Transition Metals Thermal Crystal Physics:
Cu-Sb-S, Cu-Li-Mg, Bi-Sn-Zn and Al-Fe-Ti

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ABSTRACT

This thesis focuses four different systems containing at least one transition element. A transition element is an element whose atom it has an incomplete \( d \) sub-shell, or which can give rise to cations with an incomplete \( d \) sub-shell. This characteristic gives rise to some distinctive properties that were object of this study.

All the following systems \textbf{Cu-Sb-S}, \textbf{Cu-Li-Mg}, Bi-Sn-Zn, and Al-Ti-Fe, were studied by means of experimental and/or theoretical techniques. Differential Scanning Calorimetry (DSC), Scanning Electron Microscopy (SEM) or, alternatively, Electron Probe Micro Analysis (EPMA) and X-ray diffraction (XRD). Additionally, X-ray Absorption (XANES) experiments were performed for Tetrahedrite structures of the Cu-Sb-S system, and Neutron Scattering (diffraction and spectroscopy) and hydrogen absorption studies were performed for the Cu-Li-Mg (H, D) system.

The theoretical studies are of paramount importance, not only as a auxiliary technique used in the analysis of experimental data, but also to predict worth doing experiments and to tailor new materials.

Density Function Theory (DFT), as implemented in VASP codes, was used to optimize the crystal structure of the phases in study. Electrical, mechanical, and thermodynamic properties were also studied. For the latter PHONON code was additionally used.

Phase diagrams were furthermore assessed using Thermo-Calc code.

\textbf{Cu-Sb-S}

Tetrahedrite, \( \text{Cu}_{12}\text{Sb}_4\text{S}_{13} \) is one of the ternary phases of the Cu-Sb-S system. This phase is interesting from the mineralogical point of view since Cu can be replaced by impurities like Zn, Fe, Ag, Cd, Mn, In, Tl and Ge and by that being able to store these elements. Bond distortion is the result of these replacements.

In this thesis, I’ve initiated the experimental and theoretical work leading to an understanding of the structural features conducing to this effect that is not verified in other phases like, for example, Chalcopyrite, \( \text{CuFeS}_2 \). Phase diagram experimental studies (including XRD, DSC and EPMA) were performed to characterize the Cu-Sb-S system.
**Cu-Li-Mg (H, D)**

The increasing need for materials that optimize the performance of fuel cells and batteries is becoming one of the major trends of Materials Research.

In this work, I've contributed for the experimental and theoretical study of CuLi$_{0.08}$Mg$_{1.92}$H$_5$ as a hydrogen storage material with applications in both fuel cells and Li batteries conversion electrodes. I was specially focused in studying the parent CuLi$_{0.08}$Mg$_{1.92}$ phase by means of XRD and presently I am complementing the neutron scattering studies on the Cu-Li-Mg-H system with XRD experiments. Furthermore, I am involved in the DFT and PHONON calculations developed for some of the phases of the mentioned system.

Van’t Hoff plots were obtained by means of experimental hydrogen absorption experiments, the CuLi$_{0.08}$Mg$_{1.92}$H$_5$ phase was characterized mostly by neutron diffraction and spectroscopy and DSC in synchrony with thermogravimetric analysis.

The catalytic effect of the Cu-Li-Mg-H system over Li/LiH, Mg/MgH$_2$ and Ti/TiH$_2$ was moreover studied.

The first part of this work was devoted to the study of the CuLi$_{0.08}$Mg$_{1.92}$ compound and its thermodynamic and structural characteristics.

**Bi-Sn-Zn**

Lead and lead-containing compounds are considered toxic substances due to their detrimental effect to the well-being of humans and the environment. Suitable development policy has been implemented by many countries around the world and, in order to protect the environment, the restriction of lead used in industry has been strongly promoted. Sn-Zn is one of the systems that has been used as solder as a substitute of the traditional Sn-Pb solder.

We have studied the Sn-Zn and Bi-Sn-Zn systems experimentally. My main participation in these studies was related with the XRD studies at room and elevated temperatures.

The Sn-Zn and Bi-Sn-Zn systems were furthermore studied by means of DSC and SEM. The system was reassessed and liquid miscibility gap of the Bi-Zn system was moreover studied using phase field. Microstructures were determined as a function of temperature and composition and phase diagram assessed parameters.
**Al-Fe-Ti**

Both the Al-Fe and Al-Fe-Ti systems were experimentally studied. Nonetheless, I only present some of the results obtained for the Al-Fe system since the study of the Al-Fe-Ti system is still insipient and only contemplates experimental results (XRD, DSC and EPMA).

With respect to Al-Fe, I have mainly contributed with XRD and EPMA data and/or analysis and first principles calculations, including phonon calculations. Even if we do not present the complete study in this thesis, the study of the Al-Fe system, centered on the ε high temperature phase, is becoming mature and we just need a final reflection over the whole data (including the immediate neighboring phases such as AlFe and AlFe₂) to publish this work.
RESUMO

Na presente dissertação são abordados quatro sistemas diferentes, cada um destes sistemas contendo pelo menos um elemento de transição. Um elemento de transição é um elemento cujo átomo tem uma orbital d com preenchimento incompleto, ou que pode dar origem a catiões com uma orbital d com preenchimento incompleto. Esta configuração electrónica dá origem a elementos que exibem propriedades características e que foram objecto do meu estudo.

Os seguintes sistemas Cu-Sb-S, Cu-Li-Mg, Bi-Sn-Zn e Al-Ti-Fe, foram estudados por meio de técnicas experimentais e teóricas. Experimentalmente foram utilizadas, a Calorimetria Diferencial de Varrimento (DSC), Microscopia Electrónica de Varrimento (SEM) ou, alternativamente, a Microsonda Electrónica (EMPA) e a Difracção de Raios-X (XRD). Para o cálculo teórico recorremos aos primeiros princípios, segundo a teoria dos funcionais de densidade e fonões.

Experiências de espectroscopia de absorção de raios-X por sincrotrão foram realizadas para estudar a estrutura da tetraedrita pertencente ao sistema Cu-Sb-S.

Difracção e espectroscopia de neutrons e estudos de absorção de hidrogénio foram realizados para o sistema Cu-Li-Mg (H, D).

Os estudos teóricos são de extrema importância, não só como técnica auxiliar usada na análise dos dados experimentalmente obtidos, como também, para prever as experiências e para criar/adaptar novos materiais.

Teoria dos Funcionais de Densidade (DFT), como implementada no código VASP, foi utilizada para optimizar a estrutura cristalina das fases do estudo. Propriedades eléctricas, mecânicas e termo-dinâmicas também foram estudadas. O código Phonon foi utilizado em conjugação com o VASP.

Os diagramas de fase foram ainda avaliados usando o código Thermo-Calc.

Cu-Sb-S

A tetraedrite, Cu_{12}Sb_4S_{13}, é uma das fases pertencente ao sistema ternário Cu-Sb-S. Esta fase é interessante sob o ponto de vista mineralógico e tecnológico uma vez que o Cu pode
ser substituído por elementos como o Zn, Fe, Ag, Cd, Mn, Na, Tl e Ge na sua rede cristalina. Como resultado desta substituição ocorre uma distorção na ligação química.

Nesta tese, iniciou-se o trabalho experimental e teórico, que conduziria a uma melhor compreensão das características estruturais provocadas pelo efeito da substituição destes elementos em baixa concentração. Esta substituição não é tão amplamente verificada em outras fases, como por exemplo na calcopirite, CuFeS₂.

Estudos experimentais do diagrama de fase (incluindo XRD, DSC e EMPA) foram realizados para caracterizar o sistema Cu-Sb-S.

**Cu-Li-Mg (H, D)**

A crescente necessidade de materiais para otimizar o desempenho das células de combustível e baterias tornou-se um dos principais temas da investigação em materiais para armazenamento de energia.

Neste trabalho, contribuí para o estudo experimental e teórico do composto CuLi₀.₀₈Mg₁.₉₂H₅. Este material que tem propriedades de armazenamento de hidrogénio pode ser aplicado tanto em células de combustível como em eléctrodos de conversão baterias de Li. O meu trabalho esteve especialmente focado em estudar a liga “mãe”, a fase de composição CuLi₀.₀₈Mg₁.₉₂ por meio de difracção de Raios-X e actualmente estou a complementar os estudos de difracção de neutrons do sistema Cu-Li-Mg-H, com experiências de difracção de Raios-X. Além disso, estou envolvido nos cálculos com fonões e primeiros princípios desenvolvidos para algumas das fases do sistema mencionado.

A primeira parte deste trabalho foi dedicada ao estudo do comportamento termodinâmico e características estruturais da fase CuLi₀.₀₈Mg₁.₉₂.

Os diagramas de van't Hoff foram obtidos por meio de experiências de absorção de hidrogénio. A fase CuLi₀.₀₈Mg₁.₉₂H₂ foi caracterizada por espectroscopia e difracção de neutrons e experiências de DSC em simultâneo com análise termogravimétrica.

O efeito catalítico do sistema Cu-Li-Mg-H ao longo de Li/LiH, Mg/MgH₂ e Ti/TiH₂ foi também objecto de estudo.
**Bi-Sn-Zn**

O chumbo e compostos contendo chumbo são considerados tóxicos devido ao seu efeito prejudicial para o bem-estar de seres humanos e para o ambiente. Uma política de desenvolvimento adequado foi implementada por muitos países do mundo, a fim de proteger o meio ambiente. Uma restrição no uso de chumbo na indústria tem sido fortemente promovida. Fases do sistema Sn-Zn têm sido utilizadas como substituto da solda de Sn-Pb tradicional.

Estudamos experimentalmente os sistemas Sn-Zn e Bi-Sn-Zn. A minha principal participação nestes estudos esteve relacionada com os estudos de difração de Raio-X a temperaturas elevadas (XRD-HT).

Os sistemas Sn-Zn e Bi-Sn-Zn foram ainda estudados por meio de Calorimetria Diferencial de Varrimento (DSC) e Microscopia Electrónica de Varrimento (SEM). O sistema foi reavaliado e a lacuna miscibilidade na fase líquida do sistema Bi-Zn foi estudada usando a teoria de campo. Foram determinadas as microestruturas em função da temperatura, da composição e dos parâmetros otimizados do diagrama de fase (duas otimizações diferentes).

**Al-Fe-Ti**

Foram estudados experimentalmente tanto os sistemas Al-Fe como Al-Fe-Ti. No entanto, só são apresentados alguns dos resultados obtidos para o sistema Al-Fe, uma vez que o estudo do sistema Al-Fe-Ti é ainda insipiente e contempla apenas resultados experimentais obtidos por XRD, DSC e EMPA.

Em relação ao Al-Fe, contribuí principalmente com dados e análises obtidas por microssonda electrónica e difração de raios-X e cálculos por primeiros princípios, incluindo cálculos com fonões. Apesar do estudo não se apresentar completo nesta tese, a análise da fase de alta temperatura, ε, está quase finalizada sendo necessária uma reflexão final sobre todos os dados (incluindo os das fases vizinhas AlFe e AlFe₂) para que este trabalho seja submetido para publicação.
ACRONYMS

Chapter 1. INTRODUCTION

**IUPAC** - International Union of Pure and Applied Chemistry  
**CIGS** - Copper Indium Gallium Selenide  
**CZTS** - Copper Zinc Tin Sulfide  
**LED** - Light Emitting Diode  
**DFT** - Density Functional Theory  
**LDA** - Local Density Approximation  
**GGA** - Generalized Gradient Approximation  
**LUMO** - Lowest Occupied Molecular Orbital  
**HOMO** - Highest Occupied Molecular Orbital  
**XC** - Exchange-Correlation  
**U** - Hubbard parameter  
**J** - Strength of the exchange interaction parameter  
**DFT+U** - Density Functional Theory plus Hubbard parameter  
**LDA+U** - Local Density Approximation plus Hubbard parameter  
**GGA+U** - Generalized Gradient Approximation plus Hubbard parameter  
**MUE** - Mean Unsigned Errors  
**GGA-PBE** - Generalized Gradient Approximation-Perdew Burke Ernzerhof functional  
**HSE** - Heyd Scuseria Ernzerhof hybrid functional  
**PBE0** - Perdew Burke Ernzerhof hybrid functional  
**EOS** - Equation Of State  
**VASP** - Vienna *Ab-initio* Simulation Package  
**PW** - Planwaves

Chapter 2. Cu-Sb-S SYSTEM

**Tet** - Tetrahedrite  
**Enr** - Enargite  
**Fam** - Famantinite  
**XANES** - X-ray Absorption Near Edge Struture
Chapter 3. Cu-Li-Mg (H, D) SYSTEM

DSC - Differential Scanning Calorimetry
WETO - World Energy Technology and Climate Policy Outlook
MEM - Maximum Entropy Method
HT - High-Temperature
LT - Low-Temperature
XRD - X-ray diffraction
ND - Neutron Diffraction
INS - Incoherent Inelastic Scattering
IR - Infrared Spectroscopy
TOF - Time-of-Flight
NPDF - Neutron Powder Diffractometer
GSAS - General Structure Analysis System
PDF - Pair Distribution Function
DFT - Density Functional Theory
DSC - Differential Scanning Calorimetry
TGA - Thermal Gravimetry Analysis
HIPD - High-Intensity Powder Diffractometer
LANSCE - Los Alamos Neutron Science Center
SMARTS - Spectrometer for Materials Research at Temperature and Stress
FDS - Filter Difference Spectrometer

Chapter 4. Bi-Sn-Zn SYSTEM

RoHS - Restriction of Certain Hazardous Substances
WEEE - Waste Electrical and Electronic Equipment Legislations
COST 531 EU - Lead-free Solder Materials –EU action
COST MP0602 EU - Advanced Solder Materials for High Temperature Application – EU action

HT-XRD - High Temperatures X-ray Diffraction
RT-XRD - Room Temperatures X-ray Diffraction
SEM - Scanning Electron Microscopy
DSC - Differential Scanning Calorimetry

Chapter 5. Al-Fe-Ti SYSTEM

COST 533 EU – Thermodynamics of Alloyed Aluminides – EU action

HT-XRD - High Temperatures X-ray Diffraction
RT-XRD - Room Temperatures X-ray Diffraction
SEM - Scanning Electron Microscopy
DSC - Differential Scanning Calorimetry
EMPA - Electron Microprobe Probe Analyzer
INTRODUCTION

1.1. Transition metals and their applications

The definition of the International Union of Pure and Applied Chemistry (IUPAC) for what a transition element is: "an element whose atom has an incomplete d sub-shell, or which can give rise to cations with an incomplete d sub-shell" (McNaughton & Wilkinson, 1997).

The main characteristic of the transition elements, which can be referred as transition metals as well, is having a partially filled d sub-shell or to give rise to cations with an incomplete d sub-shell (e.g. Cu$^{2+}$). The transition elements belong to three rows in the periodic table which correspond to the progressive filling of 3d, 4d, and 5d states. The presence of the d electrons changes the "picture" of bonding in these metals considerably. The transition metals usually have high melting points and several oxidation states; they usually form colored compounds and are often paramagnetic (McNaughton & Wilkinson, 1997).
There is an extensive variety of materials that include transition metals. Such compounds, with transition metals can have different electronic behaviors. They can be conductors or semiconductors and more rarely insulators or superconductors. Materials having transition metals may have interesting magnetic, ferroelectric, antiferroelectric, and piezoelectric properties (Vaughan & Rosso, 2006), (Cramer & Truhlar, 2009).

When an anion of sulfur in its lowest oxidation state of -2 is bonded to a transition metal, a transition-metal sulfide is formed.

Transition-metal sulfides constitute an important class of inorganic compounds with diverse applications in industry, ranging from catalysis to lubrication, corrosion protection and photoconductivity. In important minerals containing sulfur, such as Chalcopyrite, Tetrahedrite (Fig. 1.3) and Blend, it is common to find some of latter properties.

These minerals can be doped with other elements enhancing the above mentioned properties (Rignanese, 2005).

Sulfides are also components of many thin-film devices and have been extensively investigated as part of the nanotechnology revolution.

Fig. 1.3 Photograph of a Tetrahedrite mineral (School of Geology - University of Aristotle’s – Greece, 2012).
A cross-section of a ZnO-CdS-CIGS solar cell is shown in Fig. 1.4. From bottom to top: Kapton foil, layer of Mo with 0.5-1.5 μm thick working as positive electrode, roughly 1-2 μm of CIGS functionalized as the positive semiconductor, layer of 3-5 μm CdS functionalized as the negative semiconductor, and a layer with 0.5-1.5 μm of ZnO working as negative electrode. In the top cell, two wire conductors based on Ni/Al alloy.

Since the beginning of the 21st century the increasing demand for renewable energies, due to the limited availability of fossil fuels and to environmental problems, resulted in an extraordinary request for photovoltaic materials.
Currently, the high cost of the materials applied in photovoltaic solar cells, (e.g. Ga and In) Fig. 1.5, is one of the main obstacles for their production and application to a larger scale.

Ternary Chalcopyrite's with the general formula $A_{I}B_{III}X_{2}$ ($A = Li, Na, Cu, Ag; B = Fe, Al, Ga, Ge, In; X = S, Se, Te; I$ is a $+1$ cation and $III$ a $+3$ cation) are of considerable interest because of their potential optoelectronic applications as solar energy converters, nonlinear optical devices, Light Emitting Diodes (LED), and detectors. Chalcopyrite is a semiconductor. Polycrystalline solar cells with $Cu(In, Ga)Se_{2}$ - Chalcopyrite (Shafarman & Zhu, 2000) absorber are reach up to 18.8 % efficiency.

The importance and application of compounds based on transition-metal sulfides have many technological applications, ranging from lubrication to the use as catalysts in sulfoo-reductive hydrotreating processes in the petroleum refining industry (Harris & Chianelli, 1984), (Topsoe et al., 1996), (Hobbs & Haffner, 1999)

In addition, transition-metal sulfides have also a fundamental scientific interest. The sulfides of the transition metals are intermediate between the transition-metal oxides, whose properties are determined by strong electronic correlation effects (Ansisimov et al., 1991), and the transition-metal selenides showing a variety of electronically induced structural phase transitions, including the formation of incommensurate phases (di Salvo & McMillan, 1977). The combined scientific and technological importance of these materials has motivated a substantial research effort directed towards an understanding of their properties at an atomistic level.

The electromagnetic properties of sulfide minerals are furthermore responsible for their contribution to geomagnetism and paleo-magnetism, since they become geophysical prospectors to be used as exploration tools in metalliferous ore deposits (Fig. 1.6). To the mineral technologist, these same properties provide methods for the separation of the metal-bearing sulfides from the associated waste minerals after mining and milling and before extraction of the metal by pyrometallurgical or hydrometallurgical treatment (Pearce et al., 2006).
In this doctoral thesis we will explore several systems including transition metals, from minerals to light weight hydrogen storage, passing through lead free solders.

1.2. Theoretical tools supporting the materials study

A great approach for studying structural and electronic properties is the Density-Functional Theory (DFT). DFT is the most popular and robust theoretical approach currently available for solving the electronic structure of materials. Although far from an answer for all physical problems in this domain, no other theoretical approach has provided as much understanding of the electronic properties. DFT has proven to be capable of computing a multitude of properties of condensed matter with a reasonable accuracy (Michaelides & Scheffler 2012).

1.2.1 The Kohn-Sham equations

Hohenberg and Kohn, 1964, and Kohn and Sham, 1965, formulated a rather outstanding theorem which states that the total energy of a system such as a solid, surface or molecule depends only on the electron density of its ground state. In other words, one can express the total energy, $E$, of an atomistic system as a functional of its electron density, $E[\rho]$.

$$E = E[\rho]$$

(1.1)

The idea of using the electron density as the fundamental entity of a quantum mechanical theory for describing matter was developed in the early days of quantum mechanics,
particularly by the work of Fermi, 1928 and Thomas, 1929, (Slater, 1951). In the following decades, it was rather the Hartree-Fock approach Hartree, 1928; Fock, 1930; Fock, 1934 (Slater, 1951) which was developed and applied to small molecular systems. Calculations on realistic solid state systems were then out of reach.

Later Slater, 1951, used ideas from the electron gas with the intention to simplify the Hartree-Fock theory to a point in which electronic structure calculations on solids became feasible. Slater’s work, which led to the so-called Xα-method (Slater, 1974) has contributed enormously to the progress of electronic structure calculations. The Xα-approach, combined with other simplifications in the entitled Scattered-Wave method have driven heated disputes about the “ab initio” character of this approach, which was carried over into the comparison of density functional theory vs. Hartree-Fock based methods. Today’s density functional methods can be considered “ab initio” (Wimmer & Freeman, 2000).

In solid-state systems, molecules, and atoms, the electron density, ρ, is a scalar function defined at each point, r, in real space,

\[ \rho = \rho(r) \]  \hspace{1cm} (1.2)

The electron density and the total energy, E, depend on the type and arrangements of the atomic nuclei. Therefore, E, can be expressed by,

\[ E = E[\rho(r), \{R_\alpha\}] \]  \hspace{1cm} (1.3)

Conventionally ( \{R_\alpha\}), represents the positions of all atoms of the element, \( \alpha \), in the system under consideration. Equation (1.2) is the key to the atomic-scale understanding of electronic, structural, and dynamic properties of matter. If (1.2) can be evaluated, then the equilibrium structure of a solid, the reconstruction of a surface, and the equilibrium geometry of molecules adsorbed on surfaces, can be predicted (Wimmer & Freeman, 2000).

Moreover, the derivative of the total energy (1.3), with respect to the nuclear position, of an atom, is the absolute value of the force acting on that atom. This enables the efficient search for stable structures and, perhaps more importantly, the study of dynamical processes such as diffusion or the reaction of molecules on surfaces.
Most of the considerations presented here are based on the Born-Oppenheimer approximation in which it is assumed that the motions of the electrons are infinitely faster than those of the nuclei. This approximation rests on the fact that the nuclei are much more massive than the electrons, which allows us to say that the nuclei are nearly fixed with respect to electron motion (Sherrill, 2005). This means that the electronic structure is calculated for a fixed atomic arrangement and the atoms are then moved according to classical mechanics.

In density functional theory, the total energy is decomposed into three parts: a kinetic energy, \( T_0 \), an electrostatic or Coulomb energy, \( U \), and exchange-correlation energy, \( E_{\text{xc}} \),

\[
E = T_0 + U + E_{\text{xc}}
\]  

(1.4)

The most straightforward term is the Coulomb energy, \( U \). It is purely classical and contains the electrostatic energy arising from the Coulomb attraction between electrons and nuclei, the repulsion between all electronic charges, and the repulsion between nuclei.

\[
U = U_{\text{en}} + U_{\text{ee}} + U_{\text{nn}}
\]  

(1.5)

With

\[
U_{\text{en}} = -e^2 \sum Z_{\alpha} \int \frac{\rho(r)}{|r-R_{\alpha}|} \, dr
\]  

(1.6)

\[
U_{\text{ee}} = e^2 \int \int \frac{\rho(r)\rho(r')}{|r-r'|} \, dr \, dr'
\]  

(1.7)

\[
U_{\text{nn}} = e^2 \sum \frac{Z_{\alpha} Z'_{\alpha'}}{|R_{\alpha} - R'_{\alpha'}|}
\]  

(1.8)

Where, \( e \) is the elementary charge of a proton, and, \( Z_{\alpha} \), is the atomic number of the atom of \( \alpha \). The summations extend over all atoms and the integrations over all space. Once the electron density and the atomic numbers and positions of all atoms are known, equations (1.6)-(1.8) can be evaluated by using the techniques of classical electrostatics, were \( U_{\text{en}} \), is the potential energy between the electrons and nuclei, \( U_{\text{ee}} \), is the potential energy...
giving from Coulombic electron-electron repulsions and \( U_{nn} \), is the potential energy giving from Coulombic nuclei-nuclei repulsions.

The kinetic energy term, \( T_0 \) in density functional theory, the physical electrons of a system are substituted by electrons with the equal charge, mass, and density distribution. However, the electrons move as independent particles in an effective potential, where the motion of a real electron is connected with that of all other electrons. \( T_0 \) is the sum of the kinetic energies of all physical electrons moving as independent particles (Wimmer & Freeman, 2000). Frequently, one does not explicitly make this distinction between real and effective electrons.

If each effective electron is described by a single particle wave function, \( \Psi_i \), then the kinetic energy of all effective electrons in the system is given by

\[
T_0 = \sum_i n_i \int \Psi_i^* (\mathbf{r}) \left( -\frac{\hbar^2}{2m} \nabla^2 \right) \Psi_i (\mathbf{r}) d\mathbf{r}
\]  

Equation (1.9) is the sum of the expectation values of one-particle kinetic energies, \( n_i \) denotes the number of electrons in state, \( I \), and \( \Psi_i^* \) designate the complex conjugate part of the wave function. By construction, dynamical correlations between the electrons are excluded from \( T_0 \).

The third term of equation (1.4), called exchange-correlation energy, \( E_{xc} \) includes all remaining electronic contributions to the total energy. The most important of these contributions is the exchange term.

Electrons are Fermions and follow the Pauli Exclusion Principle. In real space, the Pauli principle implies that, around each electron with a given spin, all other electrons with the same spin tend to avoid that electron. As a consequence, the average Coulomb repulsion acting on that electron is reduced. This energy gain is called exchange energy. Effectively each electron is surrounded by a positive exchange hole (Slater, 1963). By definition, the additional many-body interaction terms between electrons of opposite spin are called correlation energy (Wimmer & Freeman, 2000).

The Hohenberg-Kohn-Sham theorem, which is a central part of density functional theory,
states that the total energy is at its minimum value for the ground state density and that the total energy is stationary with respect to first-order variations in the density.

$$\frac{\partial E[\rho]}{\partial \rho} \bigg|_{\rho=\rho_0} = 0 \quad (1.10)$$

In conjunction with the kinetic energy, we have introduced one-particle wave functions, $\Psi_i(r)$ which generate the electron density

$$\rho(r) = \sum_i n_i |\Psi_i(r)|^2 \quad (1.11)$$

As in the expression (1.9) for the kinetic energy, $n_i$ denotes the occupation number of the eigenstate, $i$, which is represented by the one-particle wave function, $\Psi_i$. So far, one has a formally exact theory in the sense that no approximations have been made yet to the many-electron interactions. By construction, $\rho(r)$, in eq. (1.11) is the exact many-electron density.

The next step is the derivation of equations that can be used for practical density functional calculations. Through equations (1.9) and (1.11) we have introduced one-particle wave functions. A change of these wave functions corresponds to a variation in the electron density (Wimmer & Freeman, 2000). Therefore, the variational condition (1.10) can be used to derive the conditions for the one-particle wave functions that lead to the ground state density. In order to accomplish that, one substitutes equation (1.11) in equation (1.10) and varies the total energy with respect to each wave function (Wimmer & Freeman, 2000). This procedure leads to the following equations:

$$\left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{eff}}(r) \right] \Psi_i(r) = \epsilon_i \Psi_i(r) \quad (1.12)$$

With

$$V_{\text{eff}}(r) = V_c(r) + \mu_{xc}[\rho(r)] \quad (1.13)$$
Equations (1.12) and (1.13) are named the Kohn-Sham equations (Kohn & Sham, 1965). The electron density, which corresponds to these wave functions, is the ground state (1.12) density which minimizes the total energy and the, $V_{eff}(r)$, is the Kohn–Sham potential, and, $V_c(r)$, is the Coulomb potential or electrostatic potential. The solutions of the Kohn-Sham equations form an orthonormal set, i.e.

$$\int \Psi_i^*(r)\Psi_j(r) \,dr = \delta_{ij} \quad (1.14)$$

This additional constraint is achieved by introducing Lagrange multipliers, $\varepsilon_i$, in eq. (1.12). These Lagrange multipliers are effective one-electron eigenvalues and are used to determine the occupation numbers, $n_i$. The eigenstates are ordered according to increasing eigenvalues. For non-spin polarized systems each state is occupied by two electrons until all electrons are accommodated. In spin polarized systems, each state is occupied by at most one electron.

As a consequence of the partitioning of the total energy equation (1.4), the Hamiltonian operator in the Kohn-Sham equation (1.12) has three terms, one for the kinetic energy, the second for the Coulomb potential, and the third for the exchange-correlation potential.

The kinetic energy term is the standard second-order differential operator of one-particle Schrödinger equations and its construction does not require specific knowledge of a system. In contrast, the Coulomb potential, $V_c(r)$, and the exchange-correlation potential, $\mu_{xc}$, depend on the specific electron distribution in the system under consideration (Wimmer & Freeman, 2000).

The Coulomb or electrostatic potential, $V_c(r)$, at point, $r$, is generated from the electric charges of all nuclei and electrons in the system. It can be evaluated directly in real space,

$$V_c(r) = -e^2 \sum_{a} \frac{z_a}{|r-R_a|} + e^2 \int \frac{\rho(r') \,dr'}{|r-r'|} \quad (1.15)$$

In condensed systems it is more appropriate to use Poisson’s equation
to calculate the electrostatic potential. Here, \( q(r) \) denotes both the electronic charge
distribution \( \rho(r) \) and the positive point charges of the nuclei at positions, \( R_\alpha \). The
exchange-correlation potential, \( \mu_{xc} \), is related to the exchange-correlation energy, \( E_{xc}[\rho] \)
by,

$$
\mu_{xc} = \frac{\partial E_{xc}[\rho]}{\partial \rho}
$$

Equation (1.17) is formally exact in the sense that it does not contain any approximations
to the complete many-body interactions. In practice however, the exchange-correlation
energy and thus the exchange-correlation potential, is not known and approximations
must be done (Hutter, 2002).

As a result of the Kohn-Sham theorem, the exchange-correlation energy depends only on
the electron density. As a simple and, as it turns out, surprisingly good approximation one
can assume that the exchange-correlation energy depends only on the local electron
density around each volume element, \( dr \), (Wimmer & Freeman, 2000). This is called the
Local Density Approximation (LDA)

$$
E_{xc}[\rho] = \int \rho(r) \epsilon_{xc}(\rho(r)) dr
$$

There are various analytical forms with different coefficients in their representation of the
exchange-correlation terms. These coefficients are not adjustable parameters, but rather
are determined through first-principles theory. Hence, the LDA is a first-principles
approach in the sense that the quantum mechanical problem is solved without any
adjustable, arbitrary, or system depended parameters (Wimmer & Freeman, 2000).
<table>
<thead>
<tr>
<th>Energy</th>
<th>Potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\epsilon_{xc} = \epsilon_x + \epsilon_c$</td>
<td>$\mu = \frac{\partial(\rho \epsilon)}{\partial \rho}$</td>
</tr>
</tbody>
</table>

**Exchange**

$\epsilon_x = -\frac{3}{2} \left( \frac{3}{\pi \rho} \right)^{\frac{1}{3}}$

$\mu_x = -2 \left( \frac{3}{\pi \rho} \right)^{\frac{1}{3}}$

**Correlation**

$\epsilon_c = -c \left[ (1 + x^3) \ln \left( 1 + \frac{1}{x} \right) + \frac{x}{2} - x^3 - \frac{1}{3} \right]$

$\mu_c = -c \ln \left( 1 + \frac{1}{x} \right)$

$c = 0.0225$, $x = \frac{r_s}{21}$, $r_s = \left( \frac{3}{4\pi \rho} \right)^{\frac{1}{3}}$

| Table 1.1 Explicit forms for the local density exchange (LDA) adapted from (Wimmer & Freeman, 2000) |

Explicit forms for the local density exchange are given by (Kohn & Sham, 1965). Correlation terms are according to (Hedin & Lundqvist, 1971). Exchange and correlation energies per electron are denoted by, $\epsilon$, and the corresponding potentials by, $\mu$. Both quantities are given in Hartree atomic unit (1 Hartree = 2 Rydberg = 27.21165 eV). The units for the electron density are number of electrons/(Bohr radius)$^3$.

Note that there are two types of exchange-correlation terms, one term for the energy and other term for the potential. The energy, $\epsilon_{so}$, is needed to evaluate the total energy and the potential term, $\mu_{so}$, is required for the Kohn-Sham equations (Eschrig, 2003). The two terms are, following equations (1.17) and (1.18), related

$$\mu_{xc} = \frac{\partial(\rho \epsilon_{xc}(\rho))}{\partial \rho}$$

(1.19)

Using the explicit formulas given in the Table 1.1, the exchange-correlation potential for any electron density $\rho(r)$ can be evaluated. Thus, all terms of the effective one-particle operator in the Kohn-Sham equations are defined and one can proceed with a computational implementation (Eschrig, 2003).
Another approximation called Generalized Gradient Approximation (GGA) was proposed by (Perdew, 1986), (Becke, 1988), (Perdew & Wang, 1992) and (Perdew et al. 1996). The basic idea in these schemes is the inclusion of terms in the exchange-correlation expressions that depend on the gradient of the electron density and not only on its value at each point in space. Therefore, these corrections are also sometimes referred to as "non-local" potentials (Zeller, 2009).

The Table 1.2 gives the form proposed by (Becke, 1988) for the exchange part, the energy gradient corrected exchange, $E^G_X$, for the correlation (Perdew, 1986), the energy gradient corrected correlation, $E^G_C$, and where the energy for Local Spin Density (LSD) is designated by $E_{LSD}$. While dissociation energies calculated with these corrections competing in precision the best post-Hartree-Fock quantum chemistry approaches, gradient corrected density functional calculations are computationally much less demanding and more general. Gradient corrected density functional has been studied extensively for molecular systems, for example by (Andzelm & Wimmer, 1992). The results are very encouraging and this approach could turn out to be of great value in providing quantitative thermochemical data (Wimmer & Freeman, 2000).

The one-particle eigenvalues obtained from gradient-corrected exchange-correlation potentials are not significantly different from the LDA eigenvalues. Therefore, these potentials do not remove the discrepancy between calculated and measured energy band gaps.

<table>
<thead>
<tr>
<th>exchange by Becke</th>
<th>correlation by Perdew</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{GGA} = E_{LSD} + E^G_X + E^G_C$</td>
<td>$E^G_G = \int f(\rho, \rho) e^{-g(\rho)(\nabla\rho)\cdot(\nabla\rho)^2} d\rho$</td>
</tr>
</tbody>
</table>

$E^G_X = b \sum \frac{\rho_\sigma x_\sigma^2}{1 + 6b x_\sigma sinh^{-1} x_\sigma} dr$

$x_\sigma = \frac{\left| \nabla \rho \right|}{\rho^3} \sigma = \uparrow \text{ or } \downarrow$

**Table 1.2** Explicit forms for Gradient-correction to the total energy (GGA) (Wimmer & Freeman, 2000)

Energies are given in Hartree atomic units; the units for the electron and spin densities are number of electrons/(Bohr radius)$^3$. The constant $b$ in Becke’s formula is a parameter.
fitted to the exchange energy of inert gases. The explicit form of the functions $f$ and $g$ in Perdew's expression for the correlation energy is given in the original paper (Perdew, 1986).

Modern DFT provides an extremely valuable tool for predicting structures, thermodynamic, mechanical and electronic properties of new materials for both finite and periodic systems. In theory, the electron affinity and ionization potential can be obtained exactly from the ground-state energy differences of the $N+1$ and $N-1$ electron systems versus the $N$ electron system being $N$ the number of electrons of the atom.

In practice, for periodic structures, the band gap, is the difference between the ionization potential and the electron affinity, and it is obtained from the difference in the orbital energies of the Lowest Occupied Molecular Orbital (LUMO) corresponding to the conduction band minimum - and the Highest Occupied Molecular Orbital (HOMO) corresponding to the valence band maximum from a single calculation.

It is well documented in (Xiao et al., 2011) that standard DFT exchange-correlation (XC) functionals, including various Generalized Gradient Approximations (GGA), dramatically underestimate the band gaps, $E_g$, for insulators due to the existence of a derivative discontinuity of the energy with respect to the number of electrons.

The study of the materials based on transition-metal sulfides, using DFT, began with the work of (Raybaud et al., 1997), in which a complete research of the structural, cohesive and electronic properties of transition-metal sulfides in the Local Density Approximation (LDA) is made. Raybaud et al., 1997, demonstrated the overbinding tendency of the LDA (prediction of too small atomic volumes and too large cohesive energies) pronounced, in particular, for the transition-metal sulfides. For the $4d$ and $5d$ orbitals, in transition-metal sulfides, the overbinding is largely corrected by including non-local corrections in the form of a generalized gradient approximation (GGA) (Hobbs & Hafner, 1999), (Hafner, 2008).

An approximate description of strong intra-atomic correlation effects is provided by the DFT+U. The physical idea behind the LDA+U or GGA+U schemes comes from the Hubbard Hamiltonian. In practical implementations the on-site two-electron integrals, which would appear in Hartree-Fock, are expressed in terms of two parameters. These are the Hubbard parameter $U$, which reflects the strength of the on-site Coulomb interaction, and the parameter $J$, which adjusts the strength of the exchange interaction. In the somewhat simplified, yet rotationally invariant method of (Dudarev et al., 1998) these two
parameters are combined into a single parameter $U_{\text{eff}} = U - J$ (Loschen et al., 2007) approach in which on-site Coulomb and exchange interactions, described in an unrestricted Hartree–Fock approximation, are added to the DFT Hamiltonian (Lichtenstein et al., 1995).

The DFT+U as formulated by (Dudarev et al., 1998), allows investigate the structural and electronic properties of several 3d transition-metal sulfides to be calculated using both LDA and GGA as a starting point.

Using DFT+U, it is possible to deal more accurately, with electron correlations in transition metal and rare earth compounds. Its implementation within a PAW framework was developed by (Bengone et al., 2004).

The main important concept of DFT+U is to address the on-site Coulomb interactions in the localized $d$ or $f$ orbitals with an additional Hubbard-type term (Hafner, 2009). When DFT fails to account for the strong Coulomb repulsion between electrons occupying narrow bands, which leads to an enhanced exchange splitting between occupied and empty eigen states, The DFT+U method attempts to resolve this defect by adding a Hubbard-type Coulomb repulsion to the DFT Hamiltonian (Hafner, 2009).

The LDA functional already provides a good approximation for the calculation of properties in transition metal solids (Hathaway et al., 1985), and the GGA functional does not always necessarily improve the LDA results (Garcia et al., 1992). Some tests are made to evaluate the accuracy of the GGA PBE local functionals for the calculation of the unit cell volumes of Cu, Pd, W, Pt, and Au. The Mean Unsigned Errors (MUE) are 1.0% for LDA, 1.3–2.9% for GGA-PBE (Kurth et al., 1999).

In summary, according to (Kurth et al., 1999), LDA underestimates the volumes (over binding) whereas the GGA usually overestimate them (under binding). A similar effect was found for Cu, Rh, Pd, Ag, Ir, Pt, and Au with LDA and GGA. According to (Grabowski et al., 2007), the mean errors for the calculation of the bulk moduli are 19% for LDA and 8-34% for GGA (Kurth et al., 1999).

Relevant is also the work of (Heyd et al., 2005), in which they show that accurate lattice constants with the screened Coulomb hybrid functional Heyd-Scuseria-Ernzerhof (HSE) can be calculated. For example, the lattice constants of ZnS, ZnSe, and ZnTe are overestimated by HSE by an average of 0.7%, (Heyd et al., 2005), whereas the local GGA-PBE functional overestimates the same lattice constants by an average of 1.4% (Heyd et
al., 2005). This is important because HSE predicts much more accurate band structures than do local functionals.

Chevrier et al., 2010, compare the accuracy of conventional semilocal DFT, the DFT+U method and the Heyd-Scuseria-Ernzerhof (HSE06) (Heyd et al., 2005) hybrid functional for structural parameters, redox reaction energies, and formation energies of transition metal compounds.

As an example, (Sun et al., 2008) use the LDA with PBE to calculate the equation of state of Pt. The Helmholtz energy was determined as a function of the lattice constants and temperature by setting it equal to a sum of three terms: the ground-state electronic energy, the free energy of thermally excited electronic states and the vibrational free energy of the lattice (Li et al., 2007), (Sun et al., 2008).

Presently hybrids functionals like PBE0 (Perdew et al., 1996) and HSE (Heyd et al., 2003) can give more accurate band gap values, using the orbital-energy gap expression instead of using local functionals like PBE. For corroborating this assumption, (Heyd et al., 2005) presents an example, for ZnS, ZnSe, and ZnTe, in which HSE orbital energies underestimate the band gaps by an average of 0.27 eV while for the same three materials, the local PBE functional underestimates the band gaps by an average of 1.46 eV. (Heyd et al., 2005).

The ability to calculate band gaps more accurately allows us to study interesting problems such as the charge states of interstitial hydrogens in oxides like TiO$_2$, SrTiO$_3$, PbTiO$_3$, ZrO$_2$, SrZrO$_2$, ZrSiO$_4$, HfO$_2$, ZnO and CdO (Grabowski et al., 2007), (Cramer & Truhlar, 2009).

Theoretical studies are especially useful for studying materials under conditions that are hard to reproduce experimentally, for example, high-pressure conditions in the earth's mantle, and the GGA-PBE density functional was used to calculate the electronic energy, including core repulsion, as a function of volume at high pressure for three phases of FeH (Isaev et al., 2009).

Moreover, they extended their calculations to free energy as a function of pressure by adding a quasiharmonic vibrational (i.e., Phonon) contribution to the ground-state electronic energy.

Studies performed by (Umemoto et al., 2008) about the spin state of Fe in iron bearing magnesium silicate Perovskite, (Mg,Fe)SiO$_3$, under lower-mantle conditions, show that state is a crucial parameter for determining key mantle properties such as elastic and
seismic wave velocities, the post-Perovskite transition pressure, and electrical and thermal conductivities.

For calculation of phonon frequencies of solid materials with transition-metals, using full potentials or pseudo-potentials, LDA usually overestimates, and GGA-PBE usually underestimates (Grabowski et al., 2007). This author also shows that, for the calculation of thermal expansion, heat capacity, and free energy, LDA is usually more accurate than GGA-PBE (Grabowski et al. 2007). For phonon dispersion curves, the experimental results generally lie between those calculated by LDA and GGA-PBE.

These same authors suggest that for improving the accuracy of calculated thermodynamic data of solids with transition metals, pure DFT data should be combined with temperature dependent data calculated with Phonons.

The Equation of State (EOS) of a material is determined by its Helmholtz free energy $F(V,T)$, which consists of three parts:

$$ F(V,T) = U(V) + F_{\text{vib}}(V,T) + F_{\text{ele}}(V,T) \quad (1.20) $$

$$ F_{\text{vib}}(V,T) = k_B T \sum_{n,q} \ln \left[ 2 \sinh \left( \frac{\hbar \omega_{nq}}{2k_B T} \right) \right] \quad (1.21) $$

where $U(V)$ is the static energy of the lattice, $F_{\text{vib}}(V,T)$ is the vibrational free energy, and, $F_{\text{ele}}(V,T)$, accounts for the thermal excitation of the electrons, and, $k_B$ is the Boltzman constant, $n_q$ is the frequency of the phonon mode for wave vector, $q$, and volume, $V$, (Isaev et al. 2007).

**1.2.2 Phonon calculations, the PHONON code**

The software PHONON was used to perform the Phonons calculations. PHONON (Parlinski, 1999), is a code for calculating phonon dispersion curves, and phonon density spectra of crystals, surfaces and adsorbed atoms on surfaces. From either a set of force constants or from a set of Hellmann-Feynman forces calculated within an Ab-initio code as Vienna *Ab-initio* Simulation Package (VASP), (Kresse & Hafner, 1993), (Kresse et al., 1994), (Kresse & Furthmüller, 1996), (Kresse & Furthmüller, 1996a). This code is capable to optimize a
supercell and calculate the Hellmann-Feynman forces. PHONON builds a crystal structure, using one of the 230 crystallographic space groups, finds the force constant from the Hellmann-Feynman forces, builds the dynamical matrix, diagonalizes it, and calculates the phonon dispersion relations, and their intensities.

PHONON finds the polarization vectors, and the irreducible representations, Gamma point of phonon modes, and calculates the total and partial phonon density of states. It plots the internal energy, free energy, entropy, heat capacity and tensor of mean square displacements, Debye-Waller factors (Parlinski, 1999). PHONON finds the dynamical structure factor for the coherent inelastic neutron scattering and the incoherent doubly differential scattering cross section for a single crystal and polycrystal.

A detailed knowledge of lattice vibrations is critical for the understanding and quantitative prediction of a wide variety of temperature dependent physical properties of solids. The fundamental thermodynamic functions of internal and free energy, entropy, heat capacity as well as non-linear properties such as thermal expansion and heat conduction are to a considerable extent determined by the vibrations of the constituent atoms in the lattice. Fortunately, the quantum theory of lattice dynamics is well developed and has proven to be one of the most successful theories of solid state physics (Müller et al., 2008).

1.2.3 Planewave pseudopotential method, the VASP code

The ab initio calculations are performed using the planewave pseudopotential code, the Vienna Ab-initio Simulation Package (VASP), (Kresse & Hafner, 1993), (Kresse et al., 1994), (Kresse & Furthmüller, 1996), (Kresse & Furthmüller, 1996a). The VASP codes have been used to determine the equilibrium lattice parameters, heats of formation, elastic constants. The Phonon dispersions are calculated together with PHONON code (Parlinski, 1999).

The VASP approach, is based on a finite-temperature local-density approximation, with the free energy as variational quantity, and an exact evaluation of the instantaneous electronic ground state at each calculation step using efficient matrix diagonalization schemes (Kresse & Furthmüller, 1996).

Planewaves (PAW) (Blöchl, 1994) and pseudopotentials form a natural alliance in this method, and they are fundamental when DFT calculations are used. In planewave pseudopotential method, the model system is constructed in a tridimensional periodic supercell which allows Bloch’s theorem to be applied to the electron wavefunctions.
\[ \psi_{n,k} (r) = u_{n,k}(r) \exp(i k \cdot r) \] (1.22)

The function \( u(r) \) has the periodicity of a supercell. It can be of any appropriate mathematical form and habitually one chooses a series expansion in terms of a set of basis function. In planewaves pseudopotential, planewaves are used for this expansion, so that each single-electron wavefunction \( \psi_{n,k} \) is written as (Segall et al., 2002).

\[ \psi_{n,k} (r) = \sum_G u_{n,k}(G) \exp(i (k + G) \cdot r) \] (1.23)

The \( u_{n,k} \) are the expansion coefficients. The wavevectors \( G \) are such that the planewaves are commensurate with the supercell. Both the number of \( G \) vectors in the sum and the number of \( k \) considered should in principle be infinite (Kresse & Furthmüller, 1996a).

The exponential term is a planewave of wavevector \( k \) which must be commensurate with the entire system not just the periodically-replicated cell. For an infinite system there is an infinite number of \( k \) vectors, at each of which solutions for \( \psi_{n,k} \) exist. This simply reflects the fact that the number of electrons is infinite (Segall et al., 2002).
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Chapter 2 - Cu-Sb-S System
Chapter 2.

Cu-Sb-S SYSTEM

2.1. Motivations

Chalcogenides are compounds primarily formed by chalcogen elements such as sulfur, selenium or tellurium. These compounds present interesting physical properties, like photosensitivity and photoconduction and therefore can be used as photovoltaic and photoconductor materials.

The solar energy is a natural resource that can be used without limitations since it is a non-polluent and it is powered by an infinite resource.

Some alternatives to the photovoltaic materials used in thin-films solar panels are going to be described and analyzed from the semiconductor behavior and mechanical properties point of view.

An ideal solar cell absorber material should have a direct band gap (around 1.0 - 2.2 eV) and being constituted of with abundant, inexpensive and nontoxic elements.

In this chapter the Cu-Sb-S system will be analyzed. The phases in which sulfur serves as the cationic coordinator were studied. One of the latter phases - belonging to the Cu-Sb-S and playing a major role as a photosensitive material - is the cubic phase, Tetrahedrite, I4-3m, Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}. This phase together with cubic phase Tennantite, I4-3m Cu\textsubscript{12}As\textsubscript{4}S\textsubscript{13}, forms a complete solid solution series and is among the most frequent complex sulfides in Nature. The Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13} phase is important from the economical point of view, since it can be a carrier of minor useful elements (Ag, Ge, Se, Te, In).

The study of the phases, occurring in the natural form, allowed us to establish the grounds for a directional study with synthetic equivalents. These synthetics were used to improve the knowledge of the Cu-Sb-S system (Braga et. al, 2008), (Ferreira & Braga, 2010).

The Tetrahedrite-type structure, in its simplest elementary composition, can be studied within the Cu-Sb-S system. This ternary system encloses other variety of natural copper antimony Chalcogenides.
Recurrently, there are no experimental data available in the published literature or in databases. Therefore, we had to proceed with the experiments to obtain data. We have initiated the synthesis process of new samples with targeted compositions.

By relating specific properties of the elements with their position in the periodic table, we selectively manipulate the composition to obtain the optimal configuration for a particular physical property.

The electronic properties (e.g. band structure) are crucial to characterize photosensitive behaviors. For some different compositions it can be demonstrated that different elements, occupying certain crystallographic sites, will make a difference in what concerns the photosensitive behaviors of Tetrahedrites. The latter was taken into consideration and \textit{ab initio} calculations were performed to show that the electronic properties of these compounds make them promising candidates as solar cells photovoltaic materials, since they possess a direct band gap and a band gap between 1.1 eV and 2.2eV. These properties can be further optimized by doping and substituting certain ions in the structure.

![Fig 2.1 Energy vs. crystal momentum for a semiconductor with an indirect band gap](image)

**Fig 2.1** Energy vs. crystal momentum for a semiconductor with an indirect band gap (Adapted from: Wikipedia, 2012).

In Fig 2.1 it is illustrated the energy vs. crystal momentum for a semiconductor with an indirect band gap, showing that an electron cannot be removed from the lowest-energy state in the conduction band (green) to the highest-energy state in the valence band (yellow) without a change in momentum. Here, almost all the energy comes from
a photon (vertical red arrow), while almost all the momentum comes from a phonon (horizontal blue arrow) (Wikipedia, 2012)

![Figure 2.2](image.png)

**Fig 2.2** Energy vs. crystal momentum for a semiconductor with a direct band gap (Adapted from: Wikipedia, 2012).

In Fig 2.2 it is illustrated the Energy vs. Crystal Momentum for a semiconductor with a direct band gap, showing that an electron can shifted from the lowest-energy state in the conduction band (green) to the highest energy state in the valence band (yellow) without a change in crystal momentum. Depicted is a transition in which a photon excites an electron from the valence band to the conduction band (Wikipedia, 2012).

This fact is very important for photovoltaics solar cells. Silicon is the most common solar-cell material, despite the fact that it has indirect-gap and therefore it does not absorb light very well. Silicon solar cells are typically hundreds of micrometres thick; if it was much thinner, much of the light, particularly in the infrared would simply pass through. On the other hand, thin-film solar cells are made of direct band gap materials such CIGS or CZTS, which absorb the light even if much thinner, and consequently can be made with a very thin active layer, often less than 1 micrometre thick (Miles et al. 2005).

The absorption spectrum of an indirect-band gap material usually depends more on temperature than that of a direct material, because at low temperatures there are fewer phonons, and therefore it is less likely that a photon and phonon can be simultaneously
absorbed to create an indirect transition. For example, silicon is opaque to visible light at room temperature, but transparent to red light at liquid helium temperatures, because red photons can only be absorbed in an indirect transition (Dresselhaus et al. 2008).

Although Cu$_{12}$Sb$_4$S$_{13}$ presents an electronic band gap of 1.24 eV, verifying the band gap condition, we want to replace the antimony in the Tetrahedrite structure since this element and its compounds are toxic.

Chalcopyrite (Cpy), CuFeS$_2$ which crystallizes in a tetragonal scalenohedral P-42m structure was furthermore studied. Based on our calculations, the band gap of this compound is 0.89 eV; but by doping and by high-pressure synthesis this value can be changed to be within the optimal band gap energy range (Hossain, 2012).

The most common elements used to dope Fe, are In or Ga and to dope S, is Se. In reality, Cu(In,Ga)Se$_2$ (CIGS) is one of the most promising thin-film solar cell materials, demonstrating an efficiency of about 20% (Contreras et al., 2005; Chen et al., 2009). Nonetheless, In and Ga are expensive and toxic elements and the band gap is usually not optimal for high efficiency CIGS solar cells. We want to design and synthesize new, high-efficient and low cost solar absorbers to replace CIGS.

The Enargite-Famatinite (Enr-Fam) Cu$_3$AsS$_4$-Cu$_3$SbS$_4$ is inexpensive; Enargite presents photosensitive properties (Pauporté & Lincot, 1995). These systems are constituted by the toxic antimony, Sb, and arsenic, As, elements. Nonetheless, these systems are interesting to be used as control for the structural and electronic properties.

Mechanical properties were additionally calculated for all compounds and were compared.

It is clear, from the recent published literature (Chirilă et al., 2010), the continuing interest in the study of Chalcogenide materials constituted by multielement and coordinated by sulfur.

2.2. The Cu-Sb-S system and the Tetrahedrite, Cu$_{12}$Sb$_4$S$_{13}$.

Sulfur is one of the most abundant elements in the universe and the 14th most abundant element in the Earth's crust. It plays a critical role in biology, atmospheric and ocean chemistry. Sulfur is the protagonist in multiple processes in different geochemical settings (Mandeville, 2010).
Sulfur is distributed throughout the mantle and crust mainly in sulfide or sulfate minerals and it finds its way into deep geologic fluids when these mineral reservoirs are perturbed by tectonic processes. The study of the sulfur behavior in the geochemical cycle provides the understanding of the origins of these mineral phases and their different formation conditions (Wallace & Carmichael, 1994).

The latter variations of the formation conditions are due to temperature differences, or more importantly due to sulfur oxidation or reduction reactions. The oxidation or reduction reactions can occur at high temperature, such as in igneous systems, at intermediate temperatures, such as in hydrothermal systems and at low temperature during sedimentary digenesis. At high temperatures, the reactions tend to occur under equilibrium conditions, whereas at low temperatures, non-equilibrium is prevalent.

The chemical speciation of sulfur in geological fluids is a controlling factor of the geochemical processes. The two major chemical forms of sulfur in crustal fluids, over a wide range of temperature and pressure are believed to be sulfate ($\text{SO}_4^{2-}$) and sulfide ($\text{S}^{2-}$). Using Raman spectroscopy it is possible to show that the dominant stable form of sulfur in aqueous solution above 250°C and 0.5 GPa is the trisulfur ion ($\text{S}_3^-$) (Pokrovski, & Dubrovinsky, 2011). The large stability range of ($\text{S}_3^-$) enables efficient transport and concentration of sulfur by geological fluids in deep metamorphic and subduction-zone settings.

Understanding the solubility of sulfur in molten silicate masses, together with the solubility of other volatile components, is a key factor for understanding the oxidation state of magma and recycling of global elements in subduction zones. It can contribute to the interpretation of the genesis of the deposits of metallic sulfides and allows evaluating the influence of volcanic sulfur emissions on the climate (Carroll & Webster, 1994).

It is known that sulfur plays a role in diagenesis and preservation of the organic matter and its conversion into oil fields (Vairavamurthy et al., 1993).

Sulfur occurs in silicate liquids in extreme states of formal valence (Connolly & Haughton, 1972; Carroll & Rutherford, 1988); oxidized as sulfate $\text{S}^{6+}$, and reduced in the form of sulfide $\text{S}^{2-}$.

The absorption spectroscopy using X-ray synchrotron radiation, XANES (X-ray Absorption Near Edge Structure), allows us to obtain the discontinuities in the absorption. A XANES edge discontinuity occurs when a core electron absorbs energy that is equal to or greater
than its binding energy. Edges are labeled according to the shell from which the electron was excited. Sulfur K-edge correspondent energy range is 2.45 to 2.53 keV.

XANES spectroscopy is a non-destructive technique and additionally it is strongly sensitive to the chemistry (formal oxidation state and geometry) of the absorbing atom; this allows us to make inferences about the coordination state of the environment of the absorbing atom (Li et al., 1995; Morra et al., 1997; Paris et al., 2001).

The microbeam XANES consents furthermore to realize studies in fluid inclusions in crystals of Olivine and Pyroxene (Gurenko & Schmincke, 2000; Bonin-Mosbach et al., 2002) which have shown the presence of intermediate oxidation states, namely S⁴⁺ in basaltic magmas rich in water (Métrich et al., 2002).

A spectroscopic study in order to characterize the sulfur state of speciation was performed but not yet published. In this work we present the first results of the analysis of the fine structure of the S K-edge absorption discontinuity of this element by XANES.

X-ray absorption experiments at ESRF (European Synchrotron Research Facility) had the purpose of studying the influence of the environment on sulfur ions and characterizing the geometry of metal ions coordinating sulfur and their bonding effects (e.g. the local order). These goals are achieved by comparing the observed sulfur K-edge profile of the minerals in study with the correspondent profile of well-known structures, which constitute model compounds for different binding situations. Native sulfur was used to characterize the molecule S = S (double bond) in S₈, Fig. 2.1; Pyrite was used to characterize the dimer S₂⁻, Fig. 2.2, and Chalcopyrite to characterize the sulfide ion S²⁻, Fig. 2.3. The following sulfide minerals were also studied as model compounds: Galena, PbS, Fig. 2.4, Blend, ZnS, Fig. 2.5, Chalcopyrite, CuFeS₂, Fig. 2.3, and Tetrahedrites Cu₁₂Sb₄S₁₃, Fig. 2.6. These phases have a very well defined structure resulting in characteristic absorption spectra. The comparison of the latter with the samples’ spectra permits a better interpretation of these spectra. In this particular case we can understand the conjugated influence of the nature of the coordinating metal atoms and the geometry of their arrangement over the electronic configuration of sulfur.

The goal of our study is to determine how impurities - replacing Cu - in the Tetrahedrite structure, will induce changes in the ideal bond lengths and geometries when compared to the ideal.

Tetrahedrite, conversely to other structures like for example the Chalcopyrite, can hold a big variety of impurities that replace Cu, such as: Zn, Fe, Ag, Cd, Mn, In, and Ge. We want to
understand why this phenomenon occurs in Tetrahedrite making it so different with this respect.

**Fig. 2.1** Crystal structure of the molecular sulfur. Space group: Fddd.

**Fig. 2.2** Crystal structure of the Pyrite, FeS$_2$. Space group: Pa3.

**Fig. 2.3** Crystal structure of the Chalcopyrite, CuFeS$_2$. Space group: I-42d.

**Fig. 2.4** Crystal structure of the Blend, ZnS. Space group: F-43m.

**Fig. 2.5** Crystal structure of the Tetrahedrite, Cu$_{12}$Sb$_4$S$_{13}$. Space group: I-43m.

**Fig. 2.6** Crystal structure of the Galena, PbS. Space group: Fm3m.
Scans between 2.45 and 2.53 KeV were performed to collect S K-edge XANES spectra. Fig. 2.7 illustrates the general trend of S K-edge XANES spectra of natural, synthetic and simulated Tetrahedrite.

The white line shown in the spectra reproduced in Fig. 2.7 (corresponding to the maximum absorption energy which in the Tetrahedrite XANES spectra is due to the Cu-S bond - an overlap of the tetrahedral and octahedral coordination contributions), does not seem to occur with similar intensity in the spectra collected from pure synthetic Tetrahedrite. This is eventually due to the presence of non-ideal structures in which there are slightly different bond lengths.

Furthermore, the presence of a small absorption peak (in the pre-edge region of the natural Tetrahedrite) is indicative of the presence of an element that replaces Cu in Cu-S bonds. This impurity element is likely to be zinc in natural Tetrahedrites.

**Fig. 2.7** Absorption spectra obtained in XANES region for natural, synthetic and simulated Tetrahedrite.
The cubic crystal structure of Tetrahedrite has two formula units per cell, being derived from the Blend structure by replacing a tetrahedral cluster of packing vacancies (4{vac.}) in each 16 packing positions by one single S-atom according to the sequence (Figueiredo & Ferreira, 2002).

\[ [S^t_{16}] \rightarrow [S_{12} \{\text{vac.} \}_4] \rightarrow \{[S^t_{12}] [S^o]\} \]

The general crystal chemical formula of Tetrahedrite may then be written (t, tetrahedral; tr, triangular; π, pyramidal; o, octahedral), clearly specifying the particular situation of one out of thirteen sulphur atoms in the crystal structure (Figueiredo & Ferreira, 2002).

\[
(Cu,Zn,Ag,Fe,Hg,Cd)^t_6(Cu,Ag)^{tr}_6(Sb,As,Bi,Te)^{\pi}_4\{[S^t_{12}][S^o]\}
\]

This process provides pyramidal and triangular coordinations respectively to four As/Sb/Bi and to six Cu/Ag ions hosted in former tetrahedral sites within the original non-lacunar closest packing; the remaining six Cu ions are hosted in true tetrahedral interstices within the closest packing of sulfide anions, Fig. 2.8.

**Fig. 2.8** Tetrahedral and octahedral arrangements in the Tetrahedrite structure.
Theoretical calculations and spectra modeling were performed with the codes FEFF 8.40 (Ankudinov et al., 1998) and FEFF 9.05 codes (Rehr et al., 2010). We want to compare FEFF simulations on DFT optimized impure Tetrahedrites with synthetic and then natural samples measurements. Spectroscopic data for Sb and Ag atoms were also recorded using XANES spectra and will be the subject of our near future study.
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Papers on the Cu-Sb-S system

2.3. First Principles Study of Copper Sulfides (for applications as photoconductors)

2.4. Phase transitions in the Cu-Sb-S System
First Principles Study of Copper Sulfides
(for applications as photoconductors)

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\textbf{Keywords:} Band Structures, Mechanical Properties, Sulfides, Photovoltaics

\textbf{Abstract.} The Tetrahedrite’s family constitutes a complete solid-solution series, and is among the most frequent complex sulfides in Nature. This kind of structure can be generically expressed by the composition, Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}. We have calculated the electronic band structure of Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13} and Ag\textsubscript{6}Cu\textsubscript{6}Sb\textsubscript{4}S\textsubscript{13} (with band gaps of 1.24 and 1.20 eV, respectively) to demonstrate that different elements occupying certain sites of the crystal structure will make a difference in what concerns the conduction process in Tetrahedrites. We will use this effect and \textit{ab initio} calculations to show that the electronic properties of these compounds make them promising candidates as solar cells photovoltaic materials since not only they possess a direct band gap but their energy falls within the range of energies of photovoltaics. Moreover, we can optimize these properties by doping and substituting ions furthermore. Mechanical properties were also calculated for both compounds and will be compared.

\textbf{Introduction}

Tetrahedrite is a copper antimony sulfosalt mineral, Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}, with I -43m crystal symmetry, seeming to be a promising candidate for solar cells photovoltaics. The Copper-Antimony-Sulfur compound can occur as a stable mineral [1] (Fig. 1) (at ambient conditions), or being synthesized from the constituent elements in stoichiometric proportion [2,3].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{tetrahedrite.png}
\caption{A specimen of natural Tetrahedrite, from Huaron Mine, Peru.}
\end{figure}

The crystal structure of the Tetrahedrite can be interpreted as a derivation of the crystal structure of the Sphalerite, which presents a cubic structure F -43m, with composition ZnS. This compound can be transformed into a Tetrahedrite, I -43m. This transformation can be explained and supported by the principles assisting the geometrical crystallography. It only implies a transformation from F to I cell type, keeping the point group (-43m). The latter transformation requires doubling the unit cell size from a\textsubscript{0}= 5.25 Å to a = 10.50 Å. The transformation is described as following: the cubic crystal structure of the Tetrahedrite has two formula units per cell, being derived from the Sphalerite structure by replacing a tetrahedral cluster of sulfur atoms by four packing vacancies (4Vac) in each sixteen packing sulfur positions. Then the vacancies, 4Vac, are replaced by one single S-atom according to the sequence (1), where S\textsuperscript{t} corresponds to the generic tetrahedral position and S\textsuperscript{o} is the final octahedral position assumed by one in sixteen atoms of sulfur (Fig. 2).

\[ [S_{16}^t] \rightarrow [S_{12}^t \text{Vac}_4] \rightarrow \{[S_{12}^t][S^o]\} \]  
(1)
This process provides pyramidal and triangular coordination, respectively, to four Sb and to six Cu\(^{+}\) cations hosted in former tetrahedral sites within the original non-lacunar closest packing; the remaining six Cu\(^{2+}\) cations are hosted in true tetrahedral interstices within the closest packing of sulfide anions (Fig. 2).

The general crystal chemical formula of the Tetrahedrite may then be written (tr, triangular; t, tetrahedral; π, pyramidal; o, octahedral), as in the following expression:

\[
(Cu^{+})_{6}^{tr}(Cu^{2+})_{6}^{t}Sb^{π}4[(S)^{t}_{12}(S)^{o}]\tag{2}
\]

The copper tetrahedral sites accommodate Cu\(^{2+}\) (Fig. 2 – bellow middle) as well as all tetrahedral coordinated divalent cations that can eventually substitute Cu\(^{2+}\) in the center of the tetrahedra. Cu\(^{+}\) occupies the center of a triangle (Fig. 2 – bellow left) of sulfur atoms and additionally, in a more distant position, in pyramidal coordination and oriented towards the central octahedra, is the Sb cation (Fig. 2 – bellow right). The (Cu\(^{+}\))\(_{tr}\) sites share a single S\(^{o}\) atom belonging to the central octahedra (Fig. 2 – bellow left) and each (Cu\(^{+}\))\(_{tr}\) is coordinated with two additional S\(^{t}\) atoms belonging to the tetrahedral framework.

Such crystal chemical insight illustrates the decisive role that \textit{ab initio} simulations have in providing a comprehensive interpretation of the Tetrahedrite behavior since substitutions in different sites will perturb different arrangements; furthermore since the panoply of substituting ions is comprehensive, \textit{ab initio} calculations deliver valuable information on the properties of the various Tetrahedrites.

Crystal engineering will be performed by substituting ions with the same valence in Tetrahedrites and eventually by creating vacancies in order to optimize electrical properties with the ultimate motivation of developing suitable photovoltaic materials.

The 89,000TW of sunlight reaching the Earth's surface is plentiful – almost 6,000 times more than the 15TW equivalent of average power consumed by humans [4,5]. Additionally, solar electric generation has the highest power density (global mean of 170 W/m\(^2\)) [4,6] among renewable energies.

Photovoltaic materials are semiconductors used to convert solar radiation into direct current electricity. Solar photons colliding with electrons will make them jump to a higher energy state (an excited state); creating positively charged holes that in turn generate electrical current. An ideal solar cell absorber material should have a direct electronic band gap around 1.0 - 2.2 eV (in a direct band gap semiconductor, the top of the valence band and the bottom of the conduction band occur at the same value of momentum) with abundant, inexpensive and nontoxic elements. Materials
presently used for photovoltaics include monocrystalline, polycrystalline and amorphous silicon, cadmium telluride, and copper indium selenide/sulfide [7]. Among these materials, Cu$_2$ZnSnS$_4$ (CZTS) is one of the most promising materials as it consists of abundant and relatively cheap elements. This semiconductor combines the properties for an ideal absorber layer for photovoltaic applications, like a direct band gap of about 1.4-1.5 eV and an optical absorption coefficient higher than $10^4$ cm$^{-1}$ [7,8].

In this work we are going to calculate the structural and electronic properties of Tetrahedrite, Cu$_{12}$Sb$_4$S$_{13}$, and compare them with those of Ag$_6$Cu$_6$Sb$_4$S$_{13}$ to prove the viability of crystal engineering towards photovoltaics optimization.

**Calculation Methods**

The electronic band structures for the cubic crystalline Tetrahedrite, I -43m, were calculated using *ab initio* Density Functional Theory (DFT) and exchange correlation functionals. The calculations were performed using Vienna *Ab initio* Simulation Package code, VASP 5.2. [9] based on the DFT approach employing the Projector-Augmented Wave (PAW) method [10,11] within the Generalized Gradient Approximation and the Perdew-Burke-Ernzerhof (GGA-PBE) [12] functional. The PBE functional presents a simple derivation of the GGA, in which all parameters are fundamental constants, and is usually applied for calculation under periodic boundary conditions. The wave functions were expanded in the plane waves up to the kinetic energy cutoff of 500 eV, which ensures the convergence with respect to basis set for this structure. The Monkhorst-Pack [13] $k$-point generation scheme was used with a grid of $5 \times 5 \times 5$ points in the irreducible part of the Brillouin zone. All calculations were performed in the $1 \times 1 \times 1$ cell containing 58 atoms. The model structure was fully optimized (atomic and cell parameters) at hydrostatic pressures equal to 0 GPa. The electronic optimizations were continued until the energy differences between the successive electronic and ion cycles were less than $10^{-5}$ eV.

**Electronic Properties**

The band gap is a critical property for understanding the optical and electrical properties of the materials and for the design of semiconductor devices. The accurate calculation of band gaps is an active and important research area in Solid-State Physics and Theoretical Chemistry. Although Kohn–Sham DFT has been very successful in Theoretical Physics and Quantum Chemistry [14], the local density functionals such as the generalized gradient approximations GGA-PBE must be engaged in order to perform the calculation of electronic properties with greater accuracy.

**Calculation results**

The energy bands of electrons in semiconductors consist of a valence band fully occupied by electrons at low energy levels, a vacant conduction band at high energy levels and a forbidden band called - band gap - which separates the former two bands and which is not so high as that of an insulator. Fig. 2 shows the high symmetry lines within the first Brillouin zone of a cubic body centered lattice.

The band gap of Cu$_{12}$Sb$_4$S$_{13}$ was calculated to be 1.24 eV and 1.20 eV for Ag$_6$Cu$_6$Sb$_4$S$_{13}$ (Fig. 3). Generally, in Cu$_{12}$Sb$_4$S$_{13}$ and Ag$_6$Cu$_6$Sb$_4$S$_{13}$ the 3d orbitals of Cu (or Ag, respectively) and the 3p of S occupy the upper region of the valence band denoting that there is bonding between Cu (or Ag) and S atoms. The orbitals 3s and 3p of S compose the bottom of the conduction band. The peaks in the interval -7 eV to -2 eV are due to the S 3p orbital. The Cu 3d orbital is located at -7 to 0 eV. The S 1s orbital on the lower region of the valence band is divided into two intervals from -12.5 eV to -12 eV and from -16 eV to 13 eV.
Most of the states in the valence band, which is located from -5 eV to 0 eV, are mainly occupied by the Cu 3d orbital and in a small percentage by S 3p orbitals (Fig. 4b).

Following the previous analysis but now focusing only on the use of the partial density of states (pDOS), we will be able to understand the orbital contribution for the promotion of electrons to the conduction band thus facilitating the occurrence of the photovoltaic effect. Essentially, from the analysis of the partial density of states (pDOS), one can infer the contribution of the electronic valence orbitals of the atoms occupying a given crystal position as well as all its equivalent positions existing in the unit cell.

By observing the data in the Fig 4a), it can be understood that both the 3d orbitals of copper that is in tetrahedral coordination, which are formally in the divalent state ($Cu^{2+}$) (2), as the electrons of the 3d orbitals of copper in triangular coordination, which are in the monovalent state ($Cu^{+}$) (2),...
have equivalent probability to contribute to the promotion of these electrons to the conduction band, although the electrons of the 3d orbitals, which arise from the triangular positions, have a slightly more favorable electronic energy to promote the electrons to the conduction band. The 3p and 3d valence orbitals of the Cu\(^{2+}\) cation (2) are filled with fifteen electrons in the following way: 3p\(^6\) 3d\(^9\), while the 3p and 3d valence orbitals of Cu\(^+\) cation (2), are filled with sixteen electrons in the following way: 3p\(^6\) 3d\(^{10}\). As it can be perceived, the difference in one electron, which induces a decoupling in a 3d orbital, facilitates the photo excitation.

In Ag\(_6\)Cu\(_6\)Sb\(_4\)S\(_{13}\), there is a substitution of the Cu\(^+\) cation by Ag\(^+\) in the positions corresponding to the triangular coordination (2). In Fig 4b) it can be observed that the 3d orbitals of copper in the divalent state (Cu\(^{2+}\)), in tetrahedral coordination, are much more likely to contribute with electrons to the conduction band. The promotion of the monovalent silver (Ag\(^+\)) electrons to the conduction band is obtained from the 4d orbitals. In the 3d orbitals of Cu\(^{2+}\), the electronic filling of the valence orbitals is made as following: 3p\(^6\) 3d\(^9\), while for the 4d orbitals of Ag\(^+\), the electronic filling of the valence orbitals is obtained by: 4p\(^6\) 4d\(^{10}\).

It is clear from the analysis of the Fig 4b) that the Ag\(^+\) valence electrons correspond to orbitals that will contribute less to conduction, since they have lower energy. What makes them not so favorable to lose electrons capable of reaching the conduction band is, possibly, the different lengths of chemical bonds with the neighboring atoms. As shown in Table 1, the bond distances between copper and sulfur are smaller for both S\(^t\) and S\(^o\).

### Table 1: Bond distances of Cu\(^{+}\)-S\(^t\), Cu\(^{+}\)-S\(^o\), Ag\(^+\)-S\(^t\) and Ag\(^+\)-S\(^o\) when the cations Cu and Ag are in triangular coordination and the anion S in tetrahedral and octahedral positions.

<table>
<thead>
<tr>
<th>Bond Distance</th>
<th>S(^t)</th>
<th>S(^o)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cu(^+))(_{tr})</td>
<td>2.254 Å</td>
<td>2.291 Å</td>
</tr>
<tr>
<td>(Ag(^+))(_{tr})</td>
<td>2.264 Å</td>
<td>2.304 Å</td>
</tr>
</tbody>
</table>

First principles calculations allow the characterization of band gaps as direct / indirect which is of paramount importance for photovoltaic applications.

### Debye model

Elastic properties of solids are very important due to the fundamental solid-state phenomena such as equation of state, phonon spectra and atomic potentials. Elastic rigidity coefficients are essential for achieving the comprehension of the mechanical properties of a solid; such as internal strain, thermoelastic stress and load deflection. Measurements of the deformations of a solid are dependent of the coefficients of elastic rigidity (Table 2).

Table 2: Lattice parameter, enthalpy of formation at 0 K (with respect to the atomic state), elasticity tensor components C\(_{ij}\), and bulk, shear, and young’s modulus calculated using Voigt, Reuss and Hill approximations, obtained from the VASP optimization of the experimental structure.
It can be observed in Table 2. that the enthalpy of formation at 0 K is considerably different for each Tetrahedrite; Ag$_6$Cu$_6$Sb$_4$S$_{13}$ is much less stable than Cu$_{12}$Sb$_4$S$_{13}$. Conversely, the bulk modulus which measures the substance’s resistance to uniform pressure is much higher in Ag$_6$Cu$_6$Sb$_4$S$_{13}$ although Cu (140 GPa), as a pure metal, has higher bulk modulus than Ag (100 GPa), in the same conditions [15]. The latter properties and differences highlight the necessity of first principles calculations to determine the properties of photovoltaic materials candidates, prior to synthesis and measurements. Furthermore, because both electronic band gap and mechanical properties change with the external pressure, it is important to correlate these properties if pressure is to be used as an additional tool to develop crystal engineering.

**Conclusions**

In this study, we present *ab initio* calculations using DFT and GGA-PBE to prove the usefulness of the latter in the selection of a particular substituting/doping element/ion and obtain new and optimized photovoltaic materials. Using the electronic band structures, density of states and correspondent orbital energies, the probability of certain electrons to be excited from the valence to the conduction band can be inferred. It can also be determined the energy cost of such a jump. Our results for the band structure and DOS for Cu$_{12}$Sb$_4$S$_{13}$ and Ag$_6$Cu$_6$Sb$_4$S$_{13}$ show that both the compounds have similar band gaps even if the electrons that will jump to the conduction band, are formerly from atoms occupying different sites.

The energy to overcome the band gap of these semiconductors – Tetrahedrites – falls within the photovoltaic operational range of 1.0 - 2.2 eV and the band gaps can be considered direct, as required.

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Phase Transitions in the Cu-Sb-S System

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Keywords: Cu-Sb-S, Tetrahedrite, Phase diagrams, XRD, DTA/DSC, EPMA

Abstract. The aim of this study is to determine the thermodynamic influence of the presence of Cu₃SbS₃, Cu₂S and Sb₂S₃ in the formation of Cu₁₂Sb₄S₁₃ - equivalent to mineral tetrahedrite. Thus, the Cu-Sb-S system is studied. Twenty three samples, with compositions that essentially lay along the vertical section Cu₂S-Sb₂S₃, were prepared. The samples were analyzed by Electron Microprobe (EPMA) in order to determine the room temperature phases' composition. Samples were also analyzed by Differential Thermal Analysis (DTA/DSC) in order to establish thermal transitions, and by X-Ray Diffraction (XRD), at room and high temperatures, so as to determine the phases that are present in the equilibria at certain temperatures. The experimental phase diagram was established and the results were compared with those available in the literature.

Introduction

This study aims to improve the knowledge about the Cu-Sb-S system by comparing synthetic with natural materials. The compositional variation and thermodynamic properties of the synthetic phases can help to establish relations with the natural equivalent composition.

The synthetic tetrahedrite type structure, in its simplest elementary composition, can be studied with the Cu-Sb-S system. This ternary system encloses, as well, synthetics with the same composition as a large variety of natural copper antimony chalcogenides. In nature, one of these phases is a very common sulphide, and crystallises in cubic system space group (I4₃m) [1], with nominal composition M₁₂X₄S₁₃ M = Cu, Ag, Bi, Hg, Fe, Zn, Pb X = Sb, As. This phase is very important by economic reasons because it can carry in its structure useful minor elements. It can show, as well, an interesting semiconductive electronic behaviour [2]. The comprehension of the mobility and accommodation of minor elements, like Ag, Bi, Hg, Fe, Zn, Pb,..., that can replace the copper positions or form an independent nanostructure in tetrahedrite lattice, will permit to explore the applicability of this structure.

Experimental

For studying the thermodynamic behaviour of the phases, belonging to the system Cu-Sb-S, synthetic samples were prepared: analytical powder (99.9995%) pure elements of Cu, Sb and S, from Alfa Aesar Puratronic, were weighed to obtain charges of 1 g.

Twenty three samples, with compositions that lay essentially along the vertical section Cu₂S-Sb₂S₃, were sealed in evacuated silica glass containers and melted at 630±2ºC for 6 h after a slow heating that took 4h. After melting, the temperature slowly dropped to room temperature in 4h in order to allow samples' homogenisation.

The samples were mounted in epoxy resin and successively observed in reflected-light optical microscopy and analysed in an Electron Microprobe (EPMA) JEOL JXA 8500F with WDS (Wavelength-Dispersive crystal Spectrometer). Samples were also analyzed by Differential Thermal Analysis (DTA) / Differential Scanning Calorimeter (DSC) in a Setaram Labsys TG/DTA/DSC apparatus, in order to determine thermal transitions. Room (RT - XRD) and high temperature X-ray
Diffraction (HT - XRD) were performed in a Panalytical X’Pert Pro MPD with an Anton Parr chamber apparatus in order to determine the phases present in equilibrium at certain temperatures.

Fig. 1. (left) Cu-Sb-S system at 300 ºC, focussed essentially on the pseudo-binary Cu$_2$S - Sb$_2$S$_3$, as it was proposed by Skinner et al. [2]. Bullets represent the composition of the prepared samples and number its reference.

Fig. 2. (below) Photomicrographs of the samples, 23, 21 and 10.
Sample 23: light grey - (Sb), dark grey - Cu$_2$S, and medium grey - Cu$_{12.3}$Sb$_{4.3}$S$_{13}$. Sample 21: light grey - CuSbS$_2$, dark grey - Cu$_{11.5}$Sb$_4$S$_{13}$ and medium grey - Cu$_3$SbS$_4$. Sample 10: dark grey - CuSbS$_2$, and medium grey - Sb$_2$S$_3$.

Results and discussion

**EPMA/WDS.** Almost every sample was analysed by means of EPMA and the composition of each phase was determined by WDS (using pure Cu, Sb and ZnS as standards). In Fig. 2 it can be seen three of the photomicrographs taken. It was observed that samples 1, 3, 4, 5, 7, 10, 14, 15, 16, 21, 22, and 23 presented the expected phases, at room temperature, after the work of [3] (see Table 1), although in the latter work samples were obtained by solid state synthesis. Samples 8, 9, 17, 18, 19 and 20 showed phases that were not expected to be found, at room temperature. This discrepancies are, in the case of samples 8 and 9, may be due to a composition shift caused by a small loss of sulphur and, in the case of sample 9, also due to a certain heterogeneity (Sb was not completely dissolved in the sample). For the other samples, the latter discrepancies are maybe due to the fact that the samples melt at higher temperatures than 630 ± 2 ºC (they have compositions close to those of the binary Cu-S whose compounds melt between ~813 and ~1127 ºC). Hence, as S melts at 115.2 ºC and Sb at 630.6 ºC, the first compounds to be formed are richer than expected in Sb. The remaining sulphur was probably accumulated at the container walls above 444.7 ºC (boiling point of S). Although in the literature, almost all synthesis, concerning the Cu-Sb-S system, were performed in the solid state (because solid state synthesis is closer to the natural process of formation of the chalcogenides), the homogenization was not sufficient for this kind of process. For the other samples, this problem could not be detected, since the samples reach the liquid state.
Table 1. The samples and its constituent phase’s compositions, at room temperature, after EPMA/WDS and RT-XRD measurements.

<table>
<thead>
<tr>
<th>x(Cu) (%)</th>
<th>x(Sb) (%)</th>
<th>x(S) (%)</th>
<th>EPMA / WDS phases at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. 64.9</td>
<td>0.8</td>
<td>34.3</td>
<td>Cu64.6Sb0.0S35.4 (CuS)</td>
</tr>
<tr>
<td>2. 54.9</td>
<td>6.1</td>
<td>39.0</td>
<td>Cu64.4Sb0.0S35.6 (CuS)</td>
</tr>
<tr>
<td>3. 47.8</td>
<td>10.4</td>
<td>41.8</td>
<td>Cu63.5Sb1.0S35.5 (CuS)</td>
</tr>
<tr>
<td>4. 41.3</td>
<td>14.7</td>
<td>44.0</td>
<td>Cu41.6Sb14.2S44.2 (CuSbS)</td>
</tr>
<tr>
<td>5. 33.5</td>
<td>19.2</td>
<td>47.3</td>
<td>Cu42.2Sb14.3S43.5 (CuSbS)</td>
</tr>
<tr>
<td>6. 24.6</td>
<td>25.1</td>
<td>50.3</td>
<td>Cu36.8Sb12.3S50.9 (CuSbS)</td>
</tr>
<tr>
<td>7. 17.4</td>
<td>29.7</td>
<td>52.9</td>
<td>Cu24.2Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>8. 11.1</td>
<td>33.8</td>
<td>55.1</td>
<td>Cu24.8Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>9. 6.4</td>
<td>36.0</td>
<td>57.6</td>
<td>Cu24.8Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>10. 1.9</td>
<td>38.3</td>
<td>59.8</td>
<td>Cu24.8Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>11. 22.4</td>
<td>22.8</td>
<td>54.8</td>
<td>Cu24.8Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>12. 23.6</td>
<td>24.1</td>
<td>52.3</td>
<td>Cu24.8Sb25.0S50.2 (CuSbS)</td>
</tr>
<tr>
<td>13. 35.2</td>
<td>16.4</td>
<td>48.4</td>
<td>Cu40.9Sb14.0S45.1 (CuSbS)</td>
</tr>
<tr>
<td>14. 30.4</td>
<td>19.0</td>
<td>50.6</td>
<td>Cu36.2Sb12.2S51.6 (CuSbS)</td>
</tr>
<tr>
<td>15. 48.1</td>
<td>7.1</td>
<td>44.8</td>
<td>Cu62.6Sb0.0S37.4 (CuS)</td>
</tr>
<tr>
<td>16. 47.7</td>
<td>5.2</td>
<td>47.1</td>
<td>Cu25.1Sb25.1S49.8 (CuSbS)</td>
</tr>
<tr>
<td>17. 44.2</td>
<td>5.1</td>
<td>50.7</td>
<td>Cu24.5Sb14.6S42.9 (CuSbS)</td>
</tr>
<tr>
<td>18. 32.7</td>
<td>11.3</td>
<td>56.0</td>
<td>Cu39.8Sb14.1S46.1 (CuSbS)</td>
</tr>
<tr>
<td>19. 37.2</td>
<td>12.4</td>
<td>50.4</td>
<td>Cu40.4Sb14.0S45.6 (CuSbS)</td>
</tr>
<tr>
<td>20. 24.3</td>
<td>25.3</td>
<td>50.3</td>
<td>Cu42.3Sb14.5S43.2 (CuSbS)</td>
</tr>
<tr>
<td>21. 41.8</td>
<td>14.2</td>
<td>44.0</td>
<td>Cu64.8Sb0.0S35.2 (CuS)</td>
</tr>
</tbody>
</table>

* According to XRD measurements, this phase is CuSbS3.
** Not measured.

**DSC/DTA.** DTA/DSC measurements were performed on a heat flux instruments with the possibility of determining the latent heat. Alumina crucibles with covers were used and the measurements were performed under flowing argon atmosphere at approx. 2.2 bar and approx. 40 cm³ min⁻¹. The heating rates used were: 2, 5, 10 and 20 °C/min. At least three different samples of the same composition were studied. A calibration factor: C = b_0 + b_1*T + b_2*R + b_3*R² (T – temperature in °C, R – heating rate in °C/min.) was evaluated after performing eleven calibrations with five different elements. Different heating rates (from 2 to 20 °C/min.) were also used for determining the coefficients b_0, b_1, b_2 and b_3. The accuracy of all of the given temperatures is ±1 °C. The temperatures of the invariant phase reactions were taken from the extrapolated onset temperatures on heating. The liquidus surface temperatures were taken from the peaks on heating (Fig. 3). The obtained results are presented in Table 2.
Table 2. Expected transitions after [3,4], and DTA/DSC and HT-XRD measurements.

<table>
<thead>
<tr>
<th>N.</th>
<th>Expected transitions (°C) (from [3,4] and this work)</th>
<th>Transition Temperatures (°C) (from DTA/DSC and HT-DRX)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α - Cu₂S + Cu₁₀S₆ → β - Cu₂S + Cu₁₀S₆ (90) [4]; Cu₁₀S₆ → β - Cu₂S + Cu₂₂S₂ → Cu₂₂S₂ + (Sb) + Liq.2 (553 ± 3) [3]; β - Cu₂S + Cu₂₂S₂ → Cu₂₂S₂ + Liq.2 + Cu₂₂S₂ + Liq.1 (607 ± 3) [3]; Liq.2 + Cu₂₂S₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>85, 122, 172, 597, 1108, 1111</td>
</tr>
<tr>
<td>2</td>
<td>α - Cu₂S + Cu₁₀S₆ → β - Cu₂S (90) [4]; Cu₁₀S₆ → β - Cu₂S + Cu₂₂S₂ → Cu₂₂S₂ + (Sb) + Liq.2 (553 ± 3) [3]; β - Cu₂S + Cu₂₂S₂ → Cu₂₂S₂ + Liq.2 + Cu₂₂S₂ + Liq.1 (607 ± 3) [3]; Liq.2 + Cu₂₂S₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>90, 123, 142, 604, 611, 911</td>
</tr>
<tr>
<td>3</td>
<td>Cu₂Sb₂ → Cu₂Sb₂ (122 ± 3) [3]; Cu₂Sb₂ + Cu₂Sb₂ + (Sb) → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 + Cu₂Sb₂ + Liq.1 (607 ± 3) [3]; Liq.2 + Cu₂Sb₂ + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>125, 511, 604, 611</td>
</tr>
<tr>
<td>4</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 + Cu₂Sb₂ + Liq.1 (553 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>472, 495, 531, 537</td>
</tr>
<tr>
<td>5</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 + Cu₂Sb₂ + Liq.1 (553 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>464, 520, 525, 533</td>
</tr>
<tr>
<td>6</td>
<td>Cu₂Sb₂ → Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Sb₂S + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 (553 ± 2); Cu₂Sb₂ + Sb₂S + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>454, 524, 530, 538</td>
</tr>
<tr>
<td>7</td>
<td>Cu₂Sb₂ → Cu₂Sb₂ + Sb₂S + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Sb₂S + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>465, 477, 495, 508</td>
</tr>
<tr>
<td>8</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>530, 542, 572</td>
</tr>
<tr>
<td>9</td>
<td>The composition is not absolutely accurate, despite the fact that the present phases at room temperature are known</td>
<td>495, 538, 600, 618</td>
</tr>
<tr>
<td>10</td>
<td>The composition is not absolutely accurate, despite the fact that the present phases at room temperature are known</td>
<td>462, 536, 538, 613, 616</td>
</tr>
<tr>
<td>11</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>63, 72, 541, 549, 601, 603, 605</td>
</tr>
<tr>
<td>12</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>543, 560, 607, 610</td>
</tr>
<tr>
<td>13</td>
<td>Cu₂Sb₂ + Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Cu₂Sb₂ + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>463, 540, 612, 615</td>
</tr>
<tr>
<td>14</td>
<td>Cu₂Sb₂ → Cu₂Sb₂ + Sb₂S → Cu₂Sb₂ + Sb₂S + Liq.2 (476.5 ± 2); Cu₂Sb₂ + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1 + Liq.2 + Liq.1</td>
<td>90, 109, 586, 595, 606</td>
</tr>
</tbody>
</table>

**RT-XRD/HT-XRD.** Powder RT-XRD measurements were performed to identify the present phases. For some samples, powder HT-XRD measurements were also performed, under a secondary vacuum of 10⁻⁵ mbar. CuKα radiation was used to collect patterns from 10 to 90° (2θ) with steps of 0.008° and counting time of 17 s (Fig. 4). This study complemented the DTA/DSC experiments.
Summary

Although in the literature all studies concerning the system Cu-Sb-S were obtained after solid synthesis, the present results show that the samples can be studied after being melted and homogenized. The EPMA/WDS and XRD room temperature data for the samples' equilibrium phases are in good agreement with the ternary from [3], at 300 °C. The DTA/DSC results are also generally in agreement with those from [3, 4]. Nevertheless, some transitions, like that at ~465 °C (for samples 5, 6, 22, 8, 9 and 10), are still not well determined.

Fig. 3. (left) DTA/DSC curve on heating for sample 10, for a heating rate of 2 °C/min. Four transitions can be observed. The first two seem to correspond to invariant transitions and the last one seems to correspond to the liquidus point.

Fig. 4. (below) RT-XRD for Sample 7. The phases identified, using the ICDD PDF 2, 2003, database, are Cu₃SbS₄ (Famatinite, syn: 00-035-0581), CuSbS₂ (Chalcostibite: 00-002-0557) and Sb₂S₃ (Stibnite, syn: 01-078-1347).

References

Chapter 3- Cu-Li-Mg (H, D) System
Chapter 3.

Cu-Li-Mg (H, D) SYSTEM

3.1 Introduction to Cu-Li-Mg system

The Cu-Li-Mg system was studied under the scope of the COST 507 - EU Action, since it is one of the ternaries of the quaternary, Al-Cu-Li-Mg system. The Al-Cu-Li-Mg system is one of the light weight reference systems with applications in the airplane and automotive industry.

Only one ternary phase coexists in the Cu-Li-Mg ternary phase diagram, CuLi$_x$Mg$_{2-x}$ ($x = 0.08$). Lithium substitutes Mg in the ternary structure which is hexagonal, P6$_2$22, although to the binary CuMg$_2$ crystallizes in an orthorhombic Fddd structure.

The fact that NiMg$_2$ crystallizes with a hexagonal structure, P6$_2$22, made us hypothesize that, as NiMg$_2$, CuLi$_x$Mg$_{2-x}$ ($x = 0.08$) would also form a hydride (Braga & Malheiros, 2007a) conversely to what happens with CuMg$_2$ that reacts with $\text{H}_2$: $2\text{CuMg}_2 + 3\text{H}_2 \rightarrow \text{Cu}_2\text{Mg} + 3\text{MgH}_2$.

The latter motivated the following study and all publications.

The following text resulted in the book chapter:

M.H. Braga, M.J. Wolverton, M.H. Sá, J.A. Ferreira

“Hydrides of Cu and Mg Intermetallic Systems: Characterization, Catalytic Function and Applications”

Keywords: Hydrides, Neutron Diffraction, Catalysis, First Principles Calculations, Phonons, Gibbs Energies, DSC/TGA, Van’t Hoff plots


2012

3.2 Introduction to hydrogen storage

The worldwide demand for energy in the 21st century is growing at an alarming rate. The European "World Energy Technology and Climate Policy Outlook" [WETO] predicts an average growth rate of 1.8% per annum for the period 2000-2030 for the world energy
demand (European Commission, 2003). The increased demand is being met largely by reserves of fossil fuel that emit both greenhouse gases and other pollutants. Since the rate of fossil fuel consumption is higher than the rate of fossil fuel production by nature, these reserves are diminishing and they will become increasingly expensive.

Against this background, the transition towards a sustainable, carbon-free and reliable energy system capable of meeting the increasing energy demands becomes imperative. Renewable energy resources, such as wind, solar, water, wave or geothermal, can offer clean alternatives to fossil fuels. Despite of their obvious advantages renewable energy sources have also some drawbacks in their use because they are unevenly distributed both over time and geographically. Most countries will need to integrate several different energy sources and an advanced energy storage system needs to be developed.

3.3 Hydrogen storage: a brief overview

Hydrogen has also attracted intensive attention as the most promising secure energy carrier of the future (Jain, 2009) due to its prominent advantages such as being:

1. Environmentally friendly. It is a “clean, green” fuel because when it burns in oxygen there is no pollutants release, only heat and water are generated:

\[
2\text{H}_2 (g) + \text{O}_2 (g) \rightleftharpoons 2\text{H}_2\text{O} (g) \quad \Delta H = 120 \text{kJ/g} \quad (3.1)
\]

2. Easy to produce. Hydrogen is the most abundant element in the Universe and is found in great abundance in the world, allowing it to be produced locally and easily from a great variety of sources like water, biomass and organic matter;

3. Light. Hydrogen is the Nature's simplest and lightest element with only one proton and one electron with high energy per unit mass.

Nonetheless, opposing to the advantages of hydrogen as an energy carrier is the difficulty in storing it. Hydrogen storage remains a problem, in particular for mobile/vehicular applications (Felderhoff et al., 2007). High-pressure hydrogen gas requires very large volumes compared to petrol, for producing the same amount of energy. On the other hand, liquid hydrogen storage systems are not viable for vehicular applications due to safety concerns in addition to volumetric constraints. Thus, hydrogen storage viability has prompted an extensive effort to develop solid hydrogen storage systems but no fully satisfactory solutions have been achieved to date (Chuchard et al., 2011).
The goal is to find a material capable of simultaneously absorbing hydrogen strongly enough to form a stable thermodynamic state, but weakly enough to release it on-demand with a small temperature rise (Jeon et al., 2011) in a safe, compact, robust, and efficient manner. There have been many materials under development for solid hydrogen storage, including metal hydrides (MHₙ), via the chemical reaction of H₂ with a metal or metal alloy (M):

\[(x/2) \text{H}_2 (g) + M (s) \rightleftharpoons \text{MH}_x (s)\]  

(3.2)

Generally, a typical hydrogenation reaction is known to involve several steps: (3.1) gas permeation through the particle bed, (3.2) surface adsorption and hydrogen dissociation, (3.3) migration of hydrogen atoms from the surface into the bulk, (3.4) diffusion through the particle and finally (3.5) nucleation and growth of the hydride phase. Any delay in one of these steps will reduce the kinetic properties of the process (Schimmel et al., 2005).

### 3.4 Magnesium hydride

Magnesium-based hydrogen storage alloys have been considered most promising solid hydrogen storage materials due to their high gravimetric hydrogen storage densities and volumetric capacity (see Table 3.1 adapted from (Chen & Zhu, 2008) for comparison) associated to the fact that magnesium is abundant in the earth’s crust, non-toxic and cheap (Grochala & Edwards, 2004; Jain et al., 2010; Schlapbach & Züttel, 2001).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Hydrides</th>
<th>Structure</th>
<th>Mass %</th>
<th>Pₑᵥ T</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaNi₅</td>
<td>LaNi₅H₆</td>
<td>Hexagonal</td>
<td>1.4</td>
<td>2 bar, 298 K</td>
</tr>
<tr>
<td>CaNi₃</td>
<td>CaNi₃H₄.₄</td>
<td>Hexagonal</td>
<td>1.8</td>
<td>0.5 bar, 298 K</td>
</tr>
<tr>
<td>ZrV₂</td>
<td>ZrV₂H₅.₅</td>
<td>Hexagonal</td>
<td>3.0</td>
<td>10⁻¹ bar, 323 K</td>
</tr>
<tr>
<td>TiFe</td>
<td>TiFeH₁.₈</td>
<td>Cubic</td>
<td>1.9</td>
<td>5 bar, 303 K</td>
</tr>
<tr>
<td>Mg₂Ni</td>
<td>Mg₂NiH₄</td>
<td>Monoclinic (LT) / Cubic (HT)</td>
<td>3.6</td>
<td>1 bar, 555 K</td>
</tr>
<tr>
<td>Ti-V-based</td>
<td>Ti-V-based-H₄</td>
<td>Cubic</td>
<td>2.6</td>
<td>1 bar, 298 K</td>
</tr>
<tr>
<td>Mg</td>
<td>MgH₂</td>
<td>Tetragonal</td>
<td>7.6</td>
<td>1 bar, 573 K</td>
</tr>
</tbody>
</table>

**Table 3.1** Structure and hydrogen storage properties of typical metal hydrides
Magnesium can be transformed in a single step to MgH$_2$ hydride with up to 7.6 wt% of hydrogen with a volumetric storage efficiency of 110g H$_2$/l (Milanese et al., 2010a), according to:

$$\text{Mg} (s) + \text{H}_2 (g) \rightleftharpoons \text{MgH}_2 (s) \quad (3.3)$$

Magnesium metal is hexagonal with P6$_3$/mmc space group (α-structure) but the absorption of hydrogen induces a structural change into the tetragonal rutile-type structure α-MgH$_2$ (P4$_2$/mnm) (Aguey-Zinsou & Ares-Fernández, 2010) (see Fig. 3.1).

At high temperature and pressure, the latter phase undergoes polymorphic transformations to form two modifications: γ-MgH$_2$ and β-MgH$_2$, having an orthorhombic structure and a hexagonal structure, respectively (Schlapbach & Züttel, 2001). Other high-pressure metastable phases have also been reported (Cui et al., 2008; Ravindran et al., 2004). The charge density distribution in these materials has also been investigated and revealed a strong ionic character. The charge density determination of MgH$_2$ by means of synchrotron X-ray powder diffraction at room temperature, the maximum entropy method (MEM) and Rietveld refinement revealed that the ionic charge of Mg and H can be expressed by Mg$^{1.91+}$ and H$^{0.26-}$, respectively, denoting that Mg in MgH$_2$ is fully ionized, but the H atoms are in a weak ionic state (Noritake et al., 2003). The high strength of these bonds results however in an unacceptably high thermodynamic stability which diminishes the potentialities of using MgH$_2$ in practical applications. The hydrogen desorption temperature is well above 573 K, which is related to its high dissociation enthalpy (75 kJ/mol H$_2$) under standard conditions of pressure (Schlapbach & Züttel, 2001). In addition,
the high directionality of the ionic bonds in this system leads to large activation barriers for atomic motion, resulting in slow hydrogen sorption kinetics (Vajo & Olson, 2007).

Several solutions were envisaged to circumvent these drawbacks. They can be accomplished to some extent by changing the microstructure of the hydride by ball-milling it (Huot et al., 1999; Zaluski et al., 1997). In this process the material is heavily deformed, and crystal defects such as dislocations, stacking faults, vacancies are introduced combined with an increased number of grain boundaries, which enhance the diffusivity of hydrogen into and out of the material (Suryanarayana, 2008).

Alloying the system with other metallic additives, like 3d elements (Ti, Fe, Ni, Cu or Al), or LaNi$_5$, FeTi, Pd, V among others and oxides like V$_2$O$_5$ or Nb$_2$O$_5$ can also be a way of improving kinetic and/or thermodynamic properties by changing the chemical interaction between the atoms (Reule et al., 2000; Rude et al., 2011; Tan et al., 2011a). The use of a proper destabilization or catalyst element/alloy into the system has also been shown to improve adsorption/desorption kinetics and to lower the adsorption temperature (Beattie et al., 2011).

Furthermore, substantial improvements in the hydriding-dehydriding properties can be achieved by nanoengineering approaches using nanosized reactants or by nanoconfinement of it (Jeon et al., 2011; Jurczyk et al., 2011; Vajo, 2011; Zaluska et al., 1999a; Zhao-Karger et al., 2010). The latter allows shorter diffusion distances and larger surface area, resulting in faster reaction kinetics. It can also introduce alternative mechanisms to hydrogen exchange modifying the thermodynamic stability of the process.

As previously referred, an alternative approach for altering the thermodynamics of hydrogenation-dehydrogenation is achieved by using additives that promote hydride destabilization by alloy or compound formation in the dehydrogenated state. This approach is known as chemical destabilization. The principle underlying this approach is that the additives are capable to form compounds or alloys in the dehydrogenated state that are energetically favourable with respect to the products of the reaction without additives. Destabilization occurs because the system can cycle between the hydride and the additive instead of the elemental metal.

A generalized enthalpy diagram illustrating this approach - destabilization of the generic hydride AH$_2$ through alloy formation (AB$_x$) promoted by the presence of the alloying species B - was given by Vajo and Olson (Vajo & Olson, 2007), and is shown in Fig. 3.2
3.5 Cu-Mg, Ni-Mg and other MgH\textsubscript{2} destabilizing systems

The work of Reilly and Wiswall provided the first evidences of this concept (Reilly & Wiswall, 1967, 1968). In their work, they showed that MgH\textsubscript{2} can be destabilized by Cu\textsubscript{2}Mg. The formation of CuMg\textsubscript{2} occurs upon dehydrogenation at lower reaction temperatures than those obtained with just pure MgH\textsubscript{2}. The compound CuMg\textsubscript{2} crystallizes in the orthorhombic structure (Braga et al., 2010c) and has a hydrogen capacity of 2.6 wt. % at 573 K (Jurczyk et al., 2007). The hydride formation enthalpy is approximately 5 kJ/mol H\textsubscript{2} lower than that of the hydrogenation of MgH\textsubscript{2} from Mg and this process obeys to the following scheme (Reilly & Wiswall, 1967):

\[
2\text{CuMg}_2 (s) + 3\text{H}_2 (g) \rightleftharpoons 3\text{MgH}_2 (s) + \text{Cu}_2\text{Mg} (s) \tag{3.4}
\]

The intermetallic cubic compound Cu\textsubscript{2}Mg does not hydrogenate under conventional hydrogenation conditions and seems to improve dehydrogenation kinetics (as compared to MgH\textsubscript{2}) due to improve resistance towards oxygen contamination (Andreasen et al., 2006; Kalinichenka et al., 2011; Reilly & Wiswall, 1967). As to the hexagonal intermetallic compound NiMg\textsubscript{2}, Reilly and Wiswall (Reilly & Wiswall, 1968) established that it reversibly reacts with hydrogen to form a ternary hydride Mg\textsubscript{2}NiH\textsubscript{4}, with a hydrogen content of 3.6 wt. %, according to the following scheme:

\[
\text{NiMg}_2\text{Ni} (s) + 2\text{H}_2 (g) \rightleftharpoons \text{NiMg}_2\text{H}_4 (s) \tag{3.5}
\]

Results obtained by A. Zaluska and co-workers (Zaluska et al., 1999b) showed that ball-milling the mixtures MgH\textsubscript{2} and NiMg\textsubscript{2}H\textsubscript{4} results in a synergetic effect of desorption, allowing the mixture to operate at temperatures as low as 493K – 513K, with good
absorption / desorption kinetics and with total hydrogen capacity exceeding 5 wt.%. They point out however that the ball-milled mixtures of the hydrides behave differently from two metal phases that are firstly ball-milled and then hydrogenated. In the latter case volume changes occur during hydrogenation with associated volume expansion of the material, in contrast to what happen in their study in which NiMg$_2$H$_4$ promoted the hydrogen release from an adjacent MgH$_2$ matrix since they undergo a significant volume contraction, which facilitates their dehydrogenation.

Many more studies have focused on changes in the hydriding/dehydriding properties of Ni-Mg binary alloys with compositional changes and changes in processing variables. Nonetheless, we highlight the study of C. D. Yim and collaborators (Yim et al., 2007) that showed that the NiMg$_2$ compound acted as a catalyst in the dissociation of the hydrogen molecule, which resulted in a faster nucleation of magnesium hydride compared to pure Mg. It revealed also that the capacity and kinetics of hydriding were larger and faster when the average size of the hydriding phase was smaller and the volume fraction of the phase boundary was larger, since phase boundaries between the eutectic α-Mg and NiMg$_2$ phases acted as a fast diffusion path for atomic hydrogen.

In the full hydrogenated state, the NiMg$_2$H$_4$ structure consists of tetrahedral [NiH$_4$]$^4$- complexes in a framework of magnesium ions and two different forms exist, high-temperature (HT) and low-temperature (LT). Under the partial pressure of 0.1 MPa of hydrogen, the HT cubic structure phase transforms into a LT monoclinically distorted structure between 518 and 483 K (Zhang et al., 2009).

The LT phase has also two modifications the untwined (LT1) and micro-twinned (LT2), which depend on the thermomechanical history of the sample (Cermak & David, 2011). The hydride formation enthalpy for the NiMg$_2$H$_4$ has been determined experimentally for the HT form, and it is in the range from -64.3 to -69.3 kJ/mol H$_2$ for the LT form this value ranges from -68.6 to -81.0 kJ/mol H$_2$ (Tan et al., 2011b).

In the pioneer work of Reilly and Wiswall (Reilly & Wiswall, 1968) it was pointed out the catalytical effect of NiMg$_2$ on the hydrogen desorption characteristics of MgH$_2$. Recently, Cermak and David (Cermak & David, 2011) showed that NiMg$_2$, and more efficiently the LT1 phase of NiMg$_2$H$_4$, were responsible for the catalytic effect of Ni reported in the literature. The fact that NiMg$_2$ is a metal whereas NiMg$_2$H$_4$ behaves like a semiconductor has opened the way to the possibility of using this system also as a switchable mirror upon hydrogenation and dehydrogenation (Setten et al., 2007). A switchable mirror will switch
from mirror to transparent material upon hydrogenation. A more detailed study of Ni-Mg-based hydrides can be found in (Orimo & Fujii, 2001).

Despite all the interest and extensive research on the above referred systems, a problem still remains; the hydrogen holding capacities of these materials are considerably less than that of MgH$_2$ (Sabitu et al., 2010). A way to overcome this limitation was found by combining MgH$_2$ with LiBH$_4$ (which involves the formation of MgB$_2$ and Li-Mg alloy (Yu et al., 2006)) since pure LiBH$_4$ has high gravimetric and volumetric hydrogen densities, 18.5 wt. % and 121 kg H$_2$/m$^3$, respectively (Bösenberg et al., 2010; Xia et al., 2011). However, although the reaction enthalpy is lowered and the hydrogen storage capacity increases (10.5 wt. %), the sorption and absorption processes occurs at high temperatures with relatively slow kinetic even though more additives are being tested in order to overcome this problem (Fernández et al., 2011; Xia et al., 2011). Alternatively, the study of the destabilization of MgH$_2$ with TiH$_2$ has also been taken experimentally (Choi et al., 2008; Sohn et al., 2011). Observations point to a substantially reduced apparent activation energy of 107-118 kJ/mol and significantly faster kinetics, compared with the 226 kJ/mol for the similarly milled MgH$_2$. The latter system constitutes a promising material to be used in practical applications for hydrogen storage.

The combined destabilization effect of Ni-Mg and Cu-Mg intermetallics towards MgH$_2$ was also tested and the Mg-rich ternary Cu-Ni-Mg alloys were recognized to have high potential for solid state hydrogen storage and have attracted many research interests. The study recently reported by Tan and co-workers (Tan et al., 2011b) elucidates about the influence of Cu substitution on the hydrogen sorption properties of magnesium rich Ni-Mg films. This study shows a two-step hydrogen absorption process. The first step is due to the absorption of Mg not alloyed in the form of NiMg$_2$ and/or CuMg$_2$, hereafter denoted as “free Mg” and is very quick, because it is mainly catalyzed by the intermetallic phase, NiMg$_2$. But the second step, due to the hydrogen absorption of intermetallic NiMg$_2$ and/or CuMg$_2$ (“bonded Mg”) is significantly slow.

The Cu substitution shows positive effects on desorption kinetics during full capacity hydrogen cycling, but shows strongly negative effects on absorption kinetics, particularly for the second absorption step, due to the segregation of CuMg$_2$ towards the grain boundaries of MgH$_2$, forming a closed shell that traps the hydrogen in MgH$_2$. The authors also reported that the Cu substitution has no thermo-destabilization for MgH$_2$, but since a significant amount can be dissolve in NiMg$_3$ even at elevated temperatures, thermo-destabilization of NiMg$_2$H$_4$ and better desorption kinetics are observed. Hong and
collaborators (Hong et al., 2011) on their study on the hydrogen storage properties of x wt.% Cu-23.5 wt.% Ni-Mg (x = 2.5, 5 and 7.5) prepared by rapid solidification process and crystallization heat treatment have also reported that the NiMg$_2$ phase has higher hydriding and dehydriding rates than Mg under similar conditions and that the addition of a smaller amount of Cu is considered favourable to the enhancement of the hydriding and dehydriding rates of the sample. The 2.5 wt.% Cu-23.5 wt.% Ni-Mg alloy had the highest hydriding and dehydriding rates. These observations are in line with the ones previously reported by the group of Milanese (Milanese et al., 2010b; 2008), who also observed the high sorption capacity and good sorption performance of Cu-Ni-Mg mixtures and proposed a two steps sorption process with different kinetics.

The first step corresponds to the quick hydrogenation of “free Mg”, according to reaction (3.3). After this step, absorption keeps on with a slower rate corresponding to the second step, hydrogenation of the “bonded Mg” phases, NiMg$_2$ and CuMg$_2$, according to reactions (3.4) and (3.5). They also showed that Ni is more effective than Cu in catalyzing the desorption reactions and that NiMg$_2$H$_4$ and Cu$_2$Mg phases destabilized each other with the beneficial effect of decreasing the dissociation temperature of about 50 K in comparison to the MgH$_2$, from “free Mg”. The positive effect of Cu as a catalyst on the hydrogenation and thermodynamic properties of NiMg$_2$ mixed by ball milling technique was also studied and recently reported by Vyas and co-workers (Vyas et al., 2011) showing that hydrogen storage capacity and enthalpy of formation of NiMg$_2$ with 10 wt.% Cu reduces to 1.81 wt.% and 26.69 kJ (mol H)$^{-1}$ from 3.56 wt.% and 54.24 kJ (mol H)$^{-1}$ for pure NiMg$_2$ at 573 K, respectively. They attributed the decrement in the absorption capacity to the formation of the intermetallic phase Cu$_2$Mg, which does not absorb the hydrogen but itself behaves like a catalyst.

However, in the case of nanocrystalline Cu$_x$Ni$_{10-x}$Mg$_{20}$ (x = 0-4) alloys synthesized by melt-spinning technique, it was found (Zhang et al., 2010a, 2010b) that the substitution of Ni by Cu does not change the major phase NiMg$_2$ although it leads to a refinement of grains with increased cell volume and the formation of a secondary phase CuMg$_2$. This in turn leads to a decrease of the hydride stability with a clear improve of the hydrogen desorption capacity and kinetics of the alloys.

The presence of CuMg$_2$ seems to act as a catalyst for the hydride-dehydride reactions of Mg and Mg-based alloys. Similar behaviour was found in Cu$_{0.25}$Ni$_{0.75}$Mg$_2$ and Cu$_{0.4}$Ni$_{0.6}$Mg$_2$ alloys that were prepared by mechanical alloying and subsequent thermal treatment (Simičić et al., 2006). The latter effect was also investigated on Cu$_{1-x}$Ni$_x$Mg$_2$ (x = 0-1) alloys.
by Hsu and collaborators (Hsu et al., 2010). They observed that by substituting Cu by Ni in CuMg$_2$, the cell volume decreased (since the radius of Cu atom is slightly larger than Ni atom) and with increasing Ni content, the effect of Ni is actually effective in MgH$_2$ and Mg$_2$NiH$_4$ destabilization, leading to a decrease of desorption temperature in these two phases. They also showed that substituted nickel caused the hydriding reaction because absorption kinetics and hydrogen storage capacity increased with the rise of Ni-substitution contents.

### 3.6 Lithium hydride

An alternative route to be considered is to explore other hydrates besides MgH$_2$ for solid hydrogen storage. One of most interesting is lithium hydride, because it contains 12.5 wt.% hydrogen. Nonetheless, the desorption temperature is 1183 K for an equilibrium pressure of 1 bar (Vajo et al., 2004). However, it has been shown (Chen et al., 2003) that when LiH (see Fig. 3.3) reacts with lithium amide (LiNH$_2$) by thoroughly mixing the substances, hydrogen is released at temperatures around 423 K, with formation of lithium imide (Li$_2$NH) or Li-rich imide (Li$_x$NH$_{3-x}$) and lithium nitride (Li$_3$N) depending on the temperature and molar ratio of (LiH/LiNH$_2$) according to the following schemes:

- Below 593 K: $\text{LiH (s) + LiNH}_2 (s) \rightarrow 2\text{H}_2 (g) + \text{Li}_2\text{NH (s)}$ (3.6)

2$\text{LiH (s) + LiNH}_2 (s) \rightarrow (x-1) \text{H}_2 (g) + \text{Li}_x\text{NH}_{3-x} (s) + (3-x) \text{LiH(s)}$ (3.7)

- At higher temperatures: $2\text{LiH (s) + LiNH}_2 (s) \rightarrow \text{H}_2 (g) + \text{Li}_3\text{N (s)}$ (3.8)

From a detailed analysis of high-resolution synchrotron x-ray diffraction data for the lithium amide (LiNH$_2$) - lithium imide (Li$_2$NH) hydrogen storage system (David et al., 2007), the authors were able to propose an alternative mechanism that does not need to have the materials mechanically milled to enhance mixing, as previously recognized by Chen and collaborators (Chen et al., 2003) as essential.

The mechanism they propose for the transformation between lithium amide and lithium imide during hydrogen cycling is a bulk reversible reaction that occurs in a non-stoichiometric manner within the cubic anti-fluorite-like Li-N-H structure, based on both Li$^+$ and H$^+$ mobility within the cubic lithium imide. Concluding that increasing the Li$^+$
mobility and/or disorder it is likely to improve the hydrogen cycling in this and related Li-based systems. Recently, further systematical evaluation of the decompositions of LiNH₂ and Li₂NH was carried out by Zhang and Hu (Zhang & Hu, 2011), who also examined the effect of Cl⁻ anion on the decomposition process. Cl⁻ is widely employed as a promoter to improve various catalysts. As a result, decomposition mechanisms were established.

The decomposition of LiNH₂ producing Li₂NH and NH₃ occurs in two steps at the temperature range of 573-723 K. LiNH₂ decomposes into a stable intermediate species (Li₁.₅NH₁.₅) and then into Li₂NH. Furthermore, Li₂NH is decomposed into Li, H₂, and N₂ without formation of Li₃N at the temperature range of 823-1023 K. The introduction of Cl⁻ can decrease the decomposition temperature of Li₂NH by about 110 K.

![Fig. 3.3 Crystal structure of lithium hydride.](image)

### 3.7 Neutron techniques associated with hydrogen solid storage

Though some progresses have been made, the state-of-art materials are still far from meeting the aimed targets for hydrogen solid storage material (Churchard et al., 2011). This huge task can be facilitated by employing state-of-the-art techniques like, computational first-principles calculations to evaluate the thermodynamic properties of the potential materials (Alapati et al., 2007; Siegel et al., 2007; Yang et al., 2007). This allows a quick screen of a large number of potential candidates, searching for thermodynamically suitable ones (saving time and money).

Once thermodynamic appropriate materials have been found other considerations such as structure and dynamics of the materials during hydrogenation/dehydrogenation will
become crucial in order to understand the fundamental properties of hydrogen storage, in realistic conditions and hence design new hydrogen storage materials.

Neutron scattering techniques are highly suitable for structure and dynamics studies related to hydrogen in solids and bound on surfaces. The energy distribution of thermal neutrons is nearly ideal for the study of condensed matter in general because it is of the same order of magnitude as most molecular and lattice excitations and the de Broglie wavelengths of thermal neutrons match quite well with interatomic distances in most solids (Squires, 1978).

Neutrons have some unique advantages over photons and electrons as scattering media which are of particular use for the analysis of hydrides. For these purposes the two most useful neutron scattering interactions are coherent elastic scattering for Neutron Diffraction (ND) and incoherent inelastic scattering (INS) to measure vibrational density of states.

The distinction of coherent and incoherent scattering interactions is important to the unique advantages offered by ND and INS respectively. This is because the relative scattering intensity of a given interaction is dependent highly upon the nucleus involved, and as such is isotope dependant. Each isotope has a different scattering cross section for both coherent ($\sigma_{\text{coh}}$) and incoherent ($\sigma_{\text{inc}}$) interactions measured in barns (1 barn = $10^{-28}$ m$^2$).

In general these scattering cross sections do not follow any specific trend regarding nucleus size.

INS has numerous advantages to other common techniques of obtaining vibrational spectra such as infrared (IR) and Raman spectroscopy. INS spectroscopy is hyper sensitive to the presence of hydrogen. The protium ($^1$H) nucleus has respective scattering cross sections of $\sigma_{\text{coh}} = 1.8$ and $\sigma_{\text{inc}} = 80.2$ barns respectively. This means neutron scattering in materials containing natural abundance hydrogen is largely inelastic.

Additionally, the incoherent cross section of $^1$H is one to two orders of magnitude higher than any other isotope (Ross, 2008). This means that in hydrides INS spectra are dominated by vibrational modes of hydrogen almost exclusively. This hyper sensitivity to hydrogen means that hydride phases are detectible even with present in miniscule relative concentration.
Another advantage of INS is the complete absence of selection rules for the excitation of vibrational modes. External modes (lattice modes, i.e. phonons) are excited with equal opportunity to molecular vibrations. Because both IR and Raman spectroscopy rely upon different types of charge symmetry interactions, a number of vibrational modes cannot be excited in the majority of solids and molecules. In particular lattice modes are far more easily observable in INS spectra than any other type of vibrational spectroscopy.

INS is also more useful for comparison with ab initio calculated density of states because relative excitation amplitudes are simply dependent upon the magnitude of motion and $\sigma_{\text{inc}}$ of the excited nucleus (Squires, 1978; Ross, 2008). Free codes, such as a-Climax is available to generate a theoretical INS spectrum from the density of states output files from numerous common ab initio packages such as Gaussian, AbInit and Dmol (Ramirez, 2004).

For these reasons INS is extremely useful in identifying the presence of different hydride phases which may not be structurally apparent (for example, due to structural disorder). A good example is the INS study of Schimmel et al. on MgH$_2$ produced from Mg processed by high energy ball milling. Ball milling of Mg to reduce particle size, and introduce fractures, defects, and faults has a beneficial effect of increasing hydride formation rate, and reducing the temperature required for absorption. Comparison of the INS spectra of the MgH$_2$ produced from ball milled Mg with well-ordered MgH$_2$ revealed a partial composition of $\gamma$-MgH$_2$, which is metastable and normally exists only at high temperatures (Schimmel et al., 2005). Presence of $\gamma$-MgH$_2$ was indicative of internal stress from mechanical processing. However after hydrogen sorption cycling, $\gamma$-MgH$_2$ was no longer observable in the INS spectrum of the ball milled material, while the fast kinetics and low sorption temperature remained. In this way INS was indispensable in revealing that the particle size reduction is more significant in the role of lowering temperature and increasing sorption kinetics than the creation of faults and internal stresses after the high energy ball milling of Mg (Schimmel, 2005; Ross, 2008).

Neutron diffraction also provides some unique advantages versus more conventional diffraction methods such as X-ray diffraction (XRD). Elastic neutron and X-ray scattering are similar in that both result in interference patterns according to Bragg scattering conditions (Squires, 1978).

In XRD the intensity of a given Bragg reflection varies with the atomic number (Z) of the atom at the lattice site. This means that the exact position of hydrogen in a structure is practically impossible to determine with XRD. In ND the relative intensities of reflections
are independent of $Z$, and instead depend on the coherent scattering cross section ($\sigma_{\text{coh}}$). This means that deuterium ($^2\text{H}; \sigma_{\text{coh}} = 5.6, \sigma_{\text{inc}} = 2.0$) is just as readily observable as most metal atoms. This allows for the observation of hydride phase transitions which differ only by the hydrogen occupation sites, such as in interstitial hydrides.

ND also allows metals with similar $Z$ values such as Ni ($Z=28, \sigma_{\text{coh}} = 13.4$) and Cu ($Z=29, \sigma_{\text{coh}} = 7.5$) to be easily distinguished, unlike in XRD. A great deal of caution must be taken to ensure that $^2\text{H}$ is not displaced by $^1\text{H}$ during sample preparation and handling, as the large $\sigma_{\text{inc}}$ of $^1\text{H}$ will create a substantial background signal.

Another advantage of ND is that intensity does not diminish greatly with scattering angle as it does in XRD (Massa, 2004). Beyond these differences, crystal structure determination techniques are very similar for ND and XRD. Common approaches include a combination of a structure solution method and the Rietveld refinement method.

ND and INS carry some common advantages and disadvantages intrinsic with the use of neutrons as a scattering medium. Common advantages are associated with the highly penetrating quality of neutron radiation through most materials. This provides some possibilities for variable depth of measurements. If the neutron beam is directed at a relatively thin portion of the sample, a greater quantity of surface and shallow depth material is surveyed, whereas in relatively thick segments predominantly material deep within the sample is surveyed. The high penetration of neutrons also allows for relatively clear in-situ measurements in a wide range of sample environments such as high pressure gas cells, furnaces, cryogenic refrigerators, anvil cells and other environments requiring obtrusive equipment. This allows for detailed structure and dynamics studies of metastable hydride phases, and phase transitions which occur only in extreme conditions.

There are numerous inconveniences associated with neutrons as well. The most prevalent and obvious is the relative scarcity and cost of neutron sources, which typically take two forms: a research reactor or a spallation source (fed by a high energy proton accelerator).

Another drawback is the time required to conduct a measurement, which can range from hours to days (per measurement). This is due to the short range of nuclear forces and relatively low probability of a scattering event, which is the same reason neutron radiation penetrates so effectively. For these reasons beam time is allocated very carefully at neutron sources, and flight paths are rarely left idle during neutron production.

ND and INS require larger sample sizes, often multiple grams, to increase the scattering rate.
3.8 Hydrides of Cu and Mg intermetallic systems

We have studied the Cu-Li-Mg system as a hydrogen storage system and, at the same time, as a catalyst of the hydrogen storage process, namely for the Ti/TiH$_2$ system (Braga & Malheiros, 2007a, 2007b; Braga et al., 2010a, 2010b).

The only ternary compound the Cu-Li-Mg system holds is CuLi$_x$Mg$_{2-x}$ ($x = 0.08$) with hexagonal P6$_2$22 structure (Braga et al., 2010c). Since the phase diagrams of Cu-Mg and Ni-Mg are similar (see Fig. 3.4), and Cu and Ni have similar electron affinities, it was thought in the sixties that CuMg$_2$ would store hydrogen, too.

Fig. 3.4 Phase diagrams of Ni-Mg and Cu-Mg (Ansara et al., 1998)

However this is not the case (Reilly & Wiswall, 1967). NiMg$_2$ has a hexagonal structure (P6$_2$22), but CuMg$_2$ has an orthorhombic structure (Fddd), and this structural difference is assumed to be the reason that NiMg$_2$ stores H$_2$ forming a hydride, but CuMg$_2$ does not. CuMg$_2$ decomposes into Cu$_2$Mg and MgH$_2$ (Reilly & Wiswall, 1967) upon hydrogen loading as previously referred (3.4). As a result of this reaction and since CuMg$_2$ does not form a hydride, CuMg$_2$ was abandoned as a candidate material for hydrogen storage (Reilly & Wiswall, 1967; Schlapbach & Züttel, 2001) until the late destabilization studies that were previously cited. The hexagonal structure of CuLi$_x$Mg$_{2-x}$ suggested the possibility of using this phase as a hydrogen storage material (Braga & Malheiros, 2007a, 2007b) because CuLi$_x$Mg$_{2-x}$ has the same space group (P6$_2$22) as NiMg$_2$ and NiMg$_2$(H,D)$_{0.3}$ (lattice parameters are almost identical: $a = b = 0.5250$ nm and $c = 1.3621$ nm (at 300 K) for CuLi$_x$Mg$_{2-x}$ and $a = b = 0.5256$ nm and $c = 1.3435$ nm for NiMg$_2$(H,D)$_{0.3}$ (Senegas et al., 1984)). Therefore, we hypothesized that CuLi$_x$Mg$_{2-x}$ ($x = 0.08$) would be a hydrogen storage material, just like NiMg$_2$ - a hypothesis that has been confirmed by now (Braga & Malheiros, 2007a, 2007b; Braga et al., 2010a).
The change of the CuMg$_2$ orthorhombic (Fddd) structure to a hexagonal structure (P6$_3$222) upon addition of a small amount of Li has been firmly established (Braga et al., 2007). Isostructural phases to CuLi$_x$Mg$_{2-x}$ are the hexagonal phase NiMg$_2$H$_{0.24-0.30}$ and NiMg$_2$ (Senegas et al., 1984). For the NiMg-hydrides, several hydrogen positions were reported: In NiMg$_2$H$_{0.29}$ the hydrogen atoms occupy Wyckoff 6f positions and could occupy the interstitial Wyckoff 6h position (Senegas et al., 1984). Other possibilities would be that the H atoms would just occupy interstitial Wyckoff 12k position (in NiMg$_2$H$_{0.26}$) or the Wyckoff 12k and 6j positions in NiMg$_2$H$_{0.24}$ (Senegas et al., 1984). This suggests a number of possible sites for Li in CuLi$_x$Mg$_{2-x}$.

Interestingly V. Hlukhyy and collaborators (Hlukhyy et al., 2005) have reported a result closely related to our observations in the Sn-doped Ni-Mg system. These authors show that the synthesis of alloys in the Ni-Mg system is affected by the presence of small amounts of Sn (forming NiMg$_{2-x}$Sn$_x$ with x = 0.22 and 0.40). The replacement of Mg by Sn produces changes in the structure of NiMg$_2$, this time making the alloy change from the NiMg$_2$ type (hexagonal) to the CuMg$_2$ type (orthorhombic). While the structure of NiMg$_{1.85}$Sn$_{0.15}$ is still of NiMg$_2$ type, the structure of NiMg$_{1.78}$Sn$_{0.22}$ and NiMg$_{1.60}$Sn$_{0.40}$ is already of the CuMg$_2$ type. These results represent obviously the converse of our own observations in the CuMg$_2$ structure, and reaffirm our results with respect to CuLi$_x$Mg$_{2-x}$.

### 3.9 The CuLi$_{0.08}$Mg$_{1.92}$ compound

We have used neutron diffraction to refine the composition of CuLi$_x$Mg$_{2-x}$, site occupancies and lattice parameters at different temperatures. In Fig. 3.5, results from the Time-of-flight (TOF) Neutron Powder Diffractometer (NPDF) at the Los Alamos Neutron Scattering Center are shown. It was analyzed a sample containing 37.5 at.% of CuLi$_{0.08}$Mg$_{1.93}$, 45.1 at.% of CuMg$_2$ and 17.4 at.% of Cu$_2$Mg. The structure was refined using the General Structure Analysis System (GSAS), a Rietveld profile analysis code developed by A. C. Larson and R. B. von Dreele (Larson & von Dreele, 2004).

Furthermore, we’ve fitted the NPDF data using the Pair Distribution Function (PDF) in which $G(r)$ was obtained via the Fourier Transform of the total diffraction pattern as indicated below:

$$G(r) = 4\pi\left[\rho(r) - \rho_0\right] = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$  \hspace{1cm} (3.9)
where $\rho(r)$ is the microscopic pair density, $\rho_0$ is the average atomic number density, and $r$ the radial distance. $Q$ is the momentum transfer ($Q = 4\pi \sin(\theta)/\lambda$). $S(Q)$ is the normalized structure function determined from the experimental diffraction intensity (Egami & Billinge, 2003). PDF yields the probability of finding pairs of atoms separated by a distance $r$. PDF fittings were performed using the code PDFgui (Farrow et al., 2007).

**Fig. 3.5** a) Neutron diffraction pattern of a sample containing CuLi$_{0.08}$Mg$_{1.92}$, CuMg$_2$ and CuMg$_3$. The highlighted peak corresponds to the (101) reflection for the CuLi$_{0.08}$Mg$_{1.92}$ compound which is not overlapped by other phases. b) Pair Distribution Function (PDF) fitting for the same conditions of the pattern in a).

Besides Neutron Diffraction, we have used theoretical complementary methods to determine the stoichiometry of the CuLi$_x$Mg$_{2-x}$ compound. We relied on the Density Functional Theory (DFT) (Hohenberg & Kohn, 1964) to calculate the structure that minimized the Electronic Energy at 0 K, without accounting for the zero point energy.

The latter energy gives us a good estimation of the Enthalpy of Formation at 0 K especially since we were relating data for stoichiometries that did not differ too much and for similar crystal structures. The results obtained are in close agreement with those obtained from ND after Rietveld refinement - CuLi$_x$Mg$_{2-x}$ (x = 0.08).

Nonetheless, no conclusions about Li site occupancies could be drawn from the use of the referred means. DFT shows that there isn’t a clear preference, in terms of energy, for the different Li site occupancies. Then again, a technique that gives information about the average site occupancies - like the Rietveld refinement - is also inadequate to clarify this
problem; therefore we have used PDF to determine Li preferred sites. With PDF fittings we were allowed to go further (see Fig. 3.5b). PDF does not see the average but the local structure and with PDF, all results but those in which Li would substitute Mg1 sites (1/2, 0, z), gave negative occupancies for Li. For Li substituting Mg1 we’ve obtained an average composition for CuLi$_{1-x}$Mg$_{2-x}$ (x = 0.07) which is in agreement with the other obtained results. For further information please see (Braga et al., 2010c).

### 3.10 Hydrogen storage in the Cu-Li-Mg-H(D) system

To study the hydrogen storage in the Cu-Li-Mg system several techniques were used (Braga et al., 2010a). Besides absorption/desorption, Differential Scanning Calorimetry, Thermal Gravimetry Analysis (DSC/TGA), X-ray Diffraction (XRD) both at the laboratory and at the Synchrotron, we have used Neutron Diffraction and Inelastic Neutron Scattering. Owing to the low X-ray scattering power of hydrogen, neutron diffraction experiments on deuterides are necessary as previously highlighted in section 1.5.

Most atomic arrangements were determined on powders of different samples yet we have also used a bulk sample machined into a cylinder to obtain ND data in both the surface and the center of the sample during deuterium uptake.

The data were usually analyzed by the Rietveld method, yet in some cases in which the background was noisier we have used the biased method (Larson & von Dreele, 2004). For better convergence, the number of refined parameters in particular those of the atomic displacement amplitudes are reduced by constraints.

ND results obtained at HIPD at LANSCE, Los Alamos National Laboratory, for a sample initially containing 78 wt.% CuLi$_{0.08}$Mg$_{1.92}$ + 22 wt.%Cu$_2$Mg (from here on “initially containing” means before hydrogen/deuterium absorption) and that was deuterated ex situ at 473 K at $P \leq 5$MPa in order to determine the crystal structure of the first deuteride phase formed in the sample (see Fig. 3.6 left). This pattern was refined using Rietveld’s method.
Fig. 3.6 (left) Rietveld refinement of a sample containing CuLi_{0.08}Mg_{1.92}, Cu\textsubscript{2}Mg, MgD\textsubscript{2} and CuLi_{0.08}Mg_{1.92}D\textsubscript{5} obtained in HIPD. wRp and Rp are the reliability factors as defined in (Larson & von Dreele, 2004). (right) ND pattern of the center of a bulk cylinder sample containing CuLi_{0.08}Mg_{1.92}, Cu\textsubscript{2}Mg, CuMg\textsubscript{2} obtained in SMARTS during an *in situ* reaction with D\textsubscript{2} at 523 K and ~3.4 MPa. Both patterns show experimental, refined and difference between experimental and calculated intensities.

Fig. 3.7 (left and right) ND pattern of the surface of a bulk cylinder sample initially containing CuLi_{0.08}Mg_{1.92}, Cu\textsubscript{2}Mg, and CuMg\textsubscript{2} obtained in SMARTS during an *in situ* reaction with D\textsubscript{2} at 523 K and ~3.4 MPa. (right) it is highlighted that MgD\textsubscript{2} cannot justify some existing peaks. Both patterns show experimental, refined and difference between experimental and calculated intensities.
The CuLi$_{0.08}$Mg$_{1.92}$D$_5$ crystal structure was determined to be monoclinic P121, with $a = 1.514$ nm, $b = 0.688$ nm, $c = 0.555$ nm and $\beta = 91.73^\circ$ according to the formula CuLi$_{0.08}$Mg$_{1.92}$D$_5 = 0.5\{\text{Mg}^{32+} \cdot \text{[CuH}_4\}_2^{3-} \cdot \text{MgD}_2\}$ corresponding to 4.4 wt% D per formula unit. CuLi$_{0.08}$Mg$_{1.92}$D$_5$ is the first deuteride/hydride to be formed. This result is interesting by itself, but the presence of MgD$_2$ in the diffraction pattern, highlights even further the possibilities of applications of this compound. According to these results, it can be obtained MgH(D)$_2$ from a sample that did not contain “free” Mg or CuMg$_2$. Furthermore, the deuteration process occurred at 473 K, which is considerably lower than the hydrogen absorption temperature reported for CuMg$_2$ (3.4) (Reilly & Wiswall, 1967).

The experiments with the bulk sample at SMARTS, LANSCE, Los Alamos National Laboratory, show that before MgD$_2$ is observed, CuLi$_{0.08}$Mg$_{1.92}$D$_5$ is already distinguishable at the surface even in a sample that initially contained CuMg$_2$ (see Fig. 3.7). Therefore, it seems that CuLi$_{0.08}$Mg$_{1.92}$D$_5$ will have a catalytic and destabilizing roll that was additionally observed with the Ti/TiH$_2$ systems (Braga et al., 2010b).

**Fig. 3.8** ND refined pattern of the center and surface of a bulk cylinder sample initially containing CuLi$_{0.08}$Mg$_{1.92}$, Cu$_2$Mg, and CuMg$_2$ obtained in SMARTS during an *in situ* reaction with D$_2$ at 523 K and ~3.4 MPa. Besides the texture effect that might be present in a bulk sample, it seems that the center initially contained more CuLi$_{0.08}$Mg$_{1.92}$ than the surface.

Experimental information about the metal–hydrogen interactions can be obtained by measuring lattice vibrations via INS, as previously highlighted in section 3.5.
Because of the large difference between the masses of metal and H atoms in transition-metal–hydrogen systems, the acoustic dispersion branches of the phonon spectra can be attributed to the motion of the metal atoms, the optic branches to the vibrations of the light H atoms relative to the metal lattice. The densities of states of optic phonons typically show a pronounced maximum at the energy of the lattice vibrations at the \( \Gamma \) point in the center of the phonon Brillouin zone (\( q = 0 \)) e.g. in (Fukay, 1993). These phonon modes describe the vibration of the undistorted H sublattice relative to the rigid metal sublattice. Hence, they contain the metal–hydrogen interaction only.

This is usually stronger than the H–H interaction, which leads to the dispersion of the optic branches. In the limit of very low H concentrations, the H vibrations can be imagined as independent vibrations of local Einstein oscillators at interstitial H sites. For both the lattice vibrations at the \( \Gamma \) point and the local vibrations, one can observe transitions from the ground state, the quantum-mechanical zero-point vibration of the H atoms, to the first excited states, e.g. by measuring optic phonon excitations, and transitions to higher excited states.

Their energies, intensities and symmetry splittings yield an insight into the shapes of the potential and the wavefunctions for the vibrations of the light particles (Elsasser et al., 1998).

**Fig. 3.9** INS spectra for NiMg\(_2\)H\(_4\) (1\(^{st}\) and 2\(^{nd}\) hydrogenation cycles) and for two samples containing CuLi\(_{0.08}\)Mg\(_{1.92}\) (triangles correspond to a sample also contained Cu\(_2\)Mg and the circles correspond to sample that contained Cu\(_2\)Mg and CuMg\(_2\) as well). All samples show the formation of a similar monoclinic structure. As in NiMg\(_2\)H\(_4\), in which Ni is bonded to four atoms of H forming the tetrahedral complex [NiH\(_4\)]\(^4\), Cu is also bonded to four atoms...
of H forming the tetrahedral complex [CuH\textsubscript{4}]\textsuperscript{3-}, which was previously referred on (Yvon & Renaudin, 2005).

We have measured samples of the Cu-Li-Mg-H system by means of INS at FDS, LANSCE, Los Alamos National Laboratory. There is no doubt about the sequence of events; first there is the formation of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{5} (see Fig. 3.9) and then in subsequent cycles the formation of MgH\textsubscript{2}, either for disproportionation of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{5} or from hydrogenation of CuMg\textsubscript{2}.

DSC/TGA experiments show that CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{5} starts desorbing hydrogen at 313 K to 328 K. In this range of temperatures the sample can release up to 1.3 wt.% (results for a isothermal experiment with a sample initially containing approximately 78 wt.% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92} and 22 wt.% of Cu\textsubscript{2}Mg - which does not absorb hydrogen at the temperature and pressure that were used). In Fig. 3.10 it can be seen that 0.5 wt.% of a sample initially containing 61 wt.% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 23 wt.% of CuMg\textsubscript{2} and 16 wt.% of Cu\textsubscript{2}Mg can be released at T < 350 K.

In spite of the fact that there was some visible oxidation during this run, we think it was worth showing this initial desorption. This initial desorption seems to be due to CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{5}. At ~473 K, hydrogen starts to be desorbed at a different rate, probably due to the disproportionation of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{5}, with the formation of MgH\textsubscript{2}, which will start releasing hydrogen at 553-573 K.

Additionally, MgH\textsubscript{2} can be formed upon hydrogenation of CuMg\textsubscript{2}.

**Fig. 3.10** TGA of two samples initially containing approximately 61 wt.% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 23 wt.% of CuMg\textsubscript{2} and 16 wt.% of Cu\textsubscript{2}Mg. Samples were measured after hydrogenation but they are not expected to be saturated in hydrogen prior to the experiment (this figure refers to the same sample composition, where the lower curve seems to have oxidized).
The DSC/TGA results show that the system containing CuLi$_{0.08}$Mg$_{1.92}$ and Cu$_2$Mg can destabilize MgH$_2$ in a more efficient way than Cu$_2$Mg by itself can. In fact, in a DSC experiment in which kinetics must be accounted for, MgH$_2$ will release hydrogen at 553-573 K, which can only be obtained when particles are reduced to nanopowders.

### 3.11 Conclusion

The hydrogen storage world still offers a considerable amount of challenges since no universal solution has been found. Eventually, different solutions will be found to suite different applications.

The Cu-Li-Mg system provides other possibilities for catalytic and destabilization effects yet not fully explored.

There are several techniques that can be employed to study systems containing hydrogen. Nonetheless, Neutron Scattering is a very useful resource, in particular, Neutron Diffraction. In the latter, crystal structure of deuteride phases are directly studied since deuterium can be detected by ND and more accurate results can be obtained either in ex situ and in situ as shown previously.
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Papers on the Cu-Li-Mg system

3.13 A ternary phase in Cu-Li-Mg system

3.14 HT-XRD in the study of Cu-Li-Mg

3.15 Neutron powder diffraction and first-principles computational studies of CuLixMg_{2-x} (x \approx 0.08), CuMg_2, and Cu_2Mg

3.16 Study of the Cu–Li–Mg–H system by thermal analysis

3.17 First Principles Calculations and Experiments to Determine the Hydrogenation Process of Cu-Li-Mg
A ternary phase in Cu–Li–Mg system∗

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Abstract

A previous study on Cu–Li–Mg system pointed out the existence of Cu8Li2Mg15, with an orthorhombic structure. The authors of the present paper also detected the existence of a ternary phase similar to the one mentioned. Due to some doubts on the phase’s structure, a study of Cu–Li–Mg was focused in an area near to the composition of that phase. SEM/EDS measurements of the phases’ compositions in equilibrium, as well as XRD paper also detected the existence of a ternary phase similar to the one mentioned. Due to some doubts concerning its structure still prevailed. This work was developed to confirm the crystal structure and the lattice parameters of that phase, as well as, determining the crystal structure.

A comparison between Cu–Li–Mg and H–Mg–Ni systems was established because, even if NiMg2 presents, at room temperature, a hexagonal structure with space group P6 22 (1 8 0), and lattice parameters a = b = 0.5260 nm, and c = 1.3649 nm. The structure was refined by Rietveld method; a Bragg reliability factor R B = 6.36% was obtained. Similarities between CuMg2−xLi x (x ≈ 0.11) and NiMg2 (H, D)x (x ≈ 0.3) structures are detailed.

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Keywords: Intermetallics; Crystal structure; Phase diagram; X-ray diffraction; Scanning electron microscopy

1. Introduction

Cu–Li–Mg system has not been, up to now, object of many studies although it is one of the ternaries of the Al–Cu–Li–Mg system which has been deeply studied, at least near the quasicrystalline T2 (Al6Li3Cu) phase, and which has many applications in the aeronautical industry.

Mel’nik et al. [1] referred the existence of a ternary phase in the Cu–Li–Mg system: Cu8Li2Mg15 with orthorhombic structure (a = 0.524 nm, b = 0.899 nm, and c = 5.433 nm). In a previous work, the present authors pointed out the existence of a phase with a stoichiometry close to that of Cu8Li2Mg15, but some doubts concerning its structure still prevailed. This work was developed to confirm the crystal structure and the lattice parameters of that phase, as well as, determining the crystal structure.

A comparison between Cu–Li–Mg and H–Mg–Ni systems was established because, even if NiMg2 presents, at room temperature, a hexagonal structure with space group P6 22 [2], and CuMg2 an orthorhombic structure with space group Fd d d d [3], the solid solution of hydrogen in NiMg2, NiMg2 (H, D)x (x ≈ 0.3) [4–8], and CuMg2−xLi x seem to have the same space group P6 22 and very similar lattice parameters: a = b = 0.5256 nm and c = 1.3435 nm for NiMg2 (H, D)x (x ≈ 0.3), and a = b = 0.5260 (1) nm and c = 1.3649 (1) nm for CuMg2−xLi x (x ≈ 0.11). Furthermore, metallic sublattices of NiMg2 (H, D)x (x ≈ 0.3) and CuMg2−xLi x (x ≈ 0.11), NiMg2 and CuMg2, respectively, are isostuctural.

2. Experimental

For this study, the alloys (Table 1 and Fig. 1) were prepared in Baikov Institute of Metallurgy from Cu > 99.97%, Li > 99.8% and Mg > 99.96% pure elements. The alloys melting was performed in a resistance furnace using alumina crucibles under a flux, consisting of a salt mixture of 75% LiCl + 25% LiF, in order to prevent oxidation of the melt and Li losses during processing. The melting was initialized by Mg; Cu and Li were added to the Mg bath. After smelting, the molten alloys were stirred and cast into a stainless steel mould; small ingots of 15 mm in diameter and 110 mm in length were obtained.

Chemical composition of the samples was also determined in Baikov Institute of Metallurgy. Li was analysed by flame emission spectrometer using a Varian – Switzerland spectrometer (model V-875). Cu was analysed by atomic-emission spectroscopy with inductive plasma (Jobin Yvon, model JY-38 plus); Mg content was obtained by difference. Ingots were cut into ~10 g samples which were homogenised at 673 K for 3 h, using alumina crucibles, under an Ar atmosphere.

All samples were studied by SEM/EDS in a JEOL JFM 6301 F. Li could not be detected directly by EDS; its content was determined by difference [8].

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Table 1
Chemical composition (in atomic fraction) of the studied samples of the Cu–Li–Mg system

<table>
<thead>
<tr>
<th>Samples</th>
<th>x(Cu)</th>
<th>x(Li)</th>
<th>x(Mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.313</td>
<td>0.032</td>
<td>0.655</td>
</tr>
<tr>
<td>2</td>
<td>0.304</td>
<td>0.056</td>
<td>0.640</td>
</tr>
<tr>
<td>3</td>
<td>0.312</td>
<td>0.066</td>
<td>0.622</td>
</tr>
<tr>
<td>4</td>
<td>0.355</td>
<td>0.067</td>
<td>0.578</td>
</tr>
<tr>
<td>5</td>
<td>0.290</td>
<td>0.096</td>
<td>0.614</td>
</tr>
</tbody>
</table>

Fig. 1. Isothermal section, at room temperature (293 K), of the Cu–Li–Mg system [8]. The symbols represent the compositions of the studied samples as well as of CuMg2Li( x ≈ 0.34) and CuMg2−xLi x ( x ≈ 0.11).

Fig. 2. Microstructure of sample 4 (magnification 500×, energy 15 keV)—Cu2Mg: light grey and CuMg2−xLi x ( x ≈ 0.11): medium grey (sample’s micro porosity: dark grey).

Fig. 3. Microstructure of sample 1 (magnification 500×, energy 15 keV)—Cu2Mg: light grey and CuMg2−xLi x ( x ≈ 0.11) + CuMg2: medium grey (sample’s micro porosity: dark grey).

Fig. 4 is a zoom of the obtained XRD pattern (2θ = 10°–90°).

Indexing results for CuMg2−xLi x pointed out a hexagonal cell. The best fit was obtained with Dicvol (figures of merit M(20) = 50.8 and F(20) = 47.7) and with McMaille (figures of merit M(20) = 40.7 and F(20) = 40.5).

It was used Checkcell for obtaining the “best solution” for the space group, based on the ratio between the observed and the calculated peaks for a particular cell/space group combination.

3. Results and discussion

Table 2 presents the crystallographic data for sample 4 and, for comparison, the crystallographic data of NiMg2(H, D) x (with x ≈ 0.3); Fig. 4 is a zoom of the obtained XRD pattern (2θ = 10°–90°).

Indexing results for CuMg2−xLi x pointed out a hexagonal cell. The best fit was obtained with Dicvol (figures of merit M(20) = 50.8 and F(20) = 47.7) and with McMaille (figures of merit M(20) = 40.7 and F(20) = 40.5).

It was used Checkcell for obtaining the “best solution” for the space group, based on the ratio between the observed and the calculated peaks for a particular cell/space group combination.
Fig. 4. Zoom of the XRD pattern for sample 4. Reflections of CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$) (not assigned) and Cu$_2$Mg phases.

The space groups obtained for the “best solution” were those for which there were no extinguished reflections due to the lattice type, although there were limiting reflections due to the space group symmetry corresponding to $0 0 l$ with $l = 3n$. $P 6_22$ space group was in the assigned group.

Another method, Le Bail method implemented on FullProf software, was used for obtaining the space group: it was realized an extraction of intensities in a space group without extinctions ($P 6_22$). Extracted intensities were very carefully checked in order to determine systematic extinctions if any. The visual examination of a zoomed part of the pattern showing the refinement results was essential for concluding to the absence or presence of a reflection. For the obtained space groups, extracted structure factors were calculated. If the cell was false, this step of extracting structure factors would reveal it by a very bad correspondence between the observed and cell-constrained calculated patterns.

The space group was found to be $P 6_22$ (1 8 0) (Tables 2 and 3) and the corresponding structure was refined, as previously mentioned, using the Rietveld method also implemented in Fullprof.

A Rietveld refinement was carried out between 17$^\circ$ and 115$^\circ$ ($2\theta$). Although the refinement of the structure of the Cu$_2$Mg phase was not the aim of this work, it was done together with CuMg$_{2-x}$Li$_x$, only by control reasons, during the process. CuMg$_{2-x}$Li$_x$ and Cu$_2$Mg were refined out of 133 and 21 reflections, respectively; five reflections (with $I/I_0 < 1$) were discarded due to the contribution (compare Fig. 7 with Fig. 4) of some impurities present in low contents.

For Cu$_2$Mg, with Cu (Wyck = 16d) for $x = y = z = 1/2$, and Mg (Wyck = 8a) for $x = y = z = 1/8$, it was obtained, after the above mentioned Rietveld refinement for control, a Bragg reliability factor $R_B = 7.34\%$.

NiMg$_2$ and CuMg$_2$ metallic sublattices were found to be isostructural.

Several alternatives were tried for possible Li positions on the ternary phase studied:

(I) $(x, y, z)$ Wyck = 12k, with $x = 0.031 (1) \text{ nm}$, $y = 0.018 (1) \text{ nm}$, $z = 0.0515 (3) \text{ nm}$ and $B_{iso} = 0.0213 (4) \text{ nm}^2$;

(II) $(1/2, 0, z)$ Wyck = 6f, with $z = 0.01081 (1) \text{ nm}$, $B_{iso} = 0.0106 (4) \text{ nm}^2$ (with Li occupying Mg$_1$ atomic positions).

---

Table 2
Crystallographic data for CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$) (on sample 4) and for NiMg$_2$(H, D)$_x$ ($x \approx 0.3$), from Ref. [22], obtained by neutron diffraction (converted to Cu K$_{\alpha_1}$ in (PDF-2 01-085-0910, 1997))

<table>
<thead>
<tr>
<th>$hhk$</th>
<th>$d$ (nm) calc. for CuMg$_{2-x}$Li$_x$</th>
<th>$I/I_0$ obs. by XRD</th>
<th>$I/I_0$ obs. for NiMg$_2$ (H, D)$_x$ from [5] converted in Ref. [22]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 0 0</td>
<td>0.4556 (7)</td>
<td>18.7</td>
<td>20.3</td>
</tr>
<tr>
<td>0 0 3</td>
<td>0.4550 (7)</td>
<td>65.4</td>
<td>59.2</td>
</tr>
<tr>
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<td>0.4321 (6)</td>
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<td>31.2</td>
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<td>1 0 2</td>
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<td>14.3</td>
</tr>
<tr>
<td>1 0 3</td>
<td>0.3219 (3)</td>
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<td>1.6</td>
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<td>4.1</td>
</tr>
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<td>3.8</td>
<td>1.7</td>
</tr>
</tbody>
</table>

The $d$-spacings were determined from the best fitting of the raw data using the appropriate structural model.
(III) \((1/2, 0, z)\) Wyck = 6f (with Li occupying Mg\(_1\) atomic positions) and \((x, 0, 1/2)\) Wyck = 6h;
(IV) \((x, y, z)\) Wyck = 12k and \((x, 2x, 1/2)\) Wyck = 6j;
(V) \((1/2, 0, z)\) Wyck = 6f (with Li occupying Mg\(_1\) atomic positions) and \((x, 2x, 1/2)\) Wyck = 6l (with Li occupying Mg\(_2\) atomic positions).

Options I, III and IV are the same as those for hydrogen in \(\text{NiMg}_2(\text{H, D})_x\) \((x \approx 0.3)\) [4].

The best reliability factors and the most stable parameters were obtained with alternatives I and II (Table 3).

Final results of Rietveld refinement for \(\text{CuMg}_2Li_x\) \((x \approx 0.34)\) – I and \(\text{CuMg}_2Li_x\) \((x \approx 0.11)\) – II were obtained at the same time as Le Bail fit was being performed on \(\text{Cu}_2\text{Mg}\).

From SEM/EDS and XRD experiments, it can be concluded that samples 4 and 5 belong to the two-phase region:
Cu$_2$Mg + CuMg$_2$Li$_x$ (Figs. 2, 4 and 5); on the other hand, the three remaining samples are located in the three-phase region Cu$_2$Mg + CuMg$_{2-x}$Li$_x$ + CuMg$_2$ (Figs. 3 and 6). These observations are more consistent with a ternary compound's stoichiometry like CuMg$_2$Li$_x$ ($x \approx 0.34$) – I than with one like CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$) – II (Fig. 1).

Results from SEM/EDS of the relation $x$(Mg)/$x$(Cu), for the present samples and for those that were studied in Ref. [19], lead to the conclusion that $x$(Mg)/$x$(Cu)$_{av.} = 1.87$ which is more in agreement with the presence of a phase with stoichiometry CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$) – II.

The average content of Li in the phase in study, $x$(Li)$_{av.} = 0.04$ (from SEM/EDS results), has to be considered carefully because Li was obtained by difference, as detailed in Ref. [8].

In the refinement of the structure of Cu–Li–Mg ternary’s phase, the best reliability and the most stable parameters concerning Li position were obtained for ($x$, $y$, $z$) Wyck = 12k corresponding to CuMg$_2$Li$_x$ ($x \approx 0.34$) – I (Table 3). Neverthe-

### Table 3

Details of the refinement of the structure of CuMg$_2$Li$_x$ ($x \approx 0.34$) – I and CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$) – II

<table>
<thead>
<tr>
<th>Formula sum</th>
<th>CuMg$_2$Li$_x$ ($x \approx 0.34$)</th>
<th>CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula weight (g/mol)</td>
<td>Mg$_2$Cu$<em>x$J$</em>{2.046}$</td>
<td>Mg$<em>{L(1.036)}$Cu$</em>{x}$J$_{0.673}$</td>
</tr>
<tr>
<td>Crystal system</td>
<td>hexagonal</td>
<td>hexagonal</td>
</tr>
<tr>
<td>Space group</td>
<td>P 6$_3$ 2 2</td>
<td>P 6$_3$ 2 2</td>
</tr>
<tr>
<td>Unit cell length, nm</td>
<td>$a = b = 0.5260$ (1), $c = 1.3649$ (1)</td>
<td>$a = b = 0.5260$ (1), $c = 1.3649$ (1)</td>
</tr>
<tr>
<td>V (nm$^3$)</td>
<td>0.32707 (9)</td>
<td>0.32708 (9)</td>
</tr>
<tr>
<td>Z</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>$\rho_{calc}$ (g/cm$^3$)</td>
<td>3.489</td>
<td>3.360</td>
</tr>
<tr>
<td>Radiation type</td>
<td>CuK$\alpha_i$</td>
<td>CuK$\alpha_i$</td>
</tr>
<tr>
<td>Wavelength (nm)</td>
<td>0.154056</td>
<td>0.154056</td>
</tr>
</tbody>
</table>

**Atomic parameters**

CuMg$_2$Li$_x$ ($x \approx 0.34$)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Biso (nm$^2$)</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg1</td>
<td>1/2</td>
<td>0</td>
<td>0.1089 (1)</td>
<td>0.0190 (4)</td>
<td>1</td>
</tr>
<tr>
<td>Mg2</td>
<td>0.1657 (3)</td>
<td>0.3313 (7)</td>
<td>0</td>
<td>0.0155 (5)</td>
<td>1</td>
</tr>
<tr>
<td>Cu1</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>0.0125 (3)</td>
<td>1</td>
</tr>
<tr>
<td>Cu2</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0.0097 (3)</td>
<td>1</td>
</tr>
<tr>
<td>Li</td>
<td>0.31 (1)</td>
<td>0.18 (1)</td>
<td>0.515 (3)</td>
<td>0.0213 (4)</td>
<td>0.17 (1)</td>
</tr>
</tbody>
</table>

CuMg$_{2-x}$Li$_x$ ($x \approx 0.11$)

<table>
<thead>
<tr>
<th>Atom</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Biso (nm$^2$)</th>
<th>occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg1</td>
<td>1/2</td>
<td>0</td>
<td>0.1081 (1)</td>
<td>0.0105 (4)</td>
<td>0.894 (2)</td>
</tr>
<tr>
<td>Mg2</td>
<td>0.1631 (4)</td>
<td>0.3261 (7)</td>
<td>0</td>
<td>0.0191 (4)</td>
<td>1</td>
</tr>
<tr>
<td>Cu1</td>
<td>0</td>
<td>0</td>
<td>1/2</td>
<td>0.0126 (3)</td>
<td>1</td>
</tr>
<tr>
<td>Cu2</td>
<td>1/2</td>
<td>0</td>
<td>1/2</td>
<td>0.0122 (3)</td>
<td>1</td>
</tr>
<tr>
<td>Li</td>
<td>1/2</td>
<td>0</td>
<td>0.1081 (1)</td>
<td>0.0106 (4)</td>
<td>0.106 (2)</td>
</tr>
</tbody>
</table>

**Bond distances (nm)**

CuMg$_2$Li$_x$ ($x \approx 0.34$)

| Mg1  | Li  | 2x  | 0.17698 (2) | Mg1/Li | Cu1 | 2x  | 0.27489 (5) |
| Cu1  | 2x  | 0.27456 (5) | Mg1/Li | Cu2 | 2x  | 0.27489 (3) |
| Cu2  | 2x  | 0.27456 (3) | Mg2   | Cu1 | 2x  | 0.27170 (2) |
| Li   | 2x  | 0.29244 (4) | Mg2   | Cu2 | 2x  | 0.27443 (2) |

Mg2

| Mg1  | Li  | 2x  | 0.29738 (2) | Mg1/Li | Mg2 | 1x  | 0.29514 (2) |
| Cu1  | 2x  | 0.27300 (2) | Mg2   | Cu1 | 2x  | 0.26302 (5) |
| Cu2  | 1x  | 0.27375 (2) | Mg2   | Cu2 | 2x  | 0.27170 (2) |
| Cu2  | 1x  | 0.29418 (2) | Mg1/Li | Cu2 | 4x  | 0.27489 (5) |
Table 3 (Continued)

<table>
<thead>
<tr>
<th>Refinement</th>
<th>Cu1</th>
<th>Li</th>
<th>x</th>
<th>0.14301 (2)</th>
<th>Cu2</th>
<th>2x</th>
<th>0.26302 (5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2</td>
<td>2x</td>
<td>0.26302 (5)</td>
<td>Mg2</td>
<td>4x</td>
<td>0.27443 (2)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

For Cu1-Mg1 and Cu1-Mg2 data on Mg1-Cu1 and Mg2-Cu1, respectively.

Cu2 | Li  | 4x  | 0.17027 (3) |

For Cu2-Cu1, Cu2-Mg1 and Cu2-Mg2 data on Cu1-Cu2, Mg1-Cu2 and Mg2-Cu2, respectively.

Li  | Li  | 1x  | 0.16928 (3) |
| Li  | 1x  | 0.23415 (4) |
| Li  | 1x  | 0.28309 (5) |
| Li  | 1x  | 0.29309 (5) |
| Li  | 1x  | 0.29829 (6) |

For Li-Cu1, Li-Cu2, Li-Mg1, and Li-Mg2 data on Cu1-Li, Cu2-Li, Mg1-Li, and Mg2-Li, respectively.

Data collection

Diffractometer | Philips X’Pert Pro MPD
Monochromator type | primary beam symmetrical Ge (111) – Johansson
Filter (for Kβ suppressing) | Ni
2θ range | 5°–120°
Step size | 0.01°
Time per step (s) | 10

Refinement

Number of observations | 14374
Number of contributing reflections | 133
Number of refined profile parameters | 12
FWHM (2θ) | 0.05° to 0.15°

CuMgLi, (x = 0.34)

Rp (%) (without background correction) | 9.34
Rwp (%) (without background correction) | 12.4
Rp (%) | 12.8
Rwp (%) | 15.5
Rp (%) | 6.68
Rf (%) | 5.91

CuMg2Li, (x = 0.11)

Rp (%) (without background correction) | 9.34
Rwp (%) (without background correction) | 12.3
Rp (%) | 13.3
Rwp (%) | 15.6
Rp (%) | 6.36
Rf (%) | 6.11

Refinement was done together with Le Bail fit of Cu2Mg (both present in sample 4).
less, bond distances between Cu–Li seem to be rather small (Cu1–Li = 0.143 nm, Cu2–Li = 0.170 nm—Table 3). Hence, this compound was discarded at the last analysis, in spite of the fact that the literature values vary: for Li covalent radius from 0.068 nm [20] to 0.134 nm [21], and for Cu covalent radius from 0.138 nm [21] to 0.152 nm [20], making this last compound (II) as the chosen one (Fig. 8).

4. Conclusions

1. The results for the ternary phase of the Cu–Li–Mg system, when put in comparison with those for NiMg2(H, D)\textsubscript{x} (x ≈ 0.3), seem to confirm the analogy between space groups, lattice parameters and crystal structures of the metallic sublattices (CuMg2 and NiMg2, respectively).

NiMg2 presents, at room temperature, a hexagonal structure (space group \textit{P}6\textsubscript{2}22) and NiMg2(H, D)\textsubscript{x} (x ≈ 0.3) is a solid solution of hydrogen in NiMg2 that preserves the structure of the NiMg2. However, in the Cu–Li–Mg system, CuMg2 has an orthorhombic structure, with space group F\textit{ddd}, with \textit{a} = 0.9044 nm, \textit{b} = 0.5275 nm, \textit{c} = 1.8328 nm and CuMg2\textsubscript{−x}Li\textsubscript{x} is hexagonal, with space group \textit{P}6\textsubscript{2}22. It seems that Li stabilizes CuMg2 into a hexagonal structure.

2. Mel’nik et al., [1] refers the existence of a ternary phase on the Cu–Li–Mg system: Cu\textsubscript{8}Li\textsubscript{2}Mg\textsubscript{15}, with a composition of x(Cu) = 0.34, x(Li) = 0.08 and x(Mg) = 0.60.

Results obtained in this work pointed the existence of a phase CuMg2\textsubscript{−x}Li\textsubscript{x} (x ≈ 0.11) with composition: x(Cu) = 0.333, x(Li) = 0.035 and x(Mg) = 0.632 corresponding to a formula sum Cu\textsubscript{6}Mg\textsubscript{11.367}Li\textsubscript{0.633}.

Acknowledgments

The authors appreciate very much Dr. Armel Le Bail’s contribution on helpful discussions and Dr. M. Hämäläinen’s help for the supply of the samples.

References

HT-XRD in the study of Cu-Li-Mg

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Keywords: powder diffraction (RT and HT), Cu-Li-Mg, DSC/DTA, SEM/EDS

Abstract. In a previous study on Cu-Li-Mg system, the authors of the present paper concluded that the ternary phase in that system corresponds to CuMg₂₋ₓLₓ (x ~ 0.11), with a hexagonal structure, space group \(P\bar{6}22\) (180), and lattice parameters \(a = b = 0.5260\) nm, \(c = 1.3649\) nm [1]. The structure was refined by the Rietveld method [2]. In order to characterize the thermal behaviour of the ternary compound and to assess the Cu-Li-Mg phase diagram [3], HT-XRD measurements were performed on samples whose compositions were close to the one corresponding to the ternary compound. SEM/EDS measurements of the phases’ compositions in equilibrium, as well as DSC/DTA heating curves, contributed to the identification of the transition temperatures and the phases present in equilibrium. It was concluded that the ternary phase decomposes at \(\sim 702 \pm 2\)K.

Introduction

The Cu-Li-Mg system has not been, till now, the object of many studies although it is one of the ternaries of the Al-Cu-Li-Mg system which has been deeply studied, at least near the quasicrystalline T2 (Al₆Li₃Cu) phase, and which has many applications in the aeronautic industry. Mel’nik et al. [4] referred to the existence of a ternary phase in the Cu-Li-Mg system: Cu₈Li₂Mg₁₅ with an orthorhombic structure (\(a = 0.524\) nm, \(b = 0.899\) nm, and \(c = 5.433\) nm). Hämäläinen et al. [3] assessed the phase diagram of the system. Figure 1 presents two vertical sections for \(x(Li) = 0.04\) and \(x(Li) = 0.07\) from the Gibbs energy parameters obtained in [3]. In previous work, the present authors pointed out the existence of a phase with a stoichiometry close to that of Cu₈Li₂Mg₁₅ [5] and, in recent work, the latter phase was defined as being CuMg₂₋ₓLₓ (x ~ 0.11) [1]. Taking into account that there were no experimental data about the thermal behaviour of the ternary phase, nor the high temperature equilibria,
and that quenching seemed ineffective for such a narrow temperature range, some HT-XRD studies were developed.

On the other hand, an important feature for a successful assessment is the crystallographic data; thus the models used to describe the phases should be supported by the phase’s crystal structure.

**Experimental**

**DSC/DTA measurements**

In the first part of this work, thirty samples were prepared in a resistance furnace and their compositions were analysed by AAS [5]. DSC/DTA experiments were performed on samples belonging to the vertical sections \( x_{\text{Mg}} \sim 0.512, x_{\text{Cu}} \sim 0.097, x_{\text{Cu}} \sim 0.039 \) and \( x_{\text{Li}} \sim 0.050 \) of the Cu-Li-Mg system under Ar atmosphere using quasi-hermetic stainless steel crucibles. Figure 1 presents some experimental data and figure 2 shows a DSC/DTA curve for a sample with \( x(\text{Cu}) = 0.088, x(\text{Li}) = 0.19, x(\text{Mg}) = 0.717 \).

In the second part of this work, samples were prepared in order to have compositions close to \( \text{Cu}_{8}\text{Li}_{2}\text{Mg}_{15} \). Those samples were prepared and analysed in a similar way to the previous ones [1].

![Figure 1. Assessed vertical sections of the ternary system Cu-Li-Mg [3]: a) \( x(\text{Li}) = 0.04 \) and b) \( x(\text{Li}) = 0.07 \). Some of the DSC/DTA experimental data are represented by squares.](image-url)

The samples were polished and cleaned in pure ethanol in order to remove the oxide layer and to ensure a flat surface for a better thermal contact between sample and crucible. Experiments took place in a DSC of continuous flux (indeed a DTA) Shimadzu 50 that operates between room temperature and 1003 K, using stainless steel crucibles especially conceived for this propose. Crucibles were quasi-hermetic and the volume of the samples and the inner...
volume of the crucibles were very close. For each composition, at least four cycles of heating/cooling were made, always with four different samples. The heating/cooling rates used were 5, 10 and 20 K/min. Transformation temperatures in figure 1 correspond to a "0 K/min." heating rate.

**SEM/EDS measurements**

SEM/EDS analyses were also performed on each sample, at room temperature and after being annealed for 60 min. at 773 K followed by quenching into liquid N 2. The Li content was found by difference [5]; high quality standards of Cu and Mg were used as patterns. A JEOL, JSM - 35C or JFM 6301 F was used. Figure 2 shows one of the photomicrographs of the samples studied which reveals the presence of a eutectic constituent. In Table 1 it can be seen the obtained EDS results for three of the system’s component phases.

![Figure 2. A DSC/DTA heating/cooling curve for a sample with x(Cu) = 0.088, x(Li) = 0.19, x(Mg) = 0.717, for a heating/cooling rate of 5 K/min. SEM backscatter photomicrograph (x 480) of the same sample after being annealed at 773 K for 60 min. followed by quenching into liquid N 2. Two phases can be distinguished: (Mg) and/or (Li) in black and CuMg 2 in white. Li content was obtained by difference [5].](image)

<table>
<thead>
<tr>
<th>Phase</th>
<th>x(Cu)</th>
<th>x(Li)</th>
<th>x(Mg)</th>
<th>Phase</th>
<th>x(Cu)</th>
<th>x(Mg)</th>
<th>Phase</th>
<th>x(Cu)</th>
<th>x(Mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuLixMg2-x</td>
<td>±0.005</td>
<td>±0.005</td>
<td>±0.005</td>
<td>CuMg2</td>
<td>±0.006</td>
<td>±0.006</td>
<td>Cu2Mg2</td>
<td>±0.005</td>
<td>±0.005</td>
</tr>
<tr>
<td>CuLi,Mg2-x</td>
<td>0.334</td>
<td>0.040</td>
<td>0.626</td>
<td>CuMg2</td>
<td>0.674</td>
<td>0.326</td>
<td>Cu2Mg2</td>
<td>0.669</td>
<td>0.332</td>
</tr>
</tbody>
</table>

**Table 1. SEM/EDS results.** Average contents were obtained from more than twenty measurements. The error associated with the Li content cannot be precisely determined because Li was found by difference.

**RT and HT - powder XRD**

At room temperature, some powder samples were measured on a Philips X’Pert Pro MPD using CuKα radiation (λ = 0.15406 nm) primary monochromated by a symmetric Ge (111) crystal [1]. When those samples were studied at high temperatures, instead of the primary monochromated radiation CuKα, and CuKα (λ = 0.15443nm) were used, because the inten-
sity of the incident/diffracted beam was already attenuated by the protective graphite foil of the heating chamber. Intensity can become crucial when a sample is being heated because the counting time cannot be very high owing to the sample’s reactivity. The heating chamber was an Anton Parr that operates from room temperature to 1473 K. The diffraction pattern in figure 3 was obtained under the same conditions as those for high temperature. Patterns were collected from 5 to 120° (2θ) with steps of 0.01° and a counting time of 10 s.

**Figure 3.** XRD diffraction pattern of CuLi$_{x}$Mg$_{2-x}$ (x ~ 0.11) + Cu$_2$Mg + CuMg$_2$, at 300 K, after Rietveld refinement, of a sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578. (1) observed points, and calculated continuous line, (2) Bragg positions for Cu-Li$_{x}$Mg$_{2-x}$ (x ~ 0.11), Cu$_2$Mg and CuMg$_2$, respectively, (3) difference between observed and calculated patterns.

**Figure 4.** 2D film diffractogram of a sample with x(Cu) = 0.355, x(Li) = 0.067 and x(Mg) = 0.578. Above 573 K CuLi$_{x}$Mg$_{2-x}$ (x ~ 0.11) cannot be distinguished, and above 700 K CuMg$_2$ cannot be distinguished.
Discussion

DSC/DTA results denote the existence of at least three invariant transitions at \( T = 702 \pm 2 \text{ K} \), \( T = 757 \pm 2 \text{ K} \) and \( T = 804 \pm 2 \text{ K} \) (see figures 1 and 2). It seems that CuLi_{x}Mg_{2-x} (\( x \sim 0.11 \)) decomposes at \( T = 702 \pm 2 \text{ K} \), although its peaks couldn’t be distinguished at temperatures above 623 K in the HT-XRD pattern (see figures 4 and 5). SEM/EDS results assisted us to conclude about the nature of the transitions (see figure 2) and to identify the phases in equilibrium. It was very difficult to determine the Li content due to the difficulties pointed out in [5].

FullProf - WinPLOTR software [6] was used to make a Rietveld refinements of the phase CuLi_{x}Mg_{2-x} (\( x \sim 0.11 \)) for the sample with \( x(\text{Cu}) = 0.355 \), \( x(\text{Li}) = 0.067 \) and \( x(\text{Mg}) = 0.578 \) at 300 K, 473 K, 523 K, 573 K and 623 K. At 300 K (see figure 3) the lattice parameters obtained were \( a = b = 0.5262(1) \text{ nm} \) and \( c = 1.3644(1) \text{ nm} \) and \( x \sim 0.08 \) in CuLi_{x}Mg_{2-x} for an \( R_p = 13.4\% \) and \( R_{wp} = 9.71\% \) (conventional Rietveld R-factors), \( \chi^2 = 0.212 \) and \( R_B = 5.36\% \) and \( R_f = 3.91\% \). These results are in close agreement with those obtained in [1]. However, although the sample has the same composition as that analysed in [1], an extra phase (CuMg_2) was detected. A potential explanation for the presence of a third phase in equilibrium relies on the proximity of the sample's composition to the border of the two and three phase domains. The results of the lattice parameters obtained at high temperatures are shown in figure 6. For the other phases in equilibrium, a Le Bail fit was performed.

Even if there is not a straightforward correspondence between the transition temperatures obtained by DSC/DTA and by HT-XRD, HT-XRD allowed us to know what were the phases.
present at different temperatures. The linear thermal expansion parameters were calculated following the obtained lattice parameters (see figure 6) and were found to be, at 300 K, $\alpha_{a=b} = 2.89 \times 10^{-5}$ K$^{-1}$ and $\alpha_c = 3.13 \times 10^{-5}$ K$^{-1}$. As expected, these results are in good agreement with each other.

![Figure 6. Lattice parameters of the phase CuLi$_x$Mg$_{2-x}$ ($x \sim 0.11$) obtained by Rietveld refinement of the diffraction patterns of the sample with $x$(Cu) = 0.355, $x$(Li) = 0.067 and $x$(Mg) = 0.578 at different temperatures.]

Concluding remarks

The Cu-Li-Mg system was studied by DSC/DTA, SEM/EDS and XRD at room and high temperatures. Results are in good agreement and the techniques complemented each other. The crystal structure and the thermal behaviour of CuLi$_x$Mg$_{2-x}$ ($x \sim 0.11$) was studied by HT-XRD which seems to be essential for the phase diagram's assessment.

References

Neutron powder diffraction and first-principles computational studies of Cu$_{1-x}$Mg$_2$\textsubscript{x} (x $\approx$ 0.08), CuMg$_2$, and Cu$_2$Mg

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Pair distribution function

A B S T R A C T

A small addition of Li changes the orthorhombic structure of CuMg$_2$ to hexagonal Cu$_{1-x}$Mg$_2$\textsubscript{x} \textemdash (x $\approx$ 0.08). Determining the Li content of the ternary phase and Li atomic positions was our main objective for this work. For this reason we performed neutron diffraction at several different temperatures below and above room temperature. The results obtained on two neutron powder diffractometers were compared with X-ray diffraction (XRD) data, and with first-principles calculations. The first-principles calculations are in good agreement with Rietveld-refined data from neutron diffraction, but do not show a marked preference for one of several possible Li sites. The pair distribution function (PDF) fitting is consistent with Li substituting only Mg(1/2, 0, z). Interstitial spaces in the structure of CuMg$_2$ and of Cu$_{1-x}$Mg$_2$\textsubscript{x} were also considered, but are unlikely to be occupied by Li. Neutron diffraction data for binary CuMg$_2$ and Cu$_2$Mg were also obtained.

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1. Introduction

Recently, we have solved by X-ray diffraction the structure of the only known ternary phase in the Cu–Li–Mg system [1]. Yet, some details about atoms’ positions were left to be solved and so was the composition of the alloy.

The main reason for studying this system at the time was its relationship to the quaternary system Al–Cu–Li–Mg—a light alloy with possible applications in the transportation industry.

Another motivation for studying the CuLi$_2$Mg$_{2-x}$ alloy is its possible use to store hydrogen [2–4]. Because the phase diagrams of Cu–Mg and Ni–Mg are similar, and because Cu and Ni have similar electronic affinities, it was thought in the sixties that CuMg$_2$ would store hydrogen, too. However this is not the case [5]. NiMg$_2$ has a hexagonal structure (P6$_2$22), but CuMg$_2$ has an orthorhombic structure (Fddd), and this structural difference is assumed to be the reason that NiMg$_2$ stores H$_2$ and forms a hydride, but CuMg$_2$ does not. CuMg$_2$ decomposes into Cu$_2$Mg and MgH$_2$ [5] upon hydrogen loading. As a result of this reaction and since CuMg$_2$ does not form a hydride, CuMg$_2$ was abandoned as a candidate material for hydrogen storage [5,6]. The hexagonal structure of Cu$_{1-x}$Mg$_2$\textsubscript{x} suggested the possibility of using this phase as a hydrogen storage material [2,3] because Cu$_{1-x}$Mg$_2$\textsubscript{x} has the same space group (P6$_2$22) as NiMg$_2$ and NiMg$_2$(H,D)$_{0.3}$ (lattice parameters are almost identical: a=b=5.250 Å and c=13.621 Å (at 300 K) for Cu$_{1-x}$Mg$_2$\textsubscript{x} and a=b=5.256 Å and c=13.435 Å for NiMg$_2$(H,D)$_{0.3}$ [7]). Therefore, we hypothesized that Cu$_{1-x}$Mg$_2$\textsubscript{x} (x $\approx$ 0.08) would be a hydrogen storage material, just like NiMg$_2$—a hypothesis that has been confirmed by now [2–4].

In view of this it became important to determine the structure and composition of Cu$_{1-x}$Mg$_2$\textsubscript{x}. In our previous work [1], two possibilities were raised for the structure and composition of the ternary disordered alloy, Cu$_{1.3}$Mg$_2$, in which Li occupies some of the Wyckoff 12k positions of a P6$_2$22 hexagonal structure) and CuLi$_{0.1}$Mg$_{1.9}$H$_{0.3}$ (in which Mg occupies some of the Mg Wyckoff 6f positions of a P6$_2$22 hexagonal structure). It was not possible to distinguish between these possibilities using X-ray diffraction, owing to the weak scattering of X-rays by Li. While Li is not a strong coherent neutron scatterer, measurements with neutrons coupled to first-principles calculations offer a complementary approach to the determination of the most stable structure and to the most stable composition.

The change of the CuMg$_2$ orthorhombic (Fddd) structure to a hexagonal structure (P6$_2$22) upon addition of a small amount of Li has been firmly established [1]. Isostructural phases to Cu$_{1-x}$Mg$_2$\textsubscript{x} are the hexagonal phase NiMg$_2$ and NiMg$_2$H$_{0.24–0.30}$ [7]. For the NiMg-hydrides, several hydrogen positions were
Table 1
Rietveld refinement’s results at 60, 150 and 300 K obtained from NPD data.

<table>
<thead>
<tr>
<th>T=60 K (NPD)</th>
<th>CuLi0.083Mg1.917</th>
<th>CuMg2</th>
<th>CuMg1.60Sn0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt. Frac.</td>
<td>0.356 (4)</td>
<td>0.426 (4)</td>
<td>0.218 (3)</td>
</tr>
<tr>
<td>CuMg2</td>
<td>Wt. Frac.</td>
<td>Orthorhombic–Fddd (70)</td>
<td>CuMg2</td>
</tr>
<tr>
<td>a=b=5.2476 (3) A; c=13.6193 (9) A;</td>
<td>a=5.2622 (3) A; b=9.0207 (6) A; c=18.310 (1) A;</td>
<td>a=5.2625 (4) A; b=9.0233 (7) A; c=18.309 (1) A;</td>
<td></td>
</tr>
<tr>
<td>Uiso=3.404 g/cm³</td>
<td>Uiso=1.26 (4) A²</td>
<td>Uiso=0.81 (2) A²</td>
<td></td>
</tr>
<tr>
<td>Cu1: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Cu1: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Mg1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg2: x=0.1663 (4); y=0.3326 (9); z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Mg2: x=0.1666 (5); y=0.3313 (1); z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td>Li1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uiso=0.097 (3) A²</td>
<td>Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuMg3</td>
<td>CuMg2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a=b=5.2625 (4) A; b=9.0233 (7) A; c=18.309 (1) A;</td>
<td>a=5.2625 (4) A; b=9.0233 (7) A; c=18.309 (1) A;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uiso=3.404 g/cm³</td>
<td>Uiso=1.26 (4) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu1: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Cu1: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu2: x=0; y=0; z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Mg1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg2: x=0.1663 (4); y=0.3326 (9); z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td>Mg2: x=0.1666 (5); y=0.3313 (1); z=0; occ.=1; Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td>Li1: x=0; y=0; z=0.1123 (2); occ.=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uiso=0.097 (3) A²</td>
<td>Uiso=0.097 (3) A²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: \( \sum = \sum_{i=1}^{n} \) and \( wR_p = \frac{\sum_{i=1}^{n} (\text{obs}_{i} - \text{calc}_{i})^2}{\sum_{i=1}^{n} \text{w}_{i}} \) in which \( \text{obs}_{i} \) is the observed intensity, \( \text{calc}_{i} \) is the calculated one. The weights, \( \text{w} \), are derived from an error propagation scheme.
2. Material and methods

2.1. Synthesis and characterization

The Cu–Li–Mg samples were prepared with a target composition of CuLi 0.10Mg 0.90 and CuLi 0.34Mg 2. They were prepared by mixing stoichiometric amounts of Cu (electrolytic, 99.99% purity, 325 mesh), Mg (99.8% purity, 200 mesh, Alfa Aesar), and small (less than 3 mm wide) pieces of Li (99% purity, Alfa Aesar). Because of the large vapor pressure of Mg, even below its melting point, the reagents were sealed in a stainless steel crucible in a dry box with He atmosphere. This had the added advantage of minimizing possible reagent loss. The samples were heated in a tube furnace with a stirring device to ensure proper mixing of the heterogeneous starting mixture and complete dispersion of Li in the sample. Different reaction temperatures and times were used. Regardless of reaction conditions, the samples, as investigated by XRD, invariably contained Cu 2Mg, CuMg 2, or both (but no pure metals). Nonetheless, we obtained final products containing approximately up to 81.0 wt% (75.6 at%) of CuLi xMg 2/C0 x. Since the structures of Cu 2Mg and CuMg 2 are known (and they are confirmed in this paper), this complication translated merely in the refinement of two additional phases in the neutron powder diffraction pattern.

We studied two samples with very different compositions, both of them containing CuLi xMg 2/C0 x, CuMg 2 and Cu 2Mg: 70.4 at% CuLi xMg 2/C0 x, 21.0 at% CuMg 2, 8.6 at% Cu 2Mg in the first sample and 38.0 at% CuLi xMg 2/C0 x, 44.8 at% CuMg 2, 17.2 at% Cu 2Mg. By means of XRD, we have studied previously a sample with: 75.6 at% of CuLi xMg 2/C0 x and 24.4 at% of CuMg 2 [9].

Samples were first characterized by means of XRD using a Rigaku Ultima III powder diffractometer, and their composition was roughly determined by means of the Match software [10], which uses the “reference intensity ratio method” (RIR-method) [11] to obtain phase fractions. Patterns were collected with CuKα typically from 2θ=15 to 70° with steps of 0.02° and a counting time of 10 s per bin.

2.2. Powder X-ray diffraction measurements

At room temperature, some powder samples were measured on a Philips X’Pert Pro MPD using CuKα1 radiation (λ=0.15406 nm) monochromated by a symmetric Ge (111) crystal [1]. When those samples were studied at high temperatures, instead of the primary monochromated monochromatic radiation, CuKα1 and CuKα2 (λ=0.15443 nm) were used, because the intensity of the incident/diffracted beam was already attenuated by the protective graphite foil of the heating chamber. Intensity can become crucial when a sample is being heated because the counting time cannot be very high owing to the sample’s reactivity. The heating chamber was an Anton Parr that operates from room temperature to 1473 K in vacuum (≤ 10−5 mbar) or in argon atmosphere. Patterns were collected from 5 to 120° (2θ)
with steps of 0.01° and a counting time of 10 s at 303, 473, 523, 573 and 623 K [9]. Results from differential scanning calorimeter (DSC) have shown that CuLi$_{x}$Mg$_{2-x}$ decomposes at approximately 702 K [9].

2.3. Neutron powder diffraction measurements (below room temperature)

Time-of-flight (TOF) neutron diffraction data were collected on the NPDF neutron diffractometer at the Manuel Lujan Neutron Scattering Center at Los Alamos National Laboratory. This instrument is a high-resolution powder diffractometer located 32 m from the neutron spallation target. The data were collected at 60 K (for 7.7 h), 150 K (for 6.4 h) and 300 K (for 6.2 h), at an average proton beam current of 100 μA, using the 46, 90, 119 and 148° banks, which cover a d-spacing range from 0.12 to 7.2 Å. A sample powder with 38.0 at% of CuLi$_{x}$Mg$_{2-x}$, 44.8 at% of CuMg$_2$ and 17.2 at% of Cu$_2$Mg was manually grinded to a diameter of less than 37 μm and placed in a vanadium sample holder in a glove box under He. The vanadium sample holder contribution, at each T, was subsequently removed from the diffraction pattern. The structure was refined using the general structure analysis system (GSAS), a Rietveld profile analysis program developed by Larson and von Dreele [12]. Background coefficients, scale factors, phase fractions, profile function coefficients (sigma-1), sample absorption, atomic positions, lattice parameters, temperature factors, and occupancies (in the case of the phase CuLi$_{x}$Mg$_{2-x}$ and for Mg and Li) were refined for the three phases (whenever applicable) making a total of 81 variables.

For NPDF data, pair distribution function (PDF), G(r), was obtained via the Fourier Transform of the total diffraction pattern as indicated below,

\[
G(r) = 4\pi r \rho(r) - \rho_0 = \frac{2}{r_0} \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ
\]

where \(\rho(r)\) is the microscopic pair density, \(\rho_0\) is the average atomic number density, and \(r\) the radial distance. Q is the momentum transfer \((Q = 4\pi \sin(\theta)/\lambda)\), S(Q) is the normalized structure function determined from the experimental diffraction intensity [13]. PDF yields the probability of finding pairs of atoms separated by a distance \(r\). PDF fittings were performed using the software PDFgui [14].

2.4. Neutron powder diffraction measurements (above room temperature)

Time-of-flight (TOF) neutron diffraction data were also collected on the neutron powder diffractometer (HIPPO) at the Manuel Lujan Neutron Scattering Center at Los Alamos National Laboratory. This instrument achieves very high neutron count rates by virtue of a short (9 m) flight path and large detector solid angle. The data were collected at approx. 313 K (for 1.6 h), 373 K (for 6.3 h), 453 K (for 2 h) and 523 K (for 0.90 h), at an average proton beam current of 100 μA, using the 90, and 144.45° banks, which cover a d-spacing range from 0.12 to 4.80 Å.

A sample powder with 70.4 at% of CuLi$_{x}$Mg$_{2-x}$, 21.0 at% of CuMg$_2$ and 8.6 at% of Cu$_2$Mg was enclosed in an aluminum sample holder to which a resistive heater and a thermocouple was attached. A standard laboratory temperature controller maintained the desired temperature during the measurement. A capillary tube attached to the sample holder allowed for pressure measurements and gas loading during the experiments.

The aluminum sample holder contributes to the diffraction pattern. An aluminum phase was refined in all our data sets. The measured sample (including Al) had: 42.1 wt% (14.6 at%) of CuLi$_{x}$Mg$_{2-x}$, CuMg$_2$ and 57.9 wt% (86.4 at%) of Al. The structure was refined using GSAS. Background coefficients, scale factors, phase fractions, profile function coefficients (sigma-1), atomic number density, and \(r\) were refined for the three phases (whenever applicable) making a total of 81 variables.

For NPDF data, pair distribution function (PDF), G(r), was obtained via the Fourier Transform of the total diffraction pattern as indicated below,

\[
G(r) = 4\pi r \rho(r) - \rho_0 = \frac{2}{r_0} \int_0^\infty Q[S(Q) - 1]\sin(Qr)dQ
\]

where \(\rho(r)\) is the microscopic pair density, \(\rho_0\) is the average atomic number density, and \(r\) the radial distance. Q is the momentum transfer \((Q = 4\pi \sin(\theta)/\lambda)\), S(Q) is the normalized structure function determined from the experimental diffraction intensity [13]. PDF yields the probability of finding pairs of atoms separated by a distance \(r\). PDF fittings were performed using the software PDFgui [14].

**Table 2**

<table>
<thead>
<tr>
<th>T=60 K (NPDF)</th>
<th>R$_{wp}$=18.6%</th>
<th>CuLi$<em>{x}$Mg$</em>{2-x}$</th>
<th>CuMg$_2$</th>
<th>Cu$_2$Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x=0.03 ± 0.04) Hexagonal-P6$_2$22 (180)</td>
<td>a=b=5.250 (2) Å; c=13.666 (7) Å;</td>
<td>a=5.240 (5) Å; b=9.003 (8) Å; c=18.25 (2) Å;</td>
<td>a=5.248 (8) Å; b=9.01 (1) Å; c=18.25 (2) Å;</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T=150 K (NPDF)</th>
<th>R$_{wp}$=17.6%</th>
<th>CuLi$<em>{x}$Mg$</em>{2-x}$</th>
<th>CuMg$_2$</th>
<th>Cu$_2$Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x=0.10 ± 0.04) Hexagonal-P6$_2$22 (180)</td>
<td>a=b=5.258 (3) Å; c=13.67 (1) Å</td>
<td>a=5.248 (8) Å; b=9.01 (1) Å; c=18.25 (2) Å;</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>T=300 K (NPDF)</th>
<th>R$_{wp}$=17.6%</th>
<th>CuLi$<em>{x}$Mg$</em>{2-x}$</th>
<th>CuMg$_2$</th>
<th>Cu$_2$Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x=0.08 ± 0.06) Hexagonal-P6$_2$22 (180)</td>
<td>a=b=5.273 (4) Å; c=13.70 (2) Å</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
<td>a=5.30 (2) Å; b=9.00 (2) Å; c=17.92 (5) Å;</td>
</tr>
</tbody>
</table>

**Fig. 3.** NPDF after Rietveld refinement diffraction pattern at 300 K for 46° bank (the results at the graph are only due to the 46° bank). PDF experimental and fitted.
sample absorption, atomic positions, lattice parameters, temperature factors, and occupancies (in the case of the phase CuLi,Mg_{2-x} and for Mg and Li) were refined for the four phases (whenever applicable) making a total of 63 variables.

3. First principles data

In a solid, where there are upward of $10^{24}$ interacting electrons and nuclei per cubic centimeter, the resolution of the many body Schrödinger equation for the electronic wavefunctions and energy eigenvalues is a big challenge. However, based on the periodicity of the structure of pure elements and perfectly ordered compounds, Bloch’s theorem shows that it is only necessary to solve the many body Schrödinger equation within one unit cell; in the case of disordered compounds that is not the case and it is necessary to solve it within a supercell. The basic information that one wishes to obtain from quantum mechanical calculations in solids is the total electronic energy for various arrangements of atoms on various lattices.

One of the most sophisticated solutions to the quantum mechanical problem in solids lies within the framework of the density functional theory (DFT) [15] using the local density approximation (LDA) [16] or the Generalized Gradient Approximation (GGA) [17]. The basic notion of these theories is to replace the true interacting many-body-system with a system of one electron in an effective potential due to all of the other electrons and nuclei. From a fundamental point of view, the one-electron functions are a unique tool for calculating the total energy and the electronic density of states; these functions have no particular physical meaning. But this simplification of the problem needs a self-consistent calculation and it is one of the major technical problems in the ab initio approach [18].

Density functional theory calculations with projector augmented wave (PAW) pseudopotentials [19], as implemented in the Vienna Ab Initio Simulation Package (VASP) code [20], implemented in MedeA [21], were performed. A plane wave cutoff of 355.18 eV, and $k$-spacings of 0.230 $\times$ 0.230 $\times$ 0.230 Å$^{-1}$ were used. Calculations were done in real space and were performed with PI space group supercells containing 144 atoms (48 atoms of Cu, 96-n of Mg, and n=0 to 12 of Li). The supercells contained as many atoms as possible to allow better approximations with the real Li concentrations (but such that the time spent on calculations were not completely impractical). Since CuLi,Mg_{2-x} is a disordered structure, it had to be obtained by randomly substituting Mg by Li in several Wyckoff 6f positions (1/2, 0, z) or Wyckoff 6i positions (x, 2x, 0) or in both positions within the supercells. The generalized gradient approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) functional [22] were used, and no magnetic moments were included in the model.

The total energy was minimized with respect to the volume (volume relaxation), the shape of the unit cell (cell external relaxation), and the position of the atoms within the cell (cell internal relaxation).

The ab initio calculations furnish the total energy (or the cohesive energy) at $T=0$ K, $E^0$. The energy of formation is easily

$$U_{\text{fro}} = 8 \pi U_{\text{iso}}.$$
calculated by the relation
\[ \Delta E = E_i^0 - \sum x_i E_i^0 \] (2)
where \( E_i^0 \) is the total energy (or cohesive energy) of \( i \) in its stable state at \( T=0 \) K. In the following we will assume that the enthalpy of formation is equal to the energy of formation.

In addition to the total energies, ab initio calculations allowed us to obtain the values of the lattice parameters at 0 K. We performed most of the calculations for \( \text{CuLi}_{x} \text{Mg}_{2-x} \) at least twice (from 1 to 5 atoms of Li calculations were performed three or more times) with different random Li positions.

We also calculated the X-ray diffraction pattern from the \textit{ab initio} results. The code is implemented in MedeA and is based on the LAZY-PULVERIX computer program [23] that calculates the position of the diffraction lines from Bragg’s law and their \( d \)-spacings. The diffraction intensity \( I_{\text{hkl}} \) is calculated as,
\[ I_{\text{hkl}} = MLPF_{hkl}^2 \] (3)
where \( M \) is the multiplicity factor of a powder line, \( L \) is the Lorentz factor and \( P \) is the polarization factor. The structure factor \( F_{\text{hkl}} \) is defined by,
\[ F_{\text{hkl}} = \sum_{\text{unit-cell}} f_j O_j \exp\left[2\pi i (h x_j + k y_j + l z_j) \right] \exp \left(-B_j \sin^2 \theta / \lambda^2 \right) \] (4)
where \( f_j \) is the atomic scattering factor of atom \( j \), \( O_j \) is the occupation factor at site \( x_j, y_j, z_j \) for atom \( j \) and \( B_j \) the Debye-Waller factor in \( \AA^2 \) for atom \( j \).

### Table 3
Rietveld refinement’s results at 313, 373, 453 and 523 K obtained from NPDF data.

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>CuLi&lt;sub&gt;0.09&lt;/sub&gt;Mg&lt;sub&gt;1.91&lt;/sub&gt;</th>
<th>CuMg&lt;sub&gt;2&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>313</td>
<td>hexagonal–P6&lt;sub&gt;3&lt;/sub&gt;2&lt;sub&gt;2&lt;/sub&gt;</td>
<td>orthorhombic–Fddd (70)</td>
</tr>
<tr>
<td>373</td>
<td>hexagonal–P6&lt;sub&gt;3&lt;/sub&gt;2&lt;sub&gt;2&lt;/sub&gt;</td>
<td>orthorhombic–Fddd (70)</td>
</tr>
<tr>
<td>453</td>
<td>hexagonal–P6&lt;sub&gt;3&lt;/sub&gt;2&lt;sub&gt;2&lt;/sub&gt;</td>
<td>orthorhombic–Fddd (70)</td>
</tr>
<tr>
<td>523</td>
<td>hexagonal–P6&lt;sub&gt;3&lt;/sub&gt;2&lt;sub&gt;2&lt;/sub&gt;</td>
<td>orthorhombic–Fddd (70)</td>
</tr>
</tbody>
</table>

\( a=5.254 \pm 0.5 \text{ Å} \); \( b=5.254 \pm 0.5 \text{ Å} \); \( c=13.626 \pm 0.5 \text{ Å} \); \( \rho=3.384 \text{ g/cm}^3 \)

\( a=5.264 \pm 0.5 \text{ Å} \); \( b=9.026 \pm 0.5 \text{ Å} \); \( c=18.31 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.033 \pm 0.5 \text{ Å} \); \( c=18.327 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.076 \pm 0.5 \text{ Å} \); \( c=18.406 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.076 \pm 0.5 \text{ Å} \); \( c=18.406 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.076 \pm 0.5 \text{ Å} \); \( c=18.406 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.076 \pm 0.5 \text{ Å} \); \( c=18.406 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)

\( a=5.262 \pm 0.5 \text{ Å} \); \( b=9.076 \pm 0.5 \text{ Å} \); \( c=18.406 \pm 0.5 \text{ Å} \); \( \rho=3.422 \text{ g/cm}^3 \)
We used the MedeA empty space finder (ESF) [21] to analyze the empty spaces of the CuLi\textsubscript{1-x}Mg\textsubscript{2}/C0\textsubscript{1-x} supercell. The ESF algorithm divides the supercell into so-called Voronoi cells around each atom [24]. A Voronoi cell is defined to be the volume enclosing all points that are closer to the center atom than to all other atoms. The ESF module positions non-overlapping spheres at the vertices of the resulting polyhedral grid and maximizes their radii. In doing so the physical size of different atomic species is taken into account through a set of covalent radii.

4. Results and discussion

4.1. Analysis of the diffraction data

The results from the refined data from NPDF at 60, 150 and 300 K can be found in Table 1 and indicate very good agreement between the experimental and model powder patterns. Phase fractions were varied for each pattern; the difference between the results is less than the refinement error, indicating phase stability over the investigated range of temperatures. The same statement is valid for the Li occupation and atomic parameters for both the Cu\textsubscript{1-x}LiMg\textsubscript{2}/C0\textsubscript{1-x} and CuMg\textsubscript{2} phases. Figs. 1–3 show the diffraction patterns at 60, 150 and 300 K and the Rietveld fits.

Results from PDF fittings at 60, 150 and 300 K can be found in Table 2 and Figs. 1–3. They indicate good agreement between the experimental and fitted curves. The error associated with each parameter obtained by PDF fitting is always higher than obtained with Rietveld, still, for 300 K where this difference is more valuable, the associated errors are $\Delta a/\alpha=0.45\%$ and $\Delta c/c=0.55\%$ (Fig. 4).

In Fig. 4 it can be observed the result of the calculation of the lattice parameters after obtaining the slop of the interplanar distance $d$ (Å) of the peak corresponding to the reflection (101) for Cu\textsubscript{1-x}LiMg\textsubscript{2}/C0\textsubscript{1-x} as a function of temperature using different values for...
a and c at T=0 K. Although this peak, as the other more intense non-overlapping ones, depends on both a and c lattice parameters and thus the extrapolation for a and c temperature dependence is not straightforward, we wanted to ensure that the calculations of the parameters of CuLiMg2−x were not interfering too much with those of CuMg2 since these two phases have many overlapping peaks.

The lattice parameters of the phase CuLiMg2−x and the isotropic thermal parameters seem to depend linearly on temperature (Figs. 4 and 5) between 60 and 300 K.

A harmonic crystal does not undergo thermal expansion since its equilibrium size does not depend on temperature. The thermal expansion of solids is a consequence of the anharmonicity of the lattice vibrations. The earliest approach to lattice vibrations was Einstein’s [25]. He proposed that all the lattice vibrations. The earliest approach to lattice vibrations was Einstein’s [25]. He proposed that all the lattice vibrations to the thermal expansion of solid crystals [27]. The Debye–Waller factors, Biso, that can be obtained from Uiso (Fig. 5), by making Biso=8π2/Uiso were also found to vary linearly between 60 and 300 K; additionally, all atoms seem to behave in a similar way with increasing temperature since the slope of the straight lines in Fig. 5 is very similar.

The results from the refined data from HIPPO at approximately, 313, 373, 453 and 523 K can be found in Table 3 and show good agreement between experimental and model powder patterns. On HIPPO the aluminum sample holder diffracts strongly, and the weight fraction of CuMg becomes relatively low (4–5 wt%). Refinement results for this phase were not included in Table 3 because the isotropic temperature factors became unstable and we were forced to constrain them. Still, the results seem to be very consistent vide, for example, Li occupancy and the atomic parameters for both the CuLiMg2−x and CuMg2 phases. Figs. 6–9 show the diffraction patterns at 313, 373, 453 and 523 K together with the Rietveld fits.

Fig. 4 shows the difference between the XRD data and the neutron diffraction data obtained on HIPPO. Notice that the relative difference between results obtained with X-ray and with neutrons never exceeds 0.4% in the case of a and 0.5% in the case of c. Additionally, the slope of the fitting line between 300 and 523 K seems to be similar in both cases. Small differences between neutron diffraction and X-ray diffraction are expected since these two techniques “see” different constituents of the atom.

The NPDF 300 K results are very similar to the 313 K HIPPO results, which is one more indicator of the results’ coherence.

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**Fig. 10.** First principles (ab initio) calculated enthalpies of formation for a molecule with 144 atoms of the phase CuLiMg2−x, in which 48 atoms are of Cu, 96−n are of Mg and n of Li (x=n/48). It can be observed that the most stable composition corresponds to n between 3 and 4 (x=[0.0625,0.0833]).

**Fig. 11.** Supercell of the phase CuLiMg2−x (x=0) with calculated empty spaces (in light grey: empty spaces, in dark grey: Cu atoms, in red: Mg atoms). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
4.2. Analysis of the first-principles data

We studied the enthalpy of formation of the alloy CuLi,Mg_{2-x} as a function of the number of Li atoms in a supercell with 144 atoms in which 48 atoms are of Cu, 96-n are of Mg and n of Li (x=n/48). The most stable composition (that has the lowest enthalpy of formation) corresponds to n between 3 and 4 (x=0.0625-0.0833) (Fig. 10).

One of the purposes of this work was to determine which structure was more stable: CuLi_{0.33}Mg_{2} (where Li occupies some of the Wyckoff 12k position of a P6_322 hexagonal structure) or CuLi_{0.66}Mg_{2-x} (with x=0.1, in which Li occupies some of the Mg Wyckoff 6f position of a P6_322 hexagonal structure). For that, we have used the minimized structure of a supercell (Fig. 11) with n=0 (x=0; CuMg_{2} with P6_322 hexagonal structure) and with n=4 (x=0.0833; CuLi_{0.0833}Mg_{1.9167} with P6_322 hexagonal structure) and calculated the empty space using the ESF MedeA module (Fig. 11). Results show that in the first case the radii of the empty spaces found are 0.410 Å < r < 0.650 Å and in the second case 0.397 Å < r < 0.666 Å. As the covalent radius of Li is 0.68 Å [31], we do not expect to have Li occupy interstitial sites, even if some atoms of Li substitute the Mg atoms. Still, we have tried to refine the NDPF data at 60 and 150 K for several possibilities that always contained Li atoms in interstitial sites (just in interstitial and both substituting Mg and in an interstitial site) and we have always obtained negative occupancies for these atoms.

Upon using first-principles calculations, it was not possible to determine which Mg sites are occupied with Li (Fig. 10).

In a 2007 article, Zhou et al. [32] calculated the enthalpy of formation of a mole of CuMg_{2}: ΔH = -13.20 KJ/mol within the Fddd space group. In the present work we have obtained for CuMg_{2} with hexagonal structure belonging to the P6_322 space group ΔH = -11.66 KJ/mol, which is consistent with the results of Zhou et al. [32] since the orthorhombic Fddd structure is the stable structure for pure CuMg_{2}. What we expected is that the substitution of Mg by Li would make the Fddd structure the solid solution of CuMg_{2} less stable until CuLi_{0.08}Mg_{1.92} (x=0.08) in the hexagonal P6_322 structure became more stable (note that the difference between the enthalpies of formation is small, of 1.5 KJ/mol of atoms).

In the same article [32] the enthalpy of formation of CuMg_{2} at 298 K was also determined using the CALPHAD method [33]: ΔH = -9.6 KJ/mol (CALPHAD uses experimental results and theoretical models for the structure of the phases and for its Gibbs energies). The experimental value from [34] is ΔH = -9.55 KJ/mol. As the enthalpy of formation of CuMg_{2} will vary from -13.20 KJ/mol (T=0 K) to -9.6 KJ/mol (T=298 K), it still seems possible that at room temperature CuLi_{0.08}Mg_{1.92} (x=0.08) in the hexagonal P6_322 structure will be more stable than the orthorhombic solid solution of CuMg_{2} for the same composition of Li. In Fig. 12, the XRD calculated pattern of CuLi_{0.08}Mg_{1.92} is compared with an experimental one for a sample containing both CuLi_{0.08}Mg_{1.92} and Cu_{2}Mg.

5. Summary

Prepared samples were invariably contaminated with Cu_{2}Mg, CuMg_{2}, or both. Nonetheless, the final product contained approximately 81.0 wt% (75.6 at%) of CuLi,Mg_{2-x}, the phase we wanted to study. Thermodynamics is probably responsible for this limitation on sample composition. Indeed, preliminary tests indicate that the final amount of CuLi,Mg_{2-x} material recovered depends (at the very least) on the reaction temperature and (to a lesser extent) on reaction time. We have taken advantage of this fact to extract refined parameters of CuMg_{2} between 60 and 523 K, and of Cu_{2}Mg between 60 and 300 K as well as of CuLi,Mg_{2-x} between 60 and 523 K.

Both neutron diffraction and first-principles calculations indicate that the composition of the ternary compound should be CuLi_{0.08}Mg_{1.92} (x=0.08).

Neither with first-principles calculations, nor with neutron diffraction, was it possible to distinguish between structures where Li substituted Mg at each of its sites individually or at both

![Fig. 12](image-url). Comparison between the diffraction pattern obtained using first principles and the LAZY PULVERIX code implanted in MedeA and XRD obtained at room temperature with a sample powder containing 81.0 wt% (75.6 at%) of CuLi,Mg_{2-x} and 19.0 wt% (24.4 at%) of Cu_{2}Mg. The calculated pattern was obtained for a B_{iso}=1.00 Å² for all the atoms.
sites. The refinement of the diffraction data revealed that the reliability factors did not change much for the three different structures, and nothing unusual happened with the other parameters (such as, for example, the Li occupancy). The calculated enthalpy of formation curve also shows differences for different occupancies of Li for the same number of Li atoms that are within the error bar. Thus we cannot draw any conclusions regarding the substituted Mg sites based on Rietveld refinement and first-principles calculations. The neutron data agrees best with the results of first-principles calculations when Li occupies Mg1 sites (1/2, 0, z). In this case, the Li occupancy corresponds to $x=0.08$ (in CuLi$_{x}$Mg$_{2-x}$) when this value is calculated by means of Rietveld refinement and using first-principles methods. This agreement does not happen for the other possibilities. With PDF fittings we were allowed to go further. PDF does not see the average but the local structure and with PDF all results but those in which Li would substitute Mg1 sites, gave negative occupancies for Li. For Li substituting Mg1 we have obtained an average composition for CuLi$_{x}$Mg$_{2-x}$ ($x=0.07$) which is in agreement with the other obtained results.

By calculating empty space in our structures, we found that it was unlikely that Li can occupy interstitial sites, but we note that it is possible for H to occupy these empty spaces.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.09.010.

References

Abstract  Finite fossil-fuel supplies, nuclear waste and global warming linked to CO2 emissions have made the development of alternative/’green’ methods of energy production, conversion and storage popular topics in today’s energy-conscious society. These crucial environmental issues, together with the rapid advance and eagerness from the electric automotive industry have combined to make the development of radically improved energy storage systems a worldwide imperative.

CuMg2 has an orthorhombic crystal structure and does not form a hydride: it reacts reversibly with hydrogen to produce Cu2Mg and MgH2. However, CuLiMg2-x (x = 0.08) has a hexagonal crystal structure, just like NiMg2, a compound known for its hydrogen storage properties. NiMg2 absorbs up to 3.6 wt% of H. Our studies showed that not only CuLiMg2-x absorbs a considerable amount of hydrogen, but also starts releasing it at a temperature in the range of 40–130 °C. In order to determine the properties of the hydrogenated CuLiMg2-x, absorption–desorption, Differential scanning calorimeter and thermogravimetric experiments were performed. Neutron spectra were collected to elucidate the behavior of hydrogen in the Li-doped CuMg2 intermetallic. Using DFT calculations we were able to determine the best value for x in CuLiMg2-x and compare different possible structures for the CuLiMg2-x hydride.

Keywords  DSC/TG · INS · Mg based alloys · Energy storage · Hydrides

Introduction  Efficient hydrogen storage remains a major technological obstacle toward the development of a hydrogen-based energy economy. Electric and hybrid vehicles use metal hydrides as the negative electrode (instead of cadmium) in their batteries [1, 2]. In fact, metal hydrides are widely used in consumer electronics rechargeable batteries. In Ni–MH, M is an intermetallic compound. The most common one has the AB5 type, where A is a rare-earth mixture (e.g., La, Ce, Nd, Pr) and B is Ni, Co, Mn, and/or Al. Note that LaNi5H6, which is commonly used in batteries, stores only a maximum of 1.4 wt% of H. Another disadvantage of these materials for hydrogen storage is that lanthanides tend to be expensive and heavy.

We are currently investigating the Cu–Li–Mg–H system. The lighter and cheaper metals and our recent discovery that hydrogen can be reversibly stored in these compounds make them a very attractive alternative to lanthanide-based systems.

CuMg2 has an orthorhombic crystal structure and does not form a hydride: it reacts reversibly with hydrogen to produce Cu2Mg and MgH2 [3]. However, CuLiMg2-x (x = 0.08) has a hexagonal crystal structure [4] (ICSD database [5]), just like NiMg2, a compound known for its hydrogen storage properties. NiMg2 absorbs up to 3.6 wt% H (of the hydride’s weight) [6]. In spite of the fact that the percentage of hydrogen absorbed by NiMg2 is enough to propitiate practical applications, the temperature at which the alloy desorbs hydrogen (282 °C (555 K) at 1 bar) is much too high for practical applications.
A comparison between the phase diagrams of the systems Cu–Mg and Ni–Mg shows that these binary systems form compounds with similar stoichiometry. NiMg₂ is formed by peritectic reaction of the elements at 759 °C (1,032 K) and CuMg₂ by congruent melting at 568 °C (841 K). The presence of Li lowers even further the melting point of CuMg₂ [7].

Since the enthalpy of formation of the hydride is related to that of the primary alloy [8], it was hypothesized that Cu₄LiₓMg₂₋ₓ might also be a hydrogen storage material similar to NiMg₂ [9]. Presumably, its advantage would be that it would release hydrogen at a lower temperature (possibly close to room temperature) [10].

Preliminary studies at the Los Alamos Neutron Scattering Center (LANSCE) showed that hydrogen unsaturated samples could desorb up to 4.4–5.3 wt% of hydrogen. Experiments furthermore shown that samples containing CuₓLiₓMg₂₋ₓ will start desorbing hydrogen at a temperature from 40–130 °C where applications are easier to develop. Hence it should be possible to use this alloy with fuel cells or in batteries and hydrogen storage devices.

**Sample preparation**

The Cu–Li–Mg samples were prepared from the pure elements with a target composition of CuₓLi₀.₁Mg₁.₉. They were prepared by mixing stoichiometric amounts of Cu (electrolytic, 99.99% purity, 325 mesh), Mg (99.8% purity, 200 mesh, Alfa Aesar), and granules (approx. 2 × 2 × 3 mm) of Li (99% purity, Alfa Aesar). Because of the large vapour pressure of Mg, even below its melting point, the reagents were sealed in a stainless steel crucible in a dry box (He atmosphere). This eliminated possible reagent loss. The samples were heated in a tube furnace with a stirring device to ensure proper mixing of the heterogeneous starting mixture and complete dispersion of Li in the sample. Different reaction temperatures and times were used (from 450 °C for 24 h to 1,200 °C for 1–2 h). Regardless of reaction conditions, the samples invariably contained Cu₃Mg, CuMg₂, or both. Nonetheless, we obtained final products containing up to 82.5 at% (77.5 wt%) of CuₓLiₓMg₂₋ₓ. Since the structure of Cu₃Mg and CuMg₂ is known as well as their hydrogen storage behaviour; this complication translated merely in the refinement of additional phases in the neutron/X-ray powder diffraction patterns.

Samples were firstly characterized by means of X-ray diffraction (XRD) using a Rigaku Ultima III powder diffractometer, and their composition was roughly determined by means of the Match software, [11] which uses the “Reference Intensity Ratio method” RiR method [12] to obtain phase fractions. Patterns were collected with CuKα radiation with 2θ typically from 15° to 70° with steps of 0.02° and a counting time of 10 s per bin.

**Hydrogen absorption experiments**

A sample with approx. 74 at% of CuₓLi₀.₀₈Mg₂₋₀.₀₈, 20 at% of CuMg₂ and 6 at% of Cu₃Mg was grinded to obtain a powder with particle size of the order of 37 μm. The sample was then studied in a HPVA high pressure absorption analyser [13]. The latter gas adsorption analysers are designed to obtain high pressure adsorption isotherms of gases, such as hydrogen, using the static volumetric method. Two additional samples with ~79 at% of CuₓLi₀.₀₈Mg₁.₉₂ and 21 at% of Cu₃Mg and ~57 at% of CuₓLi₀.₀₈Mg₁.₉₂, 34 at% of CuMg₂ and 9 at% of Cu₃Mg– were measured too, to determine H₂ equilibrium pressure at different temperatures during the absorption process (Fig. 1).

The plot of the natural logarithm of the equilibrium pressure of hydrogen versus 1,000/T in which T is the absolute temperature in Kelvin allows us to understand that to equal equilibrium pressures will correspond very different temperatures when Cu–Li–Mg–H samples (with high initial content of CuₓLi₀.₀₈Mg₁.₉₂) are compared with MgH₂, NiMg₂H₄, or even with Cu₃Mg + 3MgH₂ [13]. Additionally, when the equilibrium pressure, at 200 °C, for a sample containing CuₓLi₀.₀₈Mg₁.₉₂–H is compared with
the equilibrium pressure of a sample containing CuMg₂, at 295 °C, the difference between plateau pressures can be higher than 21 bar [13] (Fig. 1). The latter means that CuLi₀.₀₈Mg₁.₉₂–H will release hydrogen at a much lower temperature.

Calculations of the decomposition temperature can be done, using:

\[ G_{MH} - G_{H_2} = \Delta G = 0 \Leftrightarrow C_{MH}^0 - C_{H_2}^0 - R \cdot T \cdot \ln \left( \frac{P_{eq}}{P_0} \right) = 0 \]  
\[ (1) \]

\[ \Delta G^0 = R \cdot T \cdot \ln \left( \frac{P_{eq}}{P_0} \right) = \Delta H^0 - T \cdot \Delta S^0 \]  
\[ (2) \]

\[ \ln \left( \frac{P_{eq}}{P_0} \right) = \frac{\Delta H^0}{R} \cdot \frac{1}{T} - \frac{\Delta S^0}{R} \]  
\[ (3) \]

For \( P_{eq} = P_0 \Rightarrow T_{dec} = \frac{\Delta H^0}{\Delta S^0} \) (per mol of H₂) \[ (4) \]

in which \( G \) is the Gibbs energy, MH (metal-hydride), \( R \) the ideal gas constant, \( P_{eq} \) and \( P_0 \) is the equilibrium and atmospheric pressure, respectively, \( H^0 \) the enthalpy and \( S^0 \) the entropy when \( P_{eq} = P_0 \).

The previous calculations for the Cu–Li–Mg–H system lead to decomposition temperatures of 400 K (127 °C) for a sample containing −79 at% of CuLi₀.₀₈Mg₁.₉₂ and 21 at% of Cu₂Mg– and of 402 K (129 °C) for a sample containing −57 at% of CuLi₀.₀₈Mg₁.₉₂, 34 at% of CuMg₂ and 9 at% of Cu₂Mg. Cu₂Mg does not absorb hydrogen at the temperatures shown in Fig. 1.

Hydrides stability depends mostly on the enthalpy term (\( \Delta H^0 \)) as \( \Delta S^0 \) is usually around −130 J (mol H₂)⁻¹ K⁻¹, which roughly corresponds to the H₂ molecule losing its translational degrees of freedom upon transformation from the gas phase into the solid state of the hydride. Nevertheless, in this system, \( \Delta S^0 \) is higher than usually but still into the boundaries of the entropy of formation of the hydrides studied in the literature: \( \Delta S(\text{FeTi}) \approx −0.104 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{LaNi}_5) \approx −0.105 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{VH}_2) \approx 0.141 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{PdH}_{0.7}) \approx −0.098 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{CuLiMg-H}) \approx −0.170 \text{kJ/mol H}_2 \); \( \Delta S(\text{CuMg}_2) \approx 0.138 \text{kJ/mol H}_2 \) [15]; \( \Delta S(\text{NiMg}_2) \approx −0.123 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{MgH}_2) \approx −0.135 \text{kJ/mol H}_2 \) [16]; \( \Delta S(\text{NaH}) \approx −0.164 \text{kJ/mol H}_2 \) [16]; \( \Delta S(\text{K}) \approx −0.169 \text{kJ/mol H}_2 \) [16]; \( \Delta S(\text{UH}_3) \approx −0.179 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{TiH}_2) \approx −0.178 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{LiH}) \approx −0.126 \text{kJ/mol H}_2 \) [14]; \( \Delta S(\text{SrH}_2) \approx −0.141 \text{kJ/mol H}_2 \) [16]. \( \Delta S^0 \) is mostly the responsible by the difference between the Cu₂Mg + MgH₂ and the CuLi₀.₀₈Mg₁.₉₂–H desorption temperatures.

For all of the hydrides to be discussed, \( \Delta H^0 \) and \( \Delta S^0 \) are negative, i.e., the hydrogenation reaction is exothermic and the dehydrogenation reaction is endothermic.

**Inelastic neutron scattering**

Time-of-flight (TOF) inelastic incoherent neutron scattering was collected at low temperatures at LANSCE, in FDS.

A sample with approximately 76 at% of CuLi₀.₀₈Mg₁.₉₂ and 24 at% of Cu₂Mg– was loaded with H₂ at 200 °C, at different pressures and loading times, before collecting a neutron vibrational spectrum (cycling treatments were performed over the same sample after each measurement. Between loadings, H₂ pressure was ~1 bar and temperature dropped to room temperature). The sample was loaded: once for 1 h under 36 bar of H₂; twice for 6 h under 100 bar of H₂ and once for 21 h; once for 17 h and 25 min. and twice for 3 h (100 bar).

All data were collected at 10 K. Figure 2 shows the first Inelastic Neutron Scattering (INS) experiment in comparison with measurements of other samples of the same system – 33 at% of CuLi₀.₀₈Mg₁.₉₂, 35 at% of CuMg₂ and 32 at% of Cu₂Mg– and 42 at% of CuLi₀.₀₈Mg₁.₉₂, 32 at% of CuMg₂ and 26 at% of Cu₂Mg- after being submitted to one hydrogenation cycle and of NiMg₂H₄. The latter hydride exhibits the same spectra whatever the hydrogenation treatment used or number of cycles. It seems that the lattice vibrations happen at similar wavenumbers possibly indicating a similar monoclinic structure comprising a [CuH₄]³⁻ anion complex.

INS spectra show that cycling has a strong effect on structure and ion distribution. On the other hand, this effect on the structure can moreover be due to the loading time or to the waiting time (time the sample waited, at ambient pressure, before being measured). In other words, there
might be a phase transition during hydrogen loading/releasing. These results show that during the first loading the structure was monoclinic with the Cu (bonded to H) ion probably occupying C1 sites like in [NiH₄]⁴⁻ in NiMg₂H₄ (monoclinic) [17], and that after 3 and 6 cycles the sample is likely to present a tetragonal structure similar to CoMg₂H₅ in which [CoH₅]⁴⁻ occupies square-based pyramidal C₄v sites [18] or to present an extra phase with a tetragonal structure that can actually be MgH₂ [19] (Fig. 3).

Differential scanning calorimetry (DSC) and Thermogravimetry (TG)

Several samples were analysed by DSC/TG using a Netzsch instrument. Samples were heated from room temperature to 450 °C at 5 and 10 °C/min. Alumina crucibles with lids were used at all times under high-purity argon gas flowing at 27 mL/min. Samples in the form of powder were hydrogenised before measured.

A literature search shows that MgH₂ in form of powder releases hydrogen in DSC instruments at temperatures that vary from the minimum of 325 °C [20] to a maximum of 433 °C [21] (Table 1). Although for MgH₂ the equilibrium desorption temperature (1–4) should be approximately 280 °C (553 K), in DSC the effect of kinetics counts as well, and therefore the lowest temperature found in the literature was 325 °C. Several DSC studies, that aimed to determine at which temperature MgH₂ releases hydrogen, were reported in the literature [20–28] (Table 1). Most of them focus on the effect of a catalyst on the desorption temperature of MgH₂.

One of the studies refers to nanoparticles of CuMg₂ [28]. CuMg₂ is hydrogenised to form MgH₂ and Cu₂Mg (5).

According to Shao et al. [28] nanoparticles of MgH₂ + Cu₂Mg will start releasing H₂ at 409 °C when the sample is at 4 MPa (40 bar) of H₂, while the equilibrium desorption temperature is 385 °C. The same study reports that Mg nanoparticles under the previous conditions desorb hydrogen at 472 °C (Table 1), while the equilibrium desorption temperature is 442 °C [28].

![Fig. 3a INS results show similar spectra for the third hydrogenation cycle for a Cu–Li–Mg–H sample (76 at% of CuLi₀·₀₈Mg₁·₉₂ and 24 at% of Cu₂Mg-loaded at 200 °C, twice for 6 h and once for 21 h under 100 bar of H₂). b INS spectra for MgH₂. After the first hydrogenation cycle results seem to indicate that MgH₂ is formed even in samples that do not contain CuMg₂.](image)

![Table 1 Desorption temperature of MgH₂ (with tetragonal structure), obtained by means of DSC](image)
In addition, the amount of desorbed hydrogen is not only related with the capacity of the hydride, its kinetics, grain size, possible catalysts added, but also with the way powders are milled [21]. Moreover, if the samples are not saturated, the amounts of released hydrogen cannot be compared or controlled.

Results show that hydrogenated samples containing CuLi_{0.08}Mg_{1.92}, start releasing hydrogen at \( T < 50 \degree C \) \( / \) \( 323 K \), then have a second release rate at around \( \sim 200 \degree C \) \( / \) \( 473 K \) and finally a third release rate at about \( \sim 280 \degree C \) \( / \) \( 553 K \) (Figs. 4 and 5). The first and second releases seem to be related with CuLi_{0.08}Mg_{1.92}–H and the third could be due to MgH2 desorption. If this assumption is correct, this means that CuLi_{0.08}Mg_{1.92}–H will disproportionate into other hydrides. Furthermore, if only CuMg2 had contributed for the formation of MgH2 (Fig. 4 mass losses and peaks at 282 and 287 \degree C), the maximum loss in weight percentage of the sample should be \( \sim 0.6 \) wt% since CuMg2 is not present with more than \( \sim 23 \) wt%. The theoretical amount of hydrogen that can be released by CuMg + 3MgH2 (5) is 2.6 wt% in a sample containing 100% of the mixture.

Likewise, if MgH2 desorbs hydrogen at 282 \degree C, then the catalytic effect of CuMg2/Cu2Mg is likely present and in addition a catalytic effect of CuLi_{0.08}Mg_{1.92}–H, CuMg2 samples, without activation process as in the case of this study, reveal that this compound will start absorbing hydrogen at \( \sim 250 \degree C \) [28]. All our samples absorbed hydrogen at 200 \degree C.

Using the total amount of hydrogen released by the sample during heating in Fig. 4 (left), the stoichiometry of CuLi_{0.08}Mg_{1.92}–H can be determined. Nonetheless, the absorption of hydrogen by CuMg2 has to be taken into account, as well as the fact that Cu2Mg will not absorb

![Fig. 4](image1.png)

**Fig. 4** DSC/TG curve of a sample containing 60 wt% of CuLi_{0.08}Mg_{1.92}, 28 wt% of CuMg2 and 12 wt% of Cu2Mg (62 at% of CuMg2 and 10 at% of Cu2Mg) that was hydrogenated at 200 \degree C and of a sample containing 69 wt% of CuLi_{0.08}Mg_{1.92}, 18 wt% of CuMg2 and 13 wt% of Cu2Mg (72 at% of CuMg2 and 10 at% of Cu2Mg) that was also hydrogenated at 200 \degree C. Samples do not seem to be saturated with hydrogen since they still present a peak corresponding to the parent’s phase melting point (426 and 416 \degree C). Nonetheless, XRD patterns of the sample corresponding to the left curve have showed saturation

![Fig. 5](image2.png)

**Fig. 5** DSC/TG curves of different samples from the Cu–Li–Mg–H system that prior from hydrogenation contained the phases and compositions signalized in the figures’ captions. Samples were not saturated with hydrogen and suffered different hydrogenation cycles, at different pressures of H2 and all at 200 \degree C. It can be observed a peak at low temperature (\( T < 50 \) \degree C), at approximately 208–220 \degree C, at 280–300 \degree C and finally the melting point of the parent CuLi_{0.08}Mg_{1.92} at 420–426 \degree C.
hydrogen at 200 °C. We have obtained a value of ~5.3 wt% that corresponds to CuLi_{0.08}Mg_{1.92}H_6 (wH% = 5.2%).

**Ab initio calculations**

Parent phase, CuLi_{0.08}Mg_{1.92}

Density Functional Theory (DFT) calculations with Projector Augmented Wave (PAW) pseudopotentials [29], as implemented in the Vienna Ab Initio Simulation Package code (VASP) [30–32], were performed. A plane wave cutoff of 355.18 eV, and k-spacings of 0.230 × 0.230 × 0.230 Å⁻¹ were used. Calculations were done in real space and were performed with P1 space group supercells containing 144 atoms (48 atoms of Cu, 96-n of Mg, and n = 0–12 of Li). The supercells contained as many atoms as possible to allow better approximations with the real Li concentrations (but such that the time spent on calculations were not completely impractical). Since CuLi_{0.08}Mg_{2–x} is a disordered structure, it had to be obtained by randomly substituting Mg by Li in several 6f Wyckoff positions (1/2, 0, z) or 6i Wyckoff positions (x, 2x, 0) or in both positions within the supercells. The Generalized Gradient Approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) functional [33] were used, and no magnetic moments were included in the model. We have concluded that the stoichiometry that minimizes the energy of formation is CuLi_{0.08}Mg_{1.92}, which is in agreement with the experimental results [34]. Phonon calculations were also implemented and results of the phonon Density of States (DOS) are in agreement with the INS experimental results for the parent phase (Fig. 6).

Using DFT and the same conditions described for the parent phase (with one exception: we did not use supercells), several possible structures of CuMg_{2}H_{x} were optimized. We did not replace Mg with Li because that would mean building a supercell and spend a large computational time. The goal was to obtain a starting point for further studies.

Therefore, since most of the hydrides are cubic structures or structures that can be considered as distortions of a cubic structure [17], we have started calculations with tetragonal and monoclinic structures, similar to that of the hydrides formed by the nearest neighbours of copper in the periodic table and Mg: NiMg_{2}H_{4} and CoMg_{2}H_{5} (e.g., CuMg_{2}H_{4}, as monoclinic C 2/c similar to NiMg_{2}H_{4} structure—low temperature; CuMg_{2}H_{5} as tetragonal P 4/nmm similar to CoMg_{2}H_{5} structure). In Fig. 7 it can be observed that the most stable configuration corresponds to CuMg_{2}H_{5} with a monoclinic C 2/c structure. Using this structure, we have built a supercell and replaced Mg atoms by Li atoms in three different sites of the initial configuration. The new optimized structure is even more stable (ΔE_f = -4 kJ/mol of H$_2$).

Knowing what the most stable structure of the hydride is, is necessary, but not sufficient. To make a statement about what will be the reaction occurring upon hydrogen absorption more information is needed since the compound may disproportionate into other compounds/hydrides like in the case of CuMg$_2$. Nonetheless, when we compare these results with neutron diffraction [12] and inelastic neutron spectroscopy, we observe that it is highly possible that the first structure formed upon hydrogenation is a monoclinic one.

- **Fig. 6** Unweighted phonon DOS spectra, after ab initio, for the CuLi_{0.08}Mg_{1.92} and Cu$_2$Mg crystal structures in comparison with the experimental INS spectrum of a sample containing both phases (without hydrogenation treatments)
- **Fig. 7** Energy of formation of the hydride CuMg$_2$H$_n$ as a function of n (zero point energy was not included), for different types of crystal structures
Conclusions

After analysing the data obtained by hydrogen absorption, inelastic neutron spectroscopy, DSC/TG and first principles calculations we conclude that it is very likely that CuLi$_{0.08}$Mg$_{1.92}$ will react with hydrogen to form CuLi$_{0.08}$Mg$_{1.92}$H$_5$. Nonetheless, according to DSC’s results, it is also clear that the stoichiometry of the product is CuLi$_{0.08}$Mg$_{1.92}$H$_6$.

The monoclinic C 2/c structure for the CuLi$_{0.08}$Mg$_{1.92}$ hydride (or a nearly derived structure) is in agreement with the results obtained both using neutron scattering techniques and first principles calculations.

Additionally, it can be concluded that even in samples that did not initially contain CuMg$_2$, it is clear the presence of MgH$_2$ formed after hydrogen uptake.

In this work it is also clear the role of the Cu–Li–Mg–(H) as a catalyst for both CuMg$_2$ and MgH$_2$ during absorption and desorption.

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First Principles Calculations and Experiments to Determine the Hydrogenation Process of Cu-Li-Mg

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Keywords: Cu-Li-Mg-H, Density Functional Theory (DFT), Phonons, Neutron Scattering

Abstract. Density Functional Theory (DFT) calculations were performed. They were firstly implemented to optimize the structure and refine the stoichiometry of the only ternary compound, \textit{CuLi\textsubscript{0.08}Mg\textsubscript{1.92}} of the Cu-Li-Mg system. Furthermore using DFT, several possible structures of \textit{CuMg\textsubscript{2}H\textsubscript{x}} were optimized. Since most of the hydrides are cubic structures or can be considered as distortions of a cubic structure, we have started calculations for \textit{CuMg\textsubscript{2}H\textsubscript{x}} (x = 4 - 6) with tetragonal and monoclinic structures, similar to those of the hydrides formed by the nearest neighbors of Cu and Mg in the periodic table: \textit{NiMg\textsubscript{2}H\textsubscript{4}} and \textit{CoMg\textsubscript{2}H\textsubscript{5}} (e.g. monoclinic C2/c and tetragonal P4/nmm, respectively). It can be concluded that the most stable configuration corresponds to \textit{CuMg\textsubscript{2}H\textsubscript{5}} with C2/c structure. We have performed several neutron scattering experiments that are in agreement with the first principles calculations.

Introduction

Efficient hydrogen storage remains a major technological obstacle toward the development of a hydrogen-based energy economy. We are currently investigating the Cu-Li-Mg-H system. The lighter and cheaper metals and our recent discovery that hydrogen can be reversibly stored in these compounds make them a very attractive alternative to lanthanide-based systems that still constitute Ni-MH batteries nowadays. Preliminary studies at the Los Alamos Neutron Scattering Center (LANSCE) showed that hydrogen unsaturated samples could desorb up to 4.4-5.3 wt\% of hydrogen. Experiments furthermore shown that samples containing \textit{CuLi\textsubscript{x}Mg\textsubscript{2-x}} (x = 0.08) will start desorbing hydrogen at a temperature from 50 – 130 ºC where applications are easier to develop. Hence it should be possible to use this alloy as a hydrogen storage material for fuel cells, batteries and other hydrogen storage devices.

Experimental Methods

Sample Preparation. The Cu-Li-Mg samples were prepared from the pure elements with a target composition of \textit{CuLi\textsubscript{0.08}Mg\textsubscript{1.92}}. They were prepared by mixing stoichiometric amounts of Cu (electrolytic, 99.99\% purity, 325 mesh), Mg (99.8\% purity, 200 mesh, Alfa Aesar), and small granules (approx. 2 x 2 x 3 mm) of Li (99\% purity, Alfa Aesar). Because of the large vapor pressure of Mg, even below its melting point, the reagents were sealed in a stainless steel crucible in a dry box (He atmosphere). This eliminated possible reagent loss. The samples were heated in a tube furnace with a stirring device to ensure proper mixing of the heterogeneous starting mixture and complete dispersion of Li in the sample. Different reaction temperatures and times were used (from 450 ºC for 24h to 1200 ºC for 1-2 h). Regardless of reaction conditions, the samples invariably contained \textit{Cu\textsubscript{2}Mg}, \textit{CuMg\textsubscript{2}}, or both. Nonetheless, we obtained final products containing up to 82.5 at\% (77.5 wt\%) of \textit{CuLi\textsubscript{x}Mg\textsubscript{2-x}}. Since the structure of \textit{Cu\textsubscript{2}Mg} and \textit{CuMg\textsubscript{2}} is known as well as their hydrogen storage behaviour; this complication translated merely in the refinement of additional phases in the neutron/x-ray powder diffraction patterns. Samples were firstly
characterized by means of x-ray diffraction (XRD) using a Rigaku Ultima III powder diffractometer, and their composition was roughly determined by means of the Match software, [1] which uses the “Reference Intensity Ratio method” (RiR) [2] to obtain phase fractions. Patterns were collected with CuK-alpha typically from 20 = 15 to 70º with steps of 0.02º and a counting time of 10 s per bin.

**Neutron scattering in deuteride and hydride samples.** Time-of-flight (TOF) neutron diffraction data were collected at low and room temperatures on NPDF and HIPD neutron diffractometers at LANSCE.

**Neutron diffraction.** Neutron diffraction was firstly performed in order to characterize the phase CuLi$_{1-x}$Mg$_{2-x}$. Rietveld refinements using GSAS [3] and Pair Distribution Function (PDF) refinements using PDFgui [4] were carried out to characterize the phases present in the samples. Results obtained show that Li will substitute Mg in (1/2,0,z) forming a hexagonal P6$_2$2$_2$ compound CuLi$_{0.08}$Mg$_{1.92}$ with lattice parameters, a = b = 5.250 (1) Å and c = 13.621(1) Å (at T = 300 K). A detailed study of the CuLi$_{0.08}$Mg$_{1.92}$, CuMg$_2$ and Cu$_2$Mg phases of the Cu-Li-Mg system can be found in [5]. Samples of the Cu-Li-Mg-D system were also studied in NPDF and HIPD Fig. 1. Samples were always deuterized at 200 ºC. The sample correspondent to Fig. 1 (left) was deuterized for 55h30min. under 69 bar (D$_2$). Before being deuterized, it had around 38 at% of CuLi$_{0.08}$Mg$_{1.92}$, 45 at% of CuMg$_2$ and 17 at% of Cu$_2$Mg. The sample correspondent to Fig. 1 (right) suffered different hydrogen sorption/desorption cycles before being measured in HIPD; however before being cycled it had around 76 at% of CuLi$_{0.08}$Mg$_{1.92}$, and 24 at% of Cu$_2$Mg. During cycling, the gas pressure was never higher than 100 bar H$_2$/D$_2$. When measured in HIPD, the sample correspondent to Fig. 1 (right) was not fully saturated (parent phases were still present). In the case of this last sample the presence of CuLi$_{0.08}$Mg$_{1.92}$D$_5$ is clear although the compound contributes in a small percentage for the final weight of the sample.

**Inelastic Neutron Scattering.** A sample with 76 at% of CuLi$_{0.08}$Mg$_{1.92}$ and 24 at% of Cu$_2$Mg was loaded with H$_2$ at 200 ºC, at different pressures and with different loading times, before collecting a neutron vibrational spectrum (cycling treatments were performed over the same sample after each measurement. Between loadings, H$_2$ pressure was ~ 1 bar and temperature dropped to room temperature). The sample was loaded:

![Graphs showing neutron scattering data and Rietveld refinement results for different samples.](image)

**Fig. 1** (left) Sample containing around 28 at% of CuLi$_{0.08}$Mg$_{1.92}$, 33 at% of CuMg$_2$, 19 at% of Cu$_2$Mg and 20 at% of MgD$_2$. This sample was not refined with CuLi$_{0.08}$Mg$_{1.92}$D$_5$ since the presence of this phase was too small to make a difference in the refinement. (right) Sample containing around 59 at% of CuLi$_{0.08}$Mg$_{1.92}$, 27 at% of Cu$_2$Mg, 11 at% of MgD$_2$ and 3 at% of CuLiMg$_{0.08}$Mg$_{1.92}$D$_5$. All phases had to be present to allow a reliable Rietveld refinement.
- under 36 bar of H\textsubscript{2} for 1 hour once;
- twice under 100 bar of H\textsubscript{2} for 6 hours and once for 21 h;
- once for 17 h and 25 min. and twice for 3 hours (100 bar).

All data were collected at 10 K. Fig. 2 shows the first and third experiment.

Inelastic neutron scattering (INS) spectra show that cycling has a strong effect on structure and ion distribution. On the other hand, this effect on the structure can moreover be due to the loading time or to the waiting time (time the sample waited, at ambient pressure, before being measured). In other words there might be a phase transition during hydrogen loading / unloading. These results show that during the first loading the structure was monoclinic with the Cu-H, eventually forming [CuH\textsubscript{3}]\textsuperscript{3-} and probably occupying C\textsubscript{1} sites like [NiH\textsubscript{4}]\textsuperscript{4+} in NiMg\textsubscript{2}H\textsubscript{4} (monoclinic) [6], and that after 3 and 6 cycles the sample is likely to present a tetragonal structure similar to CoMg\textsubscript{2}H\textsubscript{5} in which [CoH\textsubscript{4}]\textsuperscript{4+} occupies square-based pyramidal C\textsubscript{4v} sites [7] or a tetragonal structure that can actually be MgH\textsubscript{2} [8].

**Differential scanning calorimetry (DSC) and Thermogravimetry (TG).** Several samples were analyzed by DSC/TG using a Netzsch instrument. Samples were heated from room temperature to 450 °C, at 5 and 10 °C/min. Alumina crucibles and lids were used at all times under high-purity argon gas flowing at 27 ml/min. Samples in the form of powder were hydrogenised before measured.

A literature search shows that MgH\textsubscript{2} in form of powder releases hydrogen in DSC instruments at temperatures that vary from the minimum of 325 °C [9] to a maximum of 433 °C [10]. Although for MgH\textsubscript{2} the equilibrium desorption temperature should be approximately 280 °C (553 K), in DSC the effect of kinetics counts as well, and therefore the lowest temperature found in the literature was 325 °C. Several DSC studies, that aimed to determine at which temperature MgH\textsubscript{2} releases hydrogen, were reported in the literature [9-17]. Most of them focus on the effect of a catalyst on the desorption temperature of MgH\textsubscript{2}.

One of the studies refers to nanoparticles of CuMg\textsubscript{2} [17]. CuMg\textsubscript{2} is hydrogenised to form MgH\textsubscript{2} and Cu\textsubscript{2}Mg (2CuMg\textsubscript{2} + 3H\textsubscript{2} ↔ Cu\textsubscript{2}Mg + 3MgH\textsubscript{2}). According to Shao et al., nanoparticles of MgH\textsubscript{2} + Cu\textsubscript{2}Mg will start releasing H\textsubscript{2} at 409°C when the sample is under 4MPa (40 bar) of H\textsubscript{2} [17], while the equilibrium desorption temperature is 385 °C. The same study reports that Mg nanoparticles under the same previous conditions absorb hydrogen at 472°C, while the equilibrium desorption temperature is 442 °C [17].

![Fig. 2 INS results for two different structures of the CuLi\textsubscript{0.08}Mg\textsubscript{1.92} hydride. Results show different structures depending on the number of cycles / hydrogenation stage.](image_url)

In addition, the amount of desorbed hydrogen is not only related with the capacity of the hydride; it has moreover to do with kinetics, grain size, possible catalysts added, and also with the way powders are grinded [10]. Furthermore, if the samples are not saturated, the amounts of released hydrogen cannot be compared or controlled.
Results show that hydrogenised samples containing CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, start releasing hydrogen at T < 55 °C / 328 K, and have a second release rate at around ~200 °C / 473 K and finally a third release rate at about ~280 °C/553 K. The first and second releases seem to be related with CuLi\textsubscript{0.08}Mg\textsubscript{1.92}-H and the third could be due to MgH\textsubscript{2} desorption. If this assumption is correct, this means that CuLi\textsubscript{0.08}Mg\textsubscript{1.92}-H will disproportionate into other hydrides. Furthermore, if only CuMg\textsubscript{2} had contributed to the formation of MgH\textsubscript{2} (mass losses and peaks at 282 °C in Fig. 3), the maximum loss in weight percentage of the sample should be ~0.6 wt% since CuMg\textsubscript{2} is not present with more than ~23 wt% (the theoretical amount of hydrogen that can be released by Cu\textsubscript{2}Mg + 3MgH\textsubscript{2} is 2.6 wt% in a sample containing 100 % of the mixture).

Likewise, if MgH\textsubscript{2} desorbs hydrogen at 282 °C, then the catalytic effect of Cu\textsubscript{2}Mg is likely present and in addition a catalytic effect of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}-H, since MgH\textsubscript{2} desorption temperature is 43 °C lower than the minimum temperature found in the literature for DSC experiments [9-17] of samples containing 100% of MgH\textsubscript{2}.

![Fig. 3 DSC/TG curve of a sample containing 60.0 wt% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 27.6 wt% of CuMg\textsubscript{2}, and 12.4 wt% of Cu\textsubscript{2}Mg (62.4 at% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 28.2 at% of CuMg\textsubscript{2} and 9.4 at% of Cu\textsubscript{2}Mg) and of a sample containing 68.6 wt% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 18.0 wt% of CuMg\textsubscript{2} and 13.4 wt% of Cu\textsubscript{2}Mg (71.4 at% of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}, 18.4 at% of CuMg\textsubscript{2} and 10.2 at% of Cu\textsubscript{2}Mg) that were hydrogenated at 200 °C beforehand. Samples do not seem to be saturated with hydrogen since they still present a peak corresponding to the parent’s phase melting point (426 °C and 416 °C). Nonetheless, XRD patterns of the sample corresponding to the left curve showed saturation.

On the other hand, the catalytic effects of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}(-H) over CuMg\textsubscript{2} were also present during hydrogen absorption. Hydrogen absorption experiments with nanostructured CuMg\textsubscript{2} samples, without prior activation process as in the case of this study, reveal that this compound will start absorbing hydrogen at ~ 250 °C (5) [17]. All our samples absorbed hydrogen at 200 °C. Using the total amount of hydrogen released by the sample during heating in Fig. 3 (left), the stoichiometry of CuLi\textsubscript{0.08}Mg\textsubscript{1.92}-H can be determined. Nonetheless, the absorption of hydrogen by CuMg\textsubscript{2} has to be taken into account; conversely, Cu\textsubscript{2}Mg will not absorb hydrogen at 200 °C. We have obtained a value of ~ 5.3 wt% that corresponds to CuLi\textsubscript{0.08}Mg\textsubscript{1.92}H\textsubscript{6} (Wt\textsubscript{H}/% = 5.2 %).

**Ab Initio Calculations**

**Parent phase, CuLi\textsubscript{0.08}Mg\textsubscript{1.92}**. Density Functional Theory (DFT) calculations with Projector Augmented Wave (PAW) pseudopotentials [18], as implemented in the Vienna Ab Initio Simulation Package code (VASP) [19], were performed. A plane wave cutoff of 355.18 eV, and k-spacings of 0.230 x 0.230 x 0.230 Å\textsuperscript{-1} were used. Calculations were done in real space and were performed with P1 space group supercells containing 144 atoms (48 atoms of Cu, 96 - n of Mg, and n = 0 to 12 of...
Li). The supercells contained as many atoms as possible to allow better approximations with the real Li concentrations (but such that the time spent on calculations were not completely impractical). Since CuLi$_{1-x}$Mg$_{2-x}$ is a disordered structure, it was obtained by randomly substituting Mg by Li in several 6f Wyckoff positions (1/2,0,z) of the initial hexagonal structure that conducted to the P1 supercells. The Generalized Gradient Approximation (GGA), and the Perdew–Burke–Ernzerhof (PBE) functional [20] were used, and no magnetic moments were included in the model. We have concluded that the stoichiometry that minimizes the energy of formation is CuLi$_{0.08}$Mg$_{1.92}$, which is in agreement with the experimental results [5].

**Hydride phase, CuLi$_{0.08}$Mg$_{1.92}$H$_x$.** Using DFT and the same conditions described for the parent phase (with one exception: we did not initially use supercells), several possible structures of CuMg$_2$H$_x$ were optimized. We did not replace Mg with Li because that would mean building a supercell and spend a large computational time. The goal was to obtain a starting point for further studies.

![Energy of formation of the hydride CuMg$_2$H$_n$ as a function of n, for different types of crystal structures.](image)

$\begin{align*}
\text{Fig. 4} & \quad \text{Energy of formation of the hydride CuMg}_2\text{H}_n \text{ as a function of } n, \\
& \text{for different types of crystal structures.}
\end{align*}$

Therefore, since most of the hydrides are cubic structures or structures that can be considered as distortions of a cubic structure [6], we have started calculations with tetragonal and monoclinic structures, similar to those of the hydrides formed by the nearest neighbours of Cu and Mg in the periodic table: NiMg$_2$H$_4$ and CoMg$_2$H$_5$ (e.g. CuMg$_2$H$_4$ was optimized as monoclinic C 2/c; CuMg$_2$H$_5$ tetragonal P 4/nmm, respectively). In Fig. 4 it can be observed that the most stable configuration corresponds to CuMg$_2$H$_5$ with a monoclinic C2/c structure. Using this structure, we have built a supercell and replaced Mg atoms by Li atoms in three different sites of the initial configuration. The new optimized structure is even more stable (the difference is: $\Delta E_f = -4$ kJ/mol of H$_2$).

Knowing what the most stable structure of the hydride is, is necessary, but not sufficient to make a statement about the reaction occurring upon hydrogen absorption. More information is needed since the compound may disproportionate into other compounds/hydrides like in the case of CuMg$_2$. Nonetheless, when we compare these results with neutron diffraction and inelastic neutron spectroscopy, we conclude that it is highly possible that the first structure formed upon hydrogenation is a monoclinic C2/c.

**Summary**

After analysing the data obtained by neutron diffraction and neutron spectroscopy, DSC and first principles calculations we conclude that it is very likely that CuLi$_{0.08}$Mg$_{1.92}$ will react with hydrogen to form CuLi$_{0.08}$Mg$_{1.92}$H$_5$. Nonetheless, according to DSC’s results, it is also possible that the stoichiometry of the product is CuLi$_{0.08}$Mg$_{1.92}$H$_6$. 

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The monoclinic C2/c structure for the CuLi0.08Mg1.92 hydride is in agreement with the results obtained both using neutron scattering techniques and first principles calculations. Additionally, it can be determined the presence of MgH2, formed after hydrogen uptake, even for those samples that did not initially contain CuMg2. In this work it is also clear the roll of the Cu-Li-Mg-(H) as a catalyst for both CuMg2 and MgH2 during absorption and desorption.

Acknowledgements
The authors would like to acknowledge Portuguese Science Foundation, FCT, for the project (PTDC/CTM/099461/2008 and and FCOMP-01-0124-FEDER-009369). This work has benefited from the use of neutron scattering instruments NPDF, HIPD and FDS at the Lujan Center at Los Alamos Neutron Science Center, funded by DOE Office of Basic Energy Sciences, USA. This work has benefited from the use of 11-beamline at the Advanced Photon Source at Argonne National Laboratory, USA.

References
Chapter 4- Bi-Sn-Zn System
Chapter 4.

Bi-Sn-Zn SYSTEM

4.1. Introduction

Lead and lead-containing compounds are considered toxic substances due to their detrimental effect to the well-being of humans and the environment. Suitable development policy has been implemented by many countries around the world and, in order to protect the environment, the restriction of lead used in industry has been strongly promoted.

In this context, since July 1st, 2006, both the European Union (RoHS — Restriction of Certain Hazardous Substances and WEEE — Waste Electrical and Electronic Equipment Legislations) and the U.S. Environmental Protection Agency have banned the lead-containing electronic products (Islam et al., 2006; Yu et al., 2000).

In order to replace the traditional Sn–Pb eutectic solder alloy by lead-free alternatives great efforts were developed. The Sn–Zn eutectic alloy is the nontoxic Pb-free solder alloy alternative having a melting temperature which is closest to that of the eutectic Sn–Pb alloy (471 K and 456 K, respectively). However, new solder alloys must fulfill a number of other requirements in both economic and physical/chemical points of view. In this context, the melting temperature should be in the same range as that of the traditional Sn–Pb eutectic alloy, strength and integrity should also be similar or superior, and manufacturing costs must be competitive (Garcia et al., 2010). Poor oxidation resistance and embrittlement behavior are the major problems with the Sn-Zn alloys.

In order to overcome these drawbacks, and further enhance the properties of Sn–Zn lead-free solder alloys, a small amount of alloying elements (rare earths, Bi, Ag, Al, Ga, In, Cr, Cu, Sb, Ni, Ge) added into Sn–Zn alloys were selected by many researchers. For example, a small amount of Al, P, Bi, Ga can improve the high-temperature oxidation resistance of Sn-Zn solders remarkably as well as Cr (Zhang et al., 2010).

We have studied the Bi-Sn-Zn as well as the Sn-Zn and Bi-Zn systems, on ambit of the COST 531 and COST MP0602, EU actions, on lead free solders. Our studies contemplated both

The need for new, improved solder alloys and a better understanding of reactions during the soldering process grows steadily as the need for smaller and more reliable electronic products increases. Information obtained from phase equilibria data and thermodynamic calculations has proven to be an important tool in the design and understanding of new lead-free solder alloys.

A wide range of candidate alloys can be rapidly evaluated for proper freezing ranges, susceptibility to contamination effects, and reactions with substrate materials before the expensive process of preparing and testing candidate alloys is initiated (Kattner, 2002). Therefore, the latter was the objective of the above mentioned COST actions that joined researchers from many European countries around the same goal.
4.2. References


Papers on the Bi-Sn-Zn system

4.3 Experimental Phase Diagram of the Ternary Bi-Sn-Zn

4.4 The experimental study of the Bi-Sn, Bi-Zn, and Bi-Sn-Zn System

4.5 Thermodynamic assessment of the Bi–Sn–Zn System

4.6 The Behaviour of the Lattice Parameters in the Bi-Sn-Zn System

4.7 Phase field simulations in miscibility gaps
Experimental Phase Diagram of the Ternary Bi-Sn-Zn

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Keywords: Lead-free solders, Bi-Sn-Zn, DTA/DSC, SEM/EDS, XRD room / high temperature, phase diagram.

Abstract. Bi-Sn-Zn is one of the systems being used as substitute of the traditional lead solders. Therefore a deeper knowledge of its phase diagram is a priority. Due to the lack of data about the thermodynamic properties of terminal solid solutions as well as on their phase boundaries, only binary contributions were utilized and the ternary terms were ignored on the published assessments [1, 2]. Samples corresponding to several vertical sections were prepared and DTA, SEM/EDS and XRD at room and high temperatures were performed. It was concluded that ternary terms should be held in consideration in a future assessment of the system.

Introduction
The known health problem that may arise from the excess of lead in the organism (especially neurological and born malformations) brought the water contamination, with lead, to the list of apprehensions with the ambient [3]. COST – 531 action: “Lead-free Solder Materials” [4] (from EU) has, as main objective, to study some systems (out of lead) that may be used as solders. There are some criteria for the selection of these systems. To select a solder alloy some properties should be measured, namely: melting temperature, wettability, surface tension, viscosity of the liquid alloys at different temperatures, oxidation behavior, thermomechanical fatigue, etc.

Experimental phase diagrams, thermodynamic properties and optimisation of the corresponding phase diagrams (using CALPHAD method) are some of the aims of COST – 531 in which this work is included.

Two references with the optimisation and assessment of the Bi-Sn-Zn system were found in the literature: one from D. V. Malakhov et al. (2000) [1] and another from N. Moelans et al. (2003) [2]. In both references, it was taken into account different parameters for the binaries (Table 2).

Table 1. References of the parameters, for the binaries, used by [1] and [2] in the assessment of Bi-Sn-Zn.

<table>
<thead>
<tr>
<th>Bi-Sn-Zn assessed by [1]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn [5]</td>
<td></td>
</tr>
<tr>
<td>Bi-Sn [6]</td>
<td></td>
</tr>
<tr>
<td>Bi-Zn [7]</td>
<td></td>
</tr>
<tr>
<td>Sn-Zn [8]</td>
<td></td>
</tr>
<tr>
<td>Bi-Sn-Zn (liquid) [1]</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bi-Sn-Zn assessed by [2]</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn [5]</td>
<td></td>
</tr>
<tr>
<td>Bi-Sn [9]</td>
<td></td>
</tr>
<tr>
<td>Bi-Zn [7]</td>
<td></td>
</tr>
<tr>
<td>Sn-Zn [10] – except for the excess Gibbs energy for (Zn) which is from [2]</td>
<td></td>
</tr>
<tr>
<td>Bi-Sn-Zn (liquid) [2]</td>
<td></td>
</tr>
</tbody>
</table>
The experimental data for the ternary Bi-Sn-Zn are not up-to-date, especially those for the phase diagram. For instance, in the references [11, 12], from Wright (1891 and 1892), experimental data aren’t very reliable. The work of Muzzaffar (1923) [13] (measurements of thermal arrests) is the most used (in spite of the lack of information about the liquid miscibility gap, since thermal arrests corresponding to liquid-liquid separation were not observed under the experimental conditions employed). Jänecke’s data from 1937 [14] are also not very reliable since they are not in agreement with the data from the binaries Bi-Sn and Sn-Zn.

**Experimental**

Vertical sections for 5 wt% (Sn), 13 wt% (Sn), 21 wt% (Sn), 40 wt% (Sn) and 60 wt% (Sn) were chosen for this study. The samples were melted in a resistance furnace, under an inert atmosphere, from Bi > 99.8%, Sn > 99.5% and Zn > 99.9% pure elements; their compositions were confirmed by XRF (X-ray fluorescence) and atomic absorption spectroscopy. Samples with ~ 20 mm of diameter, ~ 3 mm high and ~ 2 g were homogenised at 120 ºC for 60 minutes. DTA (differential thermal analysis) / DSC (differential scanning calorimeter) measurements were performed on a TA Instruments SDT 2960 in order to determine the temperatures for the phase transitions. Table 2 presents the composition of the samples and DTA/DSC results. Samples were observed by optical microscopy, as so as by SEM (scanning electron microscopy) / EDS (energy dispersive spectroscopy) on a JEOL JFM 6301 F. Finally, powder XRD (X-ray diffraction) measurements at room and high temperatures were also performed, on a Philips X’Pert Pro MPD, in order to characterize the phases involved on some equilibria.

**Results and discussion**

**Phase diagram.** A database with the assessed Gibbs energy parameters in [1, 2], the Gibbs energy parameters from the binaries (Table 1) and the unary Gibbs energies actualized from [5] was established for the ternary system to be used with the optimisation and assessment software - Thermo-Calc [15] - which was used to compare the new and the available experimental data with the assessed ones (Figs. 1, 2, 3 and 4).

**DTA/DSC measurements.** All samples were measured by means of DTA/DSC with heating rates of 10ºC/min and 5ºC/min. Values on Table 2 were obtained, on heating, at 5ºC/min. Figs.1 a), 2 a) and 3 present some of the results obtained plotted against the calculated phase diagram obtained after [1].

<table>
<thead>
<tr>
<th>wt%Bi</th>
<th>wt%Sn</th>
<th>wt%Zn</th>
<th>Phase diagram’s invariant and liquidus points (ºC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>10.1</td>
<td>57.8</td>
<td>32.1</td>
</tr>
<tr>
<td>2.</td>
<td>18.3</td>
<td>58.8</td>
<td>22.9</td>
</tr>
<tr>
<td>3.</td>
<td>29.6</td>
<td>58.2</td>
<td>12.2</td>
</tr>
<tr>
<td>4.</td>
<td>10.1</td>
<td>40.1</td>
<td>49.8</td>
</tr>
<tr>
<td>5.</td>
<td>23.3</td>
<td>38.3</td>
<td>38.4</td>
</tr>
<tr>
<td>6.</td>
<td>47.6</td>
<td>39.8</td>
<td>12.6</td>
</tr>
<tr>
<td>7.</td>
<td>19.5</td>
<td>4.0</td>
<td>76.5</td>
</tr>
<tr>
<td>8.</td>
<td>53.7</td>
<td>5.0</td>
<td>41.3</td>
</tr>
<tr>
<td>9.</td>
<td>68.4</td>
<td>6.0</td>
<td>25.6</td>
</tr>
<tr>
<td>10.</td>
<td>74.0</td>
<td>11.9</td>
<td>14.1</td>
</tr>
<tr>
<td>11.</td>
<td>55.6</td>
<td>13.7</td>
<td>30.7</td>
</tr>
<tr>
<td>12.</td>
<td>37.9</td>
<td>19.8</td>
<td>42.3</td>
</tr>
<tr>
<td>13.</td>
<td>56.7</td>
<td>12.6</td>
<td>30.7</td>
</tr>
<tr>
<td>14.</td>
<td>51.1</td>
<td>21.4</td>
<td>27.5</td>
</tr>
<tr>
<td>15.</td>
<td>32.3</td>
<td>47.1</td>
<td>20.6</td>
</tr>
</tbody>
</table>
Fig. 1 a) Vertical section of the ternary phase diagram for $w(Sn) = 5\%$. DTA/DSC data for samples 7, 8 and 9. b) Photomicrograph of sample 7 (magnification $\times 500$) at room temperature. Light grey – (Bi), medium grey – (Sn), dark grey – (Zn).

Fig. 2 a) Vertical section of the ternary phase diagram for $w(Sn) = 40\%$. DTA/DSC data for samples 4, 5 and 6. b) Photomicrograph of sample 5 (magnification $\times 500$) at room temperature. Light grey – (Bi), medium grey – (Sn), dark grey – (Zn).

Fig. 3 a) Bi-Sn-Zn at room temperature and its correspondent binaries. Samples from vertical sections in Figs. 1, 2, 3 b) b) Vertical section of the ternary phase diagram for $w(Sn) = 59\%$
SEM/EDS measurements. All samples were analysed on SEM and the composition of each phase determined by EDS. No external standards for the elements were used; the uncertainty associated with each measurement depends on the element but it is lower than 0.5 wt%. In Figs. 1 and 2 it can be seen two of the photomicrographs taken. It was observed that each sample belongs, at room temperature, to the three phase region (Bi) + (Sn) + (Zn), as it could be expected from the observation of the phase diagram (Fig. 3 a). It was also observed that, in spite of what could be expected from the calculated phase diagrams in [1, 2], (Sn) and (Bi) dissolve, in average and at room temperature, \(w(\text{Bi}) = 4.6\, \%\) and \(w(\text{Zn}) = 1.5\, \%\), and \(w(\text{Sn}) = 2.0\, \%\) and \(w(\text{Zn}) = 1.6\, \%\), respectively.

XRD at room temperature. All bulk samples were analysed by XRD at room temperature and all peaks were indexed using PDF–2 database [16]. As expected from the SEM/EDS observations, it could be detected for each phase the presence of (Bi) + (Sn) + (Zn) (Fig. 5).

XRD at high temperatures. Samples 8, 9 and 12 were analysed on XRD from 50 – 150º C, 30 – 180 ºC and 120 – 240º, respectively, with temperature increments of 10 ºC. The (Sn)’s peaks couldn’t be detected at temperatures higher than 120ºC (Fig. 6) since, at this temperature, the peaks were too small due to the eutectic reaction that occurs at 134 ºC. For higher temperatures, it can be detected on the baseline a curve corresponding to the liquid phase; its concavity grows with temperature as the quantity of liquid increases.

Fig. 4 Projection of the liquidus surface for Bi-Sn-Zn. It can be seen inside of the miscibility gap the surface corresponding to the phase boundary Liq + Liq2 / Liq + (Zn). The triangles corresponding to the sample’s composition indicate, in brackets, the temperature in (ºC) of the correspondent liquidus curve, except for those samples which are inside the miscibility gap for which the temperatures in brackets correspond to the phase boundary Liq + Liq2 / Liq + (Zn).

Fig. 5 Diffraction pattern from sample 1, at room temperature.

It can be clearly seen the displacement of the (Zn)’s peak (d = 2.9063 Å), corresponding to the reflection [002], with the temperature increase; this will be a consequence of the enlargement of the distances \(a\) and \(b\) (\(a = b\)) at the hexagonal cell.
Conclusions

Experimental results obtained are in better agreement with [1] than with [2]. Results from DTA/DSC are in agreement, not only with the assessed phase diagram from [1], but also with the experimental data from Muzzaffar (1923) [13] (measurements of thermal arrests) that were on the basis of that assessment. Nevertheless, the eutectic \( L \leftrightarrow (Bi) + (Sn) + (Zn) \) was found at 134 \(^\circ\)C, i.e. 4 \(^\circ\)C higher than in the assessed phase diagram in [1].

Results from SEM/EDS show that solvus surfaces, at room temperature, aren’t in complete agreement with calculated phase diagrams. (Bi) dissolves Sn and Zn and (Sn) dissolves Bi and Zn. Thus (Bi) and (Sn) should be assessed with ternary terms unlike it was done on [1] and [2]. XRD results, at room and high temperatures, are in agreement with what was expected from the phase diagrams. Nevertheless, the search-match for (Sn) indicated that its reflections are slightly shifted from the pure phase. It’s maybe due to a distortion of the cell parameters, probably due to the occupation of some Sn sites by Zn and Bi. The same effect was not so visible on (Bi). A special attention will be paid, in the future, to the behaviour of the plane \([002]\) with temperature increase, namely, near the eutectic ternary reaction where the interatomic distance, \(d\), has a slight decrease contradicting its tendency to increase with temperature.

References

[16] 01-085-1329 (Bi), 03-065-0296 (Sn), 01-087-0713 (Zn), ICDD PDF-2 2003.
The experimental study of the Bi–Sn, Bi–Zn and Bi–Sn–Zn systems


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Abstract

The binary Bi–Sn was studied by means of SEM (Scanning Electron Microscopy)/EDS (Energy-Dispersive solid state Spectrometry), DTA (Differential Thermal Analysis)/DSC (Differential Scanning Calorimetry) and RT-XRD (Room Temperature X-Ray Diffraction) in order to clarify discrepancies concerning the Bi reported solubility in (Sn). It was found that (Sn) dissolves approximately 10 wt% of Bi at the eutectic temperature. The experimental effort for the Bi–Zn system was limited to the investigation of the discrepancies concerning the solubility limit of Zn in (Bi) and the solubility of Bi in (Zn). Results indicate that the solubility of both elements in the respective solid solution is approximately 0.3 wt% at 200 °C.

Three different features were studied within the Bi–Sn–Zn system. Although there are enough data to establish the liquid miscibility gap occurring in the phase diagram of binary Bi–Zn, no data could be found for the ternary. Samples belonging to the isopleths with w(Bi) ~ 10% and w(Sn) ~ 5%, 13% and 19% were measured by DTA/DSC. The aim was to characterize the miscibility gap in the liquid phase. Samples belonging to the isopleths with w(Sn) ~ 40%, 58%, 77/81% and w(Zn) ~ 12% were also measured by DTA/DSC to complement the study of Bi–Sn–Zn. Solubilities in the solid terminal solutions were determined by SEM/EDS. Samples were also analyzed by RT-XRD and HT-XRD (High Temperature X-Ray Diffraction) confirming the DTA/DSC results for solid state phase equilibria.

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Keywords: Bi–Sn–Zn; Bi–Sn; DTA/DSC; SEM/EDS; (RT/HT)-XRD

1. Introduction

Health problems (especially neurological and birth malformations) may arise from an excess of lead in human bodies. The excess of lead is due to water contamination. Hence, lead was added to the list of apprehensions with the environment [1].

The objective of COST 531 action “Lead-free Solder Materials” [2] (European Cooperation in the field of Scientific and Technical Research) is the study of systems that may be used as lead-free solders. The selection of these systems is based on technical and health considerations. The crucial technological properties to be analyzed should be: melting point, wettability, surface tension, viscosity of the liquid alloys at different temperatures, oxidation behavior, thermomechanical fatigue, etc.

The evaluation of experimental phase diagrams, measurement of the thermodynamic properties and consequent optimization of the corresponding phase diagrams (using the CALPHAD method) are some of the aims of the COST 531 action. The work presented here is a part of this effort.

Bi–Sn–Zn is one of the important systems studied in scope of the above mentioned program. For this system there were no data concerning the liquidus surface in the miscibility gap region (corresponding to the phase boundary Liquid/L1 + L2). A work from Muzaffar [3], concluded in 1923, includes only temperature data for the surface corresponding to the phase boundary Liquid + L1/Liquid + (Zn).

The solvus surfaces for (Bi) and (Sn) were also uncertain. These doubts concern mainly the Sn-rich region within the
Bi–Sn binary system. Nagasaki and Fujita [4] experimentally defined a (Sn) solvus curve that was not in good agreement with that from Oelsen and Golücke [5]. Experimental results from Ohtani and Ishida [6] were also in contradiction with those from [4]. Nevertheless, Ohtani and Ishida [6] (contradicting their own experimental results) and Lee et al. [7] used only the experimental data from Nagasaki and Fujita [4] in their thermodynamic assessment.

Concerning Bi–Zn, there was a significant discrepancy between the (Bi) solvus estimated by Massalski [8] and that calculated by Malakhov [9] (few wt% of Zn). Thus, targeted experimental alloys were prepared to determine the solubility of Zn in (Bi).

With the aim of clarifying the above indicated aspects of the binaries and ternary, almost all of the samples were studied by SEM/EDS/WDS (Wavelength-Dispersive crystal Spectrometer), RT-XRD/HT-XRD and by DTA/DSC.

2. Experimental

The Bi–Sn and Bi–Sn–Zn systems were objects of two different studies. One more devoted to phase transitions as well as to temperature measurements and the other to the equilibrium study. Hence, the experimental details were different according to the objective of the study and therefore will be presented in two different sections.

2.1. Phase transitions study of the Bi–Sn system

Eight samples of ∼20 mm diameter, ∼3 mm height and weighing ∼2 g were prepared by mixing pure Bi (>99.8%) and Sn (>99.5%). The samples were then put in alumina crucibles and melted in a resistance furnace under an argon atmosphere. The nominal compositions of the samples were Bi(1 − x)Sn x (x = 12.5, 23.5, 36.5, 74.5, 80.1, 84.9, 89.9 and 95.6, wt%). These were confirmed by X-ray Fluorescence (XRF) and Atomic Absorption Spectroscopy (AAS). All samples were homogenized at 120 °C for 60 min and slowly cooled down to the room temperature at a rate less than 2 °C/min.

Samples were studied by Light Optical Microscopy (LOM) and by SEM in a JEOL JSM 6301 F. The SEM is equipped with an INCA Energy 350 EDS analyzer from Oxford Instruments. A backscattered beam with 15 keV is employed. Internal standards are used for the EDS analysis. The experimental uncertainties of the chemical analysis done by EDS are: Bi ±1.2 wt% and Sn ±0.9 wt%.

The Panalytical X’Pert Pro MPD was used for RT-XRD experiments with bulk samples. CuKα primary monochromated CuKα1 radiations were used to collect patterns from 5° to 120° (2θ) with steps of 0.01° and counting time of 10 s. The powder HT-XRD was not performed due to problems related with the samples’ grinding (the apparatus used only allows powder HT-XRD).

The DTA/DSC measurements were performed on a SETARAM Labsys TG/DTA/DSC in order to establish the transition temperatures. Alumina crucibles were used and measurements were performed under flowing argon atmosphere (approximately 40 cm3 min−1). Alumina also served as the reference material. Samples weighing between 0.1 and 0.2 g were measured at the heating rates of (in °C/min) 10.0, 5.0 and 2.0–2.5. Transition temperatures were found for “0 °C/min”.

The global composition and homogeneity of the samples was checked by SEM/EDS, before and after the DTA/DSC experiments.

2.2. Equilibrium study of the Bi–Sn system

Five alloys have been prepared for the equilibrium study. The samples were prepared by mixing pure Bi (>99.9%) and Sn (>99.9%). The nominal compositions of the samples are Bi(1 − x)Sn x (x = 50, 80, 85, 90 and 95, wt%). Samples were analyzed in a SEM from JEOL JSM 6460. The EDS is from Oxford Instruments and it is equipped with an INCA Energy and Wave. The studies were performed in the back-scattered electron mode with 20 keV. Four of the five samples were also studied by DTA/DSC in a Netzsch DTA/DSC 404. For the latter, samples weighing between 0.1 and 0.2 g were introduced into graphite crucibles. Silver was used as a reference material. The measurements were carried out under flowing argon atmosphere (approximately 40 cm3 min−1).

2.3. Equilibrium study of the Bi–Zn system

The experimental effort was limited to the investigation of the discrepancies concerning the solubility limit of Zn in (Bi) between the theoretical and experimental assessments.

Two alloys were prepared, one with approximately 0.3 wt% Zn and another one with 76.2 wt% Zn. The low Zn content alloy was expected to lie in the single-phase region of the phase diagram, according to the experimental assessment. Nevertheless, according to calculations, it was expected to lie in the two-phase area.

The experimental alloys were melted under an Argon atmosphere in an ERSCEM PV 8920 spill furnace. Samples of approximately 40 g were injected into a copper mould after 20–30 s of stirring.

The low Zn content (approximately 0.3 wt%) alloy was annealed for 336 h at a temperature of 245 °C, just below the eutectic temperature of 254.5 °C. After annealing, the sample was quenched in water and observed by SEM/EDS. The morphology of the sample did not allow the measurement of the composition of the Zn-rich phase. A second alloy was prepared with composition of 23.8 wt% Bi and 76.2 wt% Zn and was therefore cast and annealed at 200 °C for 864 h. This sample was analyzed by SEM/WDS using pure Bi and Zn as standards.

2.4. Phase transitions study of the Bi–Sn–Zn system

Vertical sections for w(Bi) ∼ 10%, w(Zn) ∼ 12%, and w(Sn) ∼ 5%, 13%, 19%, 40%, 59% and 79% were chosen for
this study. The corresponding 29 samples were prepared and annealed like those in Section 2.1. The samples with w(Sn) ~ 77/81% were re-annealed for more than 180 min at 120 °C, and cooled down at a rate of 0.5 °C/min or quenched into water from 120 °C.

Samples were studied by LOM and by SEM/EDS in the same conditions as those mentioned in Section 2.1. The experimental uncertainties for the chemical analysis obtained by EDS are: Bi ±1.2 wt%, Sn ±0.9 wt% and Zn ±1.1 wt%.

Bulk RT-XRD measurements were performed to identify the present phases. For some samples, powder HT-XRD measurements were also performed, under a vacuum of 10⁻⁵ mbar or an argon atmosphere. The furnace used is an Anton Parr Chamber applied to the Panalytical X’Pert Pro MPD (details for the XRD data collection are given in Section 2.1).

DTA/DSC measurements were performed on two heat flux instruments with the possibility of determining the latent heat: a TA Instruments SDT 2960 and a SETARAM Labsys TG/DTA/DSC (mentioned in Section 2.1). Alumina crucibles were used and the measurements were performed under flowing argon atmosphere. A graphite plate was sometimes used at the bottom of the crucible in order to improve the removal of the analyzed sample (especially in the case of those samples whose composition fell over the miscibility gap). Alumina (with a similar shape and weight as the measured samples) was used as reference. The samples were polished and cleaned just before being measured in order to improve thermal contact and to avoid spurious or shifted transition peaks due to oxidation. The heating rates mainly used were 20, 10, 5, 2.5 and/or 2.0 °C/min. Unfortunately, the lower heating rates did not allow the detection of transition temperatures (for example, in the case of liquidus surface of the miscibility gap). Consequently, it was impossible to find the transition temperatures at 0 °C/min by a linear regression. A calibration factor: \( C = b_0 + b_1^\prime T + b_2^\prime R + b_3^\prime R^2 \) (\( T \) — temperature in °C, \( R \) — heating rate in °C/min) was evaluated after performing ten calibrations with five different elements (including pure Sn and Zn). Different heating rates (from 2 to 20 °C/min) were also used for determining the coefficients \( b_0, b_1, b_2 \) and \( b_3 \). The accuracy of all of the given temperatures is ±1 °C. The temperatures of the invariant phase reactions were taken from the extrapolated onset temperatures on heating. The liquidus surface temperatures were taken from the peaks on heating.

After the DTA/DSC measurements, some Bi–Sn–Zn samples were also investigated by SEM/EDS in order to check their compositions.

2.5. Equilibrium study of the Bi–Sn–Zn system

A second set of experiments were carried out in the scope of this study with the aim of reaching states close to the thermodynamic equilibrium and confirming the previous results. Seven samples with nominal compositions (A – Bi35Sn35Zn30, B – Bi20Sn50Zn30, C – Bi10Sn70Zn20, D – Bi18.5Sn45Zn36.5, E – Bi10Sn70Zn20, F – Bi60Sn30Zn10, G – Bi25Sn37.5Zn37.4 and H – Bi25Sn47.6Zn27.4, wt%) were prepared from pure Bi, Sn and Zn (Bi, Sn, Zn > 99.9%, all supplied by Alfa Aesar). The homogeneity of all samples was checked by SEM/EDS (in a JEOL JSM 6460) in the back-scattered electron mode. The microstructure of the samples was, in all cases, found to be reasonably homogeneous in the whole sample volume. Slices of the samples were annealed at two selected temperatures during different intervals of time, before being quenched into cold water. The first set of alloys (A, B and C) was annealed at 100 °C. For a more detailed study and verification of the previously obtained results, a second set of alloys (D, E, F, G and H) was prepared. The annealing temperature for the second set of samples was 120 °C.

SEM/EDS analysis was used to identify the coexisting phases and to measure their compositions (both overall and phase compositions).

Some of the annealed samples were also studied by DTA/DSC (in a Netzsch DTA/DSC 404). The studied samples correspond to compositions that lay in phase regions where the phase equilibria were uncertain. The latter measurements were conducted on samples weighing approximately 0.3–0.4 g, which had been sealed under vacuum in quartz crucibles. Gold was used as the reference material. A heating rate of 2.0 °C/min was employed both for calibration and measurement of the prepared samples. The temperatures of the invariant phase reactions were usually taken from the extrapolated onset on heating. The accuracy of all of the given temperatures is ±2 °C.

3. Results and discussion

3.1. Bi–Sn system

The DSC/DTA results obtained for the first eight samples can be seen in Table 1. Their comparisons can be made by studying Fig. 1. The invariant temperature measured for the binary eutectic L ↔ (Bi) + (Sn) is 138.6 ± 0.6 °C, which is in agreement with that proposed in [4,6].

For the equilibrium study, the results of five samples studied are summarized in Table 2, along with the experimental uncertainties associated with the EDS work. It has been found that there are no major differences between equilibrated samples annealed at 190, 430, 600, 770, 890 and 950 h (Table 2). Therefore, an annealing time of around 400 h is

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Bi–Sn experimental data from DTA/DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td>w(Sn) (%)</td>
<td>Transition temperatures (°C)</td>
</tr>
<tr>
<td>12.5</td>
<td>138.9(^a) 230.1(^c)</td>
</tr>
<tr>
<td>23.5</td>
<td>138.9(^a) 200.9(^e)</td>
</tr>
<tr>
<td>36.5</td>
<td>139.0(^a) 160.5(^c)</td>
</tr>
<tr>
<td>74.5</td>
<td>138.7(^a) 195.7(^c)</td>
</tr>
<tr>
<td>80.1</td>
<td>138.2(^a) 202.8(^e)</td>
</tr>
<tr>
<td>84.8</td>
<td>138.4(^a) 210.5(^c)</td>
</tr>
<tr>
<td>89.9</td>
<td>138.0(^a) 219.3(^c)</td>
</tr>
<tr>
<td>95.6</td>
<td>188.9(^b) 227.0(^c)</td>
</tr>
</tbody>
</table>

\(^a\) Eutectic temperatures. \(^b\) Solidus temperatures. \(^c\) Liquidus temperatures.

Final composition was found after AAS and/or XRF and SEM/EDS.
Table 2
Bi–Sn experimental data from DTA/DSC and SEM/EDS for samples in equilibrium

<table>
<thead>
<tr>
<th>Sample</th>
<th>BS 1</th>
<th>BS 2</th>
<th>BS 3</th>
<th>BS 4</th>
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<tr>
<td>w(Sn)</td>
<td>50</td>
<td>80</td>
<td>85</td>
<td>90</td>
<td>95</td>
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<tr>
<td>Annealing at 130 °C</td>
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<td></td>
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<tr>
<td>Time (h)</td>
<td>Kin. st.</td>
<td>770</td>
<td>600</td>
<td>890</td>
<td>770</td>
</tr>
<tr>
<td>SEM/EDS results – composition measurements (wt%)</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>w(Sn)</td>
<td>49.4 ± 0.9</td>
<td>78.4 ± 0.5</td>
<td>83.8 ± 1.1</td>
<td>88.0 ± 0.4</td>
<td>93.2 ± 0.2</td>
</tr>
<tr>
<td>Sn in (Bi)</td>
<td>0.5 ± 0.2</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Bi in (Sn)</td>
<td>5.8 ± 0.1</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>5.4 ± 0.3</td>
</tr>
</tbody>
</table>

DSC results (°C)

| Invariant reactions | b | | | | |
| Solidus | b | | | | |
| Liquidus | b | | | | |

a Kinetic study: three samples were annealed for different times (190, 430 and 950 h). Bi content of BCT_A5 (Sn) analyzed by SEM + EDS (5, 6.2 and 5.8 wt%).
b Not measured.

Fig. 1. Bi–Sn experimental phase diagram after results from DTA/DSC and SEM/EDS obtained in the present work. Dashed lines were drawn according to what was expected from our results and having in consideration the literature [6].

The annealed structures of the samples are elucidated in Fig. 2(a)–(c). They may be viewed as two-phase structures consisting of (Bi) and (Sn), in all of the five alloys annealed at 130 °C. These results are thus consistent with the DTA/DSC results for alloys BS 2 and BS 3 (Table 2).

In disagreement with what was proposed by the authors [6, 7], results of this work point to a much lower solubility of Bi in (Sn) (approximately 10 wt% as against approximately 25 wt% [6,7]). On the other hand, the results presented in this paper are apparently in agreement with those proposed by Oelsen and Golücke [5].

The DSC/DTA data obtained with the equilibrated samples, using the Netzsch DTA/DSC 404, point to slightly different solubility of Bi in (Sn) (15 wt%). There are also some discrepancies concerning the Liquid + (Sn) ↔ (Sn). This could be because of the possibility of a slight shift in the corresponding samples’ composition.

The authors of the present paper gave more gravity to the data from the set of eight samples (Section 2.1), while assembling the experimental phase diagram. The DTA/DSC data for these eight samples were in agreement with the SEM/EDS and XRD results and also with the results from the ternary Bi–Sn–Zn (Section 3.3).

The microstructure of samples with w(Bi) = 74.5% and w(Sn) = 25.5%, were analyzed by SEM/EDS after being measured by DTA/DSC (and cooled down to room temperature with a rate of 5 °C/min), (Fig. 3). As expected, it confirms the existence of a pro-eutectic and eutectic structure.

The XRD pattern from a bulk sample with w(Bi) = 4.4% and w(Sn) = 95.6%, exhibiting one-phase structure (Sn), is shown in Fig. 4. All other samples from the binary Bi–Sn, detailed in Section 2.1, have been analyzed by RT-XRD. The presence of (Bi) confirms the results of DTA/DSC experiments (Table 1).

3.2. Bi–Zn system

The assessment of Massalski [8] is based on existing experimental results. It indicates a significant solubility of Zn in (Bi) (few wt% of Zn). Nevertheless, the calculations carried out by [9] indicated a much lower solubility (significantly less than 1 wt%). Therefore, the experimental program is focused on the discrepancies of the solubility of the alloying elements in the relevant terminal solid solutions.

The experimental results at 245 °C confirmed the low solubility of Zn in (Bi), as the sample with low Zn content clearly exhibits a two-phase structure (Fig. 5). The results of solubility of both the elements in the respective solid solutions, is shown in Table 3.

3.3. Bi–Sn–Zn system

Muzaffar [3], who thoroughly studied the system by means of thermal arrests, did not measure any point for the liquidus surface in the region of the miscibility gap (L1 + L2/Liquid).
Fig. 2. Microstructure (2000×) of the annealed samples – mixture of light (Bi) and dark (Sn) phases: (a) “BS 1”; (b) “BS 3” and (c) “BS 5”.

Fig. 3. Microstructure (500×) of the sample with w(Bi) = 74.5% and w(Sn) = 25.5%, after the DTA/DSC experiment with a cooling rate of 5 °C/min: (Bi) – light grey, (Sn) – medium grey.

Table 3
Composition of the phases present in the Bi–Zn alloy with w(Zn) = 76.2% after the annealing at 200 °C

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition of phases (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi)</td>
<td>Bi 99.7 ± 0.2, Zn 0.3 ± 0.1</td>
</tr>
<tr>
<td>(Zn)</td>
<td>Bi 0.3 ± 0.2, Zn 99.7 ± 0.2</td>
</tr>
</tbody>
</table>

In this work, we measured the miscibility gap in the liquid phase by using DTA/DSC at heating rates of 10–20 °C/min.

Fig. 4. The XRD pattern at room temperature for a bulk sample with composition: w(Bi) = 4.4% and w(Sn) = 95.6%. This sample was the only one, studied in the Bi–Sn system, which was monophasic (Sn), at room temperature.

Fig. 5. Microstructure (1000×) after 336 h of annealing (overall composition: w(Zn) ~ 0.3 and w(Bi) ~ 99.7%). The matrix comprises a solid solution of Zn in (Bi) phase and dark particles formed by a solid solution of Bi in (Zn).
Table 4
Bi–Sn–Zn experimental data from DTA/DSC and SEM/EDS

Results for Bi–Sn–Zn from DTA/DSC

<table>
<thead>
<tr>
<th>w(Bi) (%)</th>
<th>w(Sn) (%)</th>
<th>w(Zn) (%)</th>
<th>Transition temperatures (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.0</td>
<td>4.1</td>
<td>85.9</td>
<td>133.7²</td>
</tr>
<tr>
<td>20.1</td>
<td>5.0</td>
<td>74.9</td>
<td>133.1² 200.6</td>
</tr>
<tr>
<td>30.4</td>
<td>5.0</td>
<td>64.6</td>
<td>134.4² 217.0</td>
</tr>
<tr>
<td>32.8</td>
<td>5.1</td>
<td>62.1</td>
<td>133.7² 223.3</td>
</tr>
<tr>
<td>43.8</td>
<td>4.7</td>
<td>51.5</td>
<td>133.6² 229.4</td>
</tr>
<tr>
<td>53.3</td>
<td>4.9</td>
<td>41.8</td>
<td>134.4² 230.7</td>
</tr>
<tr>
<td>55.4</td>
<td>5.5</td>
<td>39.1</td>
<td>134.2² 236.4</td>
</tr>
<tr>
<td>68.5</td>
<td>5.7</td>
<td>25.8</td>
<td>133.4² 232.9</td>
</tr>
<tr>
<td>31.7</td>
<td>14.3</td>
<td>54.0</td>
<td>133.5² 186.0</td>
</tr>
<tr>
<td>55.6</td>
<td>13.7</td>
<td>30.7</td>
<td>133.2² 212.6</td>
</tr>
<tr>
<td>56.7</td>
<td>12.6</td>
<td>30.7</td>
<td>133.9² 217.9</td>
</tr>
<tr>
<td>74.0</td>
<td>11.9</td>
<td>25.0</td>
<td>134.0² 223.0</td>
</tr>
<tr>
<td>11.7</td>
<td>18.0</td>
<td>70.3</td>
<td>134.3² 153.7</td>
</tr>
<tr>
<td>26.5</td>
<td>18.2</td>
<td>55.3</td>
<td>135.1² 138.0</td>
</tr>
<tr>
<td>28.0</td>
<td>17.8</td>
<td>52.4</td>
<td>133.5² 148.0</td>
</tr>
<tr>
<td>37.9</td>
<td>19.8</td>
<td>42.3</td>
<td>134.4² 171.4</td>
</tr>
<tr>
<td>51.4</td>
<td>21.4</td>
<td>27.5</td>
<td>134.6² 177.6</td>
</tr>
<tr>
<td>55.0</td>
<td>28.9</td>
<td>16.1</td>
<td>134.8² 170.4</td>
</tr>
<tr>
<td>10.1</td>
<td>40.1</td>
<td>49.8</td>
<td>134.0² 182.6</td>
</tr>
<tr>
<td>23.7</td>
<td>38.5</td>
<td>37.8</td>
<td>135.1² 161.4</td>
</tr>
<tr>
<td>47.2</td>
<td>40.4</td>
<td>12.4</td>
<td>134.1² 137.7</td>
</tr>
<tr>
<td>30.6</td>
<td>45.8</td>
<td>23.6</td>
<td>133.4² 143.2</td>
</tr>
<tr>
<td>37.2</td>
<td>44.1</td>
<td>18.7</td>
<td>133.5² 147.1</td>
</tr>
<tr>
<td>10.1</td>
<td>57.8</td>
<td>32.1</td>
<td>134.0² 187.2</td>
</tr>
<tr>
<td>18.2</td>
<td>59.5</td>
<td>22.3</td>
<td>134.2² 181.5</td>
</tr>
<tr>
<td>29.3</td>
<td>58.5</td>
<td>12.2</td>
<td>134.8² 165.6</td>
</tr>
<tr>
<td>4.7</td>
<td>76.5</td>
<td>18.8</td>
<td>–                   168.8</td>
</tr>
<tr>
<td>9.2</td>
<td>81.0</td>
<td>9.8</td>
<td>131.0              188.2</td>
</tr>
<tr>
<td>9.6</td>
<td>81.0</td>
<td>9.4</td>
<td>131.7              182.6</td>
</tr>
</tbody>
</table>

Average compositions for the solid phases of Bi–Sn–Zn from SEM/EDS (calculated from 29 samples) (for $T ≤ 120$ °C)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition of phases (wt%)</th>
<th>w(Bi)avg ± 1.2%</th>
<th>w(Sn)avg ± 0.9%</th>
<th>w(Zn)avg ± 1.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Bi)</td>
<td>95.5</td>
<td></td>
<td>1.9</td>
<td>2.6</td>
</tr>
<tr>
<td>(Sn)</td>
<td>4.4</td>
<td>93.3</td>
<td>2.3</td>
<td>99.5</td>
</tr>
<tr>
<td>(Zn)</td>
<td>0.2</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Final composition was found after AAS and/or XRF and SEM/EDS.

The results, listed in Table 4, are plotted in Figs. 6 and 7. In some cases, the cooling curve is helpful in identifying the peak corresponding to the liquidus temperature. It is difficult to find liquidus surface peaks for samples belonging to the vertical section $w(Sn) ∼ 5\%$, with $w(Bi) ∼ 20\%$ and $70\%$; which may be due to the spinodal effect. The liquidus temperatures for these two samples are shown in Table 4 but it has to be taken into account that the experimental uncertainty can be higher for these two samples than for the rest. An example of a DTA/DSC curve obtained for a sample with $w(Bi) = 53.3\%$, $w(Sn) = 4.9\%$ and $w(Zn) = 41.8\%$ is depicted in Fig. 8.

DTA/DSC results from equilibrated samples are in agreement with the previous ones (Table 5).

The invariant temperature measured for the ternary eutectic L ↔ (Bi) + (Sn) + (Zn) is 134.1 °C ± 1.0 °C which is 4.2 °C higher than that proposed in [3].

All samples in Table 4 have been analyzed by bulk XRD at room temperature after being annealed for 60 min at 120 °C and slowly cooled down to room temperature. All peaks were searched/matched using the ICDD PDF-2 2003 database [10–12]. The results show that all samples are homogeneous and that belong to the three-phase region (Bi) + (Sn) + (Zn) (see Fig. 9). Despite the fact that XRD results are in agreement with what was expected from the phase diagrams, the search/match for (Sn) indicated that its reflections are slightly shifted with respect to their position for pure Sn. This maybe due to a
Table 5
Experimental results obtained from Bi–Sn–Zn alloys, annealed at 100 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (wt%)</td>
<td>Bi35–Sn35–Zn</td>
<td>Bi20–Sn50–Zn</td>
<td>Bi10–Sn70–Zn</td>
</tr>
<tr>
<td>Annealing at 100 °C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time (h)</td>
<td>744</td>
<td>980</td>
<td>980</td>
</tr>
<tr>
<td>SEM/EDS results – composition measurements (wt%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overall</td>
<td>Bi</td>
<td>35.5 ± 0.7</td>
<td>22.4 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>33.6 ± 0.9</td>
<td>54.8 ± 0.5</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>30.9 ± 0.9</td>
<td>22.8 ± 0.6</td>
</tr>
<tr>
<td>(Bi)</td>
<td>Bi</td>
<td>95.9 ± 0.8</td>
<td>96.6 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.4 ± 0.1</td>
<td>0.7 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>3.7 ± 0.6</td>
<td>2.7 ± 0.7</td>
</tr>
<tr>
<td>(Sn)</td>
<td>Bi</td>
<td>3.6 ± 0.9</td>
<td>4.3 ± 0.3</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>93.3 ± 1.0</td>
<td>94.0 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>3.1 ± 1.0</td>
<td>1.7 ± 0.5</td>
</tr>
<tr>
<td>(Zn)</td>
<td>Bi</td>
<td>0.7 ± 0.2</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Sn</td>
<td>0.7 ± 0.3</td>
<td>0.5 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>98.6 ± 0.3</td>
<td>99.5 ± 0.2</td>
</tr>
</tbody>
</table>

Table 4 lists the solubility of each element in all solid solutions measured by SEM/EDS. The temperature is higher temperatures (a halo – a curved baseline – is observed for 2θ between 20° and 40°). It corresponds to the liquid phase. As expected, with the increase in the amount of liquid the concavity also increases. Special attention should be given to the behavior of the [002] plane in (Zn) (T = 30 °C, 2θ = 36.37°; d = 0.247 nm) slightly above the ternary eutectic reaction where the inter-atomic distance, d, slightly decreases. This is in contradiction to the expected tendency to increase with temperature probably due to the rearrangement initiated by the appearance of liquid.
considered to be less than 120 °C because samples are annealed at 120 °C for 60 min and slowly cooled down to room temperature. Fig. 11 envisages four SEM microstructures of some selected samples showing the three different phases, in accordance with the expectation.

Three samples with w(Sn) ~ 77/81% have been subjected to two different heat treatments consisting of an annealing at 120 °C for 180 min followed by slow cooling at 0.5 °C/min and an annealing for 180 min at 120 °C, followed by water quenching. Our intention concerning the first heat treatment is to obtain phases' composition near room temperature, comparable with those already referred. For the second heat treatment, we aim at obtaining the phases' composition at 120 °C. The results show, in both cases, a similarity between phases' composition measured by EDS. This similarity could
Fig. 11. Microstructures of selected samples (500×): (Bi) – light grey, (Sn) – medium grey, (Zn) – dark grey. The composition of samples is indicated by arrows. All studied Bi–Sn–Zn samples are indicated in the figure.

Fig. 12. Microstructures (150×) of a sample with w(Bi) = 9.2%; w(Sn) = 81.0%; w(Zn) = 9.8% after: (a) slow cooling (0.5°C/min) after 180 min at 120°C and in (b) water quenched after 180 min at 120°C: (Bi) – light grey, (Sn) – medium grey, (Zn) – dark grey.

be a result of the short annealing stage, not sufficient to reach the thermodynamic equilibrium. It could also be an effect of the used cooling rate, which is not high enough to “freeze” the “high-temperature” structure. The main difference between samples annealed in different ways reflects in the grain size (Fig. 12).

Concerning the solvus of (Bi) and (Sn), SEM/EDS results from samples which previously underwent DTA/DSC experiments, followed by cooling at a rate of 5°C/min, are also in agreement with the above mentioned results.

As mentioned in Section 2.5, the Bi–Sn–Zn system is also an object of equilibrium study. Examples of the equilibrated samples resulting in microstructures are shown in Figs. 13(a)–(b) and 14(a)–(c).

The results hence obtained agree with the Bi–Sn experimental results (see Section 3.1) and confirm the errors in the predicted phase boundaries. The experimental results also confirmed the observation of Malakhov [9], that the presence of Sn increases the solubility of Zn in (Bi). This increase is significant as the value measured in the ternary alloy is several times higher than the value measured in the binary Bi–Zn system.

Tables 4 and 5 list the results of DTA/DSC measurements (namely the transition temperature found for lower Bi content, corresponding to probable ternary eutectic reaction), which confirmed a much lower Bi solubility in (Sn) than previously anticipated in [6].

4. Conclusions

1. Results from DTA/DSC, SEM/EDS/WDS, RT-XRD and HT-XRD (for some samples) are obtained for the Bi–Sn, Bi–Zn and Bi–Sn–Zn systems and critically compared. New values for the liquidus surface of the ternary miscibility gap have also been obtained.
2. Results are generally in agreement with each other. The binaries’ results confirm those obtained for the ternary and vice-versa.
Fig. 13. Microstructure (2000×) of the Bi–Sn–Zn samples (a) “A” (annealed 744 h) and (b) “C” (annealed 980 h), showing a grey matrix of a solid solution of Bi and Zn in (Sn), dark Zn-rich and light Bi-rich phases (both are also solid solutions).

Fig. 14. Microstructure (2000×) of the Bi–Sn–Zn samples (a) “D” (annealed 1175 h), (b) “E” (annealed 1175 h) and (c) “F” (annealed 1100 h), showing the grey matrix of a solid solution of Bi and Zn in BCT_A5 (Sn), dark Zn-rich and light Bi-rich phases (both are also solid solutions).

3. From the ternary and binary results obtained from different techniques, it appears that the solubility of Bi in (Sn) does not surpass w(Bi) ~ 10%, at the eutectic temperature, which is not in agreement with the assessed phase diagram in [6].

4. Results for Bi–Zn indicate that the solubility of both elements in the respective solid solution is approximately 0.3 wt% at 200 °C as in [9].

5. A reassessment of the Bi–Sn binary and also Bi–Sn–Zn ternary system is desirable. In a recent work of Vizdal et al. [14], the authors of this work reassessed the Bi–Sn and the Bi–Sn–Zn systems based, among others, on the experimental results presented in this study.

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References

Thermodynamic assessment of the Bi–Sn–Zn System

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Abstract

A thermodynamic assessment of the Bi–Sn–Zn ternary system was carried out using the CALPHAD approach along with thermodynamic descriptions from new assessments of the Bi–Sn and Bi–Zn systems. Selected experimental data from the literature and our own work were also used. New sets of optimized thermodynamic parameters were obtained that lead to a very good fit between the calculated and experimental data. The Bi–Sn–Zn system is one of the candidates for lead-free solder materials.

Keywords: Lead-free solders; Bi–Sn assessment; Bi–Sn–Zn assessment; CALPHAD approach; COST531 database

1. Introduction

It is well known that lead and lead-containing materials are toxic and dangerous to the surrounding environment. The EU Directives on Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS) prohibited the use of lead in selected electronic equipment sold in the European market. The directives came into force on 13 February 2003, giving 1 July 2006 as the date when the European electronics industry had to be lead-free. Currently, it is generally acknowledged that lead-free soldering is technologically possible (e.g. the Japanese electronics industry is virtually 100% lead-free). Nevertheless, we also have to take into account the adverse properties of possible substituting elements (e.g. toxicity, price, suitability, etc.) in the process of designing new lead-free soldering materials. Selected issues are addressed within the scope of the COST 531 action and the preparation of a self-consistent thermodynamic database for the alloy systems crucial for lead-free soldering is a major aim of this project.

Following new experimental investigations of the Bi–Sn, Bi–Zn and Bi–Sn–Zn systems, and inconsistencies between assessments of these systems already published, we have found it necessary to reassess their thermodynamic descriptions. The latest version of the SGTE unary database [1] was selected as a basis for the calculations. Phase equilibria studies were carried out in regions of the phase diagrams where the most significant differences exist and the relevant results are also reported in this paper.

This work has contributed significantly to the development of the “COST531” database [2].

2. Theoretical part

The CALPHAD method is used in this work. This procedure is based on the sequential modeling of phase equilibria and thermodynamic properties of alloy systems, starting from binary systems and leading to higher-order systems. It is
possible to obtain accurate predictions of phase equilibria of multicomponent systems using this approach. The crucial condition for the success of such a method is a good and consistent database for the calculation of the thermodynamic properties of the relevant systems.

The mathematical method for the calculation of thermodynamic equilibrium is based on modeling the Gibbs energies of all phases and minimizing the total Gibbs energy of the system. The total Gibbs energy of the system can be calculated by the formula $G^{\text{tot}} = \sum_{p} w_{p} G^{p}$, where the symbol $w_{p}$ is the amount of phase $p$ and $G^{p}$ is its Gibbs energy. The Gibbs energy for a particular solution phase is expressed by the general formula $G^{p} = \sum x_{i}^{p} \delta G_{i}^{p} + G^{\text{id}} + G^{E} + G^{\text{mag}} + \cdots$, where $x_{i}^{p}$ is the contribution of the Gibbs energy of the element $i$ in the crystallographic structure, corresponding to the phase $p$ with respect to its reference state (contribution of the pure components), $x_{i}$ is the molar fraction of element $i$, and $\delta G_{i}^{p}$ is the molar Gibbs energy of pure element $i$ in the structure, corresponding to the phase $p$. The symbol $G^{\text{id}}$ denotes the ideal mixing contribution; $G^{E}$ is the contribution due to non-ideal interactions between the components (the excess Gibbs energy of mixing) and $G^{\text{mag}}$ is the contribution of magnetic Gibbs energy if the phase exhibits magnetic properties. Other excess Gibbs energy terms can be introduced, e.g. pressure dependence ($G^{\text{press}}$), energy of the interface, energy of plastic deformation, energy of defects in the crystal lattice, etc.

Intermediate phases are usually modeled using the sublattice model [3]. This model is based on the distribution of independent lattice positions in the crystal structure into several sublattices, according to their physical properties. The amount of a particular element in the sublattice $k$ is defined by lattice fractions $y_{i}^{k}$, which are defined as

$$y_{i}^{k} = \frac{n_{i}^{k}}{\sum_{s} n_{i}^{k}},$$

where $n_{i}^{k}$ is number of moles of component $i$ in sublattice $k$, and $s$ is number of components occupying sublattice $k$.

A real crystallographic lattice can be envisaged as a superposition of several sublattices from this point of view [3]. The Thermo-Calc software [4] was used in this work for the optimization of the model parameters and calculation of phase equilibria and thermodynamic properties.

3. The Bi–Sn–Zn system and its subsystems

3.1. Introduction

An extensive experimental investigation of the Bi–Sn–Zn system has been conducted by Braga et al. [5]. The solubilities of the components in the terminal solid solutions were measured and compared with predictions using thermodynamic parameters from [6] and [7]. However, discrepancies between experimental and calculated solubilities were found for Bi in HCP\_Zn, and particularly for the solubility of Bi in BCT\_A5 (Sn). The results given in [5] indicated a much lower solubility of Bi in the BCT\_A5 (Sn) solid solution (around 10 wt% at the eutectic temperature) and confirmed the need for a new thermodynamic description for the Bi–Sn system. This fact is especially important from the point of view of the development of the “COST531” thermodynamic database [2] because other important ternary system descriptions are based on this binary. Therefore, targeted experiments using scanning electron microscopy (SEM) + energy-dispersive solid-state spectrometry (EDS) and differential scanning calorimetry (DSC) were carried out in the Sn-rich part of the Bi–Sn phase diagram as part of the experimental study [5].

Disagreement between the experimental ternary phase equilibria and the solubility limit of bismuth in HCP\_Zn calculated using the assessed thermodynamic parameters led to small changes in the description for the Bi–Zn system, too.

Experimental studies and the remodeling of the binary and ternary systems are summarized and discussed in the following sections.

3.2. Bi–Sn system

Many authors have investigated the phase equilibria and thermodynamic properties of this system experimentally, but with a certain amount of disagreement between some of the results. Nagasaki and Fujita [8] measured the specific heat, and Oelsen and Golücke [9] determined heats of mixing. More recently, Ohtani and Ishida [10] reported liquidus data and the eutectic temperature, which they measured using DSC. The agreement among these three sets of data is generally good. Many authors also investigated the enthalpies of mixing of liquid Bi–Sn alloys, e.g. [11–14]. As Ohtani and Ishida [10] pointed out, work carried out before the 1940’s (e.g. [11]) show large scatter while there is a rather good agreement amongst later data, e.g. [12–14]. Many authors have measured the activities of Sn in the liquid phase using electromotive force (EMF) methods; one of the most recent works in this field is the contribution of Asryan and Mikula [15]. Yazawa and Koike [16] also measured the activities of Bi in the liquid at 1100 °C, whereas Rickert et al. [17] measured activities at 750–1050 °C. The activities measured by the various authors were in good mutual agreement, showing a slight positive deviation from ideality. However, the calculated enthalpies showed large mutual discrepancies. Only those of Seltz and Dunkerley [18] were in good agreement with directly measured data [12–14]. Enthalpies of formation of solid alloys are also available from the calorimetric measurements made by Oelsen and Golücke [9]. A list of other related references is available in the paper of Lee et al. [19].

Thermodynamic modeling of this system has been carried out by Ohtani and Ishida [10] and Lee et al. [19]. The assessments differ in the unary data used (i.e. the Gibbs energy differences for the pure components in certain crystallographic structure – especially for their metastable states – with respect to Stable Element Reference state of that component). Therefore the phase boundaries calculated using their assessed data disagree. A different solubility of Sn in the Rhombohedral\_A7 (Bi) phase can be clearly seen (Fig. 1(a) and
Lee et al. [19] did not take into account the solubility of Sn in Rhombohedral_A7 (Bi) reported by Oelsen and Golücke [9] and obtained a much lower solubility in their assessment.

The liquid phase, Rhombohedral_A7 solid solution (Bi-rich) and BCT_A5 solid solution (Sn-rich) are stable in this system. All solid phases were modeled as regular solid solutions with one sublattice.

With respect to the different solubility of Bi in BCT_A5 (Sn-rich) solid solution, we have utilized mainly the newly obtained phase equilibrium data from [5] for the reassessment of the system (Fig. 2 shows these data superimposed on the phase diagram calculated using the thermodynamic parameters from the assessment of Ohtani and Ishida [10]). We have also taken into account new thermodynamic data measured by Asryan and Mikula [15] and the phase equilibrium data published by Oelsen and Golücke [9] concerning the solubility of Sn in the Rhombohedral_A7 (Bi) phase. The selected data of Ohtani and Ishida [10] and Nagasaki and Fujita [8] were used for the comparison with the calculated phase diagram only. We have found that binary thermodynamic parameters published in [10] (using the same unary data for all phases as in our assessment) reproduce reasonable well the phase and thermodynamic data except for the above-mentioned solubility of Bi in BCT_A5 (Sn). Therefore, it seemed reasonable to use the thermodynamic parameters published in their study as starting values in the parametric optimization in this work.

The unary data were taken from v4.4 of the SGTE unary database [1]. The parameters obtained from the present assessment are shown in Table 1. The binary Bi–Sn phase diagram calculated using these newly assessed data is shown in Fig. 3 and is compared with relevant phase equilibrium data taken from our work and those mentioned above. The calculated activity and enthalpy of mixing of liquid Bi–Sn alloys at 450 °C are compared with the calorimetric data of

(b)). Lee et al. [19] did not take into account the solubility of Sn in Rhombohedral_A7 (Bi) reported by Oelsen and Golücke [9] and obtained a much lower solubility in their assessment.

3.3. Bi–Zn system

A summary of the experimental data can be found in the papers of Okajima and Sakao [20], Malakhov [21] and Kim and Sanders [22]. Okajima and Sakao [20] studied the equilibria between the two immiscible liquid phases in this system, and the agreement between their experimental data and those of other authors is rather good. Okajima and Sakao [20] also calculated the activities of zinc in the system at 873 K using experimentally determined EMF values and compared them with Kleppa’s values [23]. The agreement between the two sets
A thermodynamic assessment of the Bi–Sn system was carried out by Malakhov [21], Oleari et al. [26], Bale et al. [27], Girard [28] and Wang et al. [29]. Recently, Kim and Sanders [22] assessed miscibility gaps and the metastable liquids in this system and published new interaction parameters for the liquid phases. We used the interaction parameters of data is good. Kawakami [24] and Wittig et al. [25] measured the enthalpies of mixing for liquid alloys.

A thermodynamic assessment of the Bi–Zn system was carried out by Malakhov [21], Oleari et al. [26], Bale et al. [27], Girard [28] and Wang et al. [29]. Recently, Kim and Sanders [22] assessed miscibility gaps and the metastable liquids in this system and published new interaction parameters for the liquid phases. We used the interaction parameters for liquid phases presented by Malakhov [21] in the current work because of better agreement with experimental data and consistency with other data used.

The liquid phase, Rhombohedral\textsubscript{A7} phase (Bi) and HCP phase (Zn) were used in the modeling. The HCP phase (Zn) is of the A3 type, but with a different c/a ratio. Therefore, we modeled it as a different phase (denoted HCP\textsubscript{Zn} instead of the standard HCP\textsubscript{A3}) in the database. To keep the consistency with other databases, this phase was modeled with two sublattices. The first sublattice is occupied by the metallic elements and the second by interstitial elements, despite the fact that no interstitial elements exist in these systems. The site-occupancy ratio given by the number of interstitial positions per site on the basic metallic sublattice is 1:0.5.

The currently accepted phase diagrams for the Bi–Zn system are shown in Fig. 5(a) and (b). There is a noticeable difference between the calculated phase diagram according to [21] (Fig. 5(a)) and the assessed experimental phase diagram [30] (Fig. 5(b)).

The assessment published in Massalski’s compendium [30], based on existing experimental results, indicates a significant solubility of Zn in Rhombohedral\textsubscript{A7} (Bi) (\textasciitilde{}2 wt\% of Zn) but the calculations carried out using Malakhov’s data [21] indicated a much lower solubility (significantly less than 1 wt\%). The calculations for the Zn-rich end of the phase diagram gave a negligible solubility of Bi in HCP\textsubscript{Zn}; less than 0.1 wt\%.

Experimental results [5] at 245 °C confirmed the low solubility of Zn in Rhombohedral\textsubscript{A7} (Bi), as the sample with a Zn content of approximately 0.3 wt\% clearly exhibits a two-phase structure. The solubility of both elements in the respective solid solution was found to be approximately 0.3 wt\% at 200 °C. This value is in good agreement with the theoretical calculation for the solubility of Zn in Rhombohedral\textsubscript{A7} (Bi), as the calculated solubility at 200 °C is 0.37 wt\% of Zn. On the other hand, the calculation according to Malakhov [21] gives much lower solubility of Bi in HCP\textsubscript{Zn} than the experiment result (Fig. 5(a)). The difference is not large in absolute numbers, as the solubility is very low, but the calculated value is about 10 times lower than the experimental result. After analysis of the experimental data, the interaction parameter $^{0}f_H^{Zn}$ was changed in the Bi–Zn binary system given by Malakhov [21] was changed from +35 000 to +25 000 J mol\textsuperscript{-1}. The resulting difference in the position of the phase boundary calculated using both parameters can be seen by comparing Fig. 6(a) and (b).

### 3.4. Sn–Zn system

An overview of the experimental data and an estimation of the phase diagram have been published by Moser et al. [31]. The available experimental data for the liquid covered both the enthalpy of mixing and chemical potentials (or activities) of Zn in the liquid state; the data are in very good agreement with each other. The activity measurements were carried using the EMF method, e.g. by Sano et al. [32] and Fiorani and Valenti [33], or by the vapor pressure method, e.g. by Scheil and Müller [34] and Kozuka et al. [35]. Kleppa [36], Oelson [37] and Schürmann and Träger [38] measured the enthalpies of mixing.

Thermodynamic modeling of this system has been carried out by Ohtani et al. [39], Lee [40] and also by Fries et al. [41]. They used the temperature dependence of the enthalpy of mixing for the liquid measured by Kleppa [36] and Bourkba et al. [42] for their assessments. The above authors used different unary data in their assessments and there are also differences in the resulting phase boundaries (Fig. 7(a) and (b)), where a different solubility of Zn in BCT\textsubscript{A5} (Sn) is clearly seen. It is difficult to decide which phase diagram is correct, as the available experimental data are limited in this region. The thermodynamic parameters from Fries et al. [41] were used in

![Fig. 3. The assessed Bi–Sn phase diagram in comparison with experimental data used in the assessment.](image-url)
the “COST531” database [2] and in our study as they exploited the unary data from the SGTE 4.4 database [1]. The standard state for Sn is BCT\textsubscript{A5}; the standard state for Zn is HCP\textsubscript{Zn} with the non-standard c/a ratio.

3.5. Bi–Sn–Zn system

The ternary Bi–Sn–Zn system was assessed by Malakhov et al. [6] and Moelans et al. [7]. Both assessments are based on the experimental work of Muzaffar [43], who carried out thermal analysis of a large number of liquid alloys. The experimental information gave a eutectic temperature of \( T = 129.87 \pm 0.15 ^\circ\text{C} \). Malakhov et al. [6] also took into account the results of Ohtani and Ishida [10] and Ohtani et al. [39]. Moelans et al. [7] used thermochemical properties determined from EMF measurements made by a number of authors, e.g. [27, 44–46]. Both Malakhov et al. and Moelans et al. introduced ternary corrections for the liquid only. Unfortunately, the assessments of this system are not mutually consistent as the authors used different unary data (e.g. \( G_{\text{Bi-Bi}}^{\text{Rhom-A7}} - G_{\text{Bi}}^{\text{Rhom-A7}} = +184.07 \text{ J mol}^{-1} \) from [10] and +13 526.3 J mol\(^{-1}\) from [19] in the Bi–Sn system). They either took these values from various versions of the SGTE unary database [10,19] or, in some cases, carried out their own assessment of the unary data [7]. Recently, Luef et al. [47] published an experimental study of this ternary system and determined partial and integral enthalpies of mixing of liquid Bi–Sn–Zn alloys at 500 °C by a drop calorimetric technique. Experiments were
conducted using compositions along six sections in the Sn-rich part of the ternary diagram. They also reported DSC data (liquidus temperatures and ternary eutectic reactions) along three sections (3, 5 and 7 at. % of Zn). Braga et al. [5] published new and significant experimental results focusing on the miscibility gap (and also the Sn-rich part of the diagram). DSC, X-ray diffraction (XRD), and SEM in conjunction with EDS were used in the study. For quantitative analysis they used X-ray fluorescence (XRF) and atomic absorption spectrometry (AAS).

Both Malakhov et al. [6] and Moelans et al. [7] have used the older thermodynamic description of the Bi–Sn system for their assessments, and therefore it was necessary to reassess the Bi–Sn–Zn system using the newly assessed Bi–Sn system (Section 3.2) together with the Bi–Sn–Zn experimental results presented in [5,43]. These experimental data were supplemented with new experimentally determined integral enthalpies of mixing of liquid Bi–Sn–Zn alloys [47] and the activities [45].

Ternary interaction parameters were introduced both for the liquid and Rhombohedral_A7 (Bi) phases modifying the ternary system behavior. No ternary interaction parameters were necessary for the BCT_A5 (Sn) phase, as the predicted solubility of Bi and Zn in this phase agreed well with the experimental results. Using the Parrot module [4] of the Thermo-Calc thermodynamic calculation software, a new set of thermodynamic parameters was optimized for the ternary system, which is summarized in Table 2.
Fig. 8. Calculated (a) integral enthalpies of mixing at 500 °C, compared with the experimental data of Luef et al. [47], and (b) activities of Zn at 450 °C, compared with the experimental data of Oleari and Fiorani [45].

Fig. 9. Calculated isothermal sections at (a) 100 °C and (b) 120 °C in comparison with experimental data from Braga et al. [5].

Table 2
Summary of the ternary corrections for the Bi–Sn–Zn system used in the present assessment

<table>
<thead>
<tr>
<th>Phase</th>
<th>Thermodynamic parameters (J mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid</td>
<td>0 ( \mu_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -17,690.6 + 33T )</td>
</tr>
<tr>
<td></td>
<td>( 1 \mu_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -2757.2 - 13T )</td>
</tr>
<tr>
<td></td>
<td>( 2 \mu_{\text{Bi,Sn,Zn}}^{\text{Liq}} = -19,259.1 + 0.5T )</td>
</tr>
<tr>
<td>Rhombohedral_A7 (Bi)</td>
<td>0 ( \mu_{\text{Rhom,A7}}^{\text{Bi,Sn,Zn}} = +387,000.0 )</td>
</tr>
<tr>
<td></td>
<td>( 1 \mu_{\text{Rhom,A7}}^{\text{Bi,Sn,Zn}} = 0 )</td>
</tr>
<tr>
<td></td>
<td>( 2 \mu_{\text{Rhom,A7}}^{\text{Bi,Sn,Zn}} = 0 )</td>
</tr>
</tbody>
</table>

The results of this assessment have been verified by comparing calculated isopleths with selected phase equilibrium data from Braga et al. [5] and Muzaffar [43] as well as with more recent data from Luef et al. [47]. They are shown in Figs. 8–15.

4. The theoretical results and discussion

4.1. Bi–Sn system

Very good agreement was reached between the calculation and experimental phase and thermodynamic data for this system (Figs. 3 and 4). The calculated solubility of the Bi in the BCT_A5 (Sn) solid solution agreed with the results of SEM measurements and the phase boundaries confirmed by the DTA measurements. The eutectic temperature obtained in the calculation is 138.4 °C, which is in very good agreement with the value measured by Braga et al. [5] (138.6 °C). For
Fig. 10. Calculated vertical sections at constant ratios (a) $W(\text{Bi})/W(\text{Zn}) = 1/2$ and (b) $W(\text{Bi})/W(\text{Sn}) = 2$ in comparison with experimental data from Braga et al. [5].

Fig. 11. Calculated vertical sections at constant ratios (a) $W(\text{Sn})/W(\text{Zn}) = 1$ and (b) $W(\text{Sn})/W(\text{Zn}) = 2$ in comparison with experimental data from Braga et al. [5].

comparison, Ohtani and Ishida [10] calculated the eutectic temperature to be 140.7 °C and Lee et al. [19] determined a value of 138.8 °C. A very good agreement between calculated and experimentally measured [15] activities of Sn in liquid Bi–Sn alloys at 450 °C is shown in Fig. 4(a).

The reliability of the new Bi–Sn description was also verified by calculations of the ternary Bi–Sn–Zn system (see Sections 3.5 and 4.3).

4.2. Bi–Zn system

It is clear from the experimental results that the estimated phase boundary [30] in the Bi-rich region is not correct and that the theoretically calculated solubility of Zn in Rhombohedral_A7 (Bi) solid solution using the data from the work of Malakhov [21] is more accurate. The calculated solubility of Bi in HCP_Zn, based on the current reassessment of the relevant interaction parameter, agrees well with experiment; the temperatures and composition of the phases in the invariant reactions are almost unchanged. Further improvement can be achieved by introducing a parameter for temperature dependence, but owing to a lack of experimental data and the spread in the experimentally determined values of the eutectic temperature given in the literature, this would be inappropriate.
The experimentally measured thermodynamic properties and phase equilibria are very well reproduced using the new thermodynamic description in Figs. 8–15. The calculated integral enthalpies of mixing and activities of Zn are compared with experimental data in Fig. 8 (a) and (b), and the agreement is very good.

Fig. 9(a) and (b) show the calculated isothermal sections at 100 and 120 °C, which are in very good agreement with the experimental data [5]. The agreement between the modeling and experimental data (DTA results) from [5] and [43] is also shown in the relevant vertical sections in Figs. 10–14. It should be noted that smaller weight was given to the experimental data of Muzaffar [43] in comparison with the data of Braga et al. [5] in this assessment. The phase equilibrium data from [5] were given priority in the optimization owing to their reliability and consistency. Muzaffar’s thermal analysis results are slightly different (e.g. the temperature of invariant reaction), but the
results are still in reasonable agreement with more recent work. The data of Muzaffar are also very useful because of the number of alloys studied (104!). These alloys covered a major part of the ternary diagram. The ternary eutectic temperature from the work of Muzaffar [43] is 129.87 ± 0.15 °C, but Braga et al. [5] determined this temperature to be 134.1 ± 0.5 °C [5]. The calculated ternary eutectic temperature is 131.7 °C.

We also obtained very good agreement between the calculations and recent experimental results taken from [47] for selected vertical sections. This comparison is shown in Fig. 15.

5. Conclusions

A critical evaluation of the thermodynamic parameters and experimental data available in the literature was carried out for the Bi–Sn, Bi–Zn, Sn–Zn and Bi–Sn–Zn systems.

Our own experimental results [5] led to the verification of the Bi-rich part of the Bi–Zn phase diagram and to a reassessment of the interaction parameter for the HCP Zn phase in the Zn-rich corner.

In the case of the Bi–Sn system, attention was focused on the Sn-rich part of the diagram, where a different solubility of
Bi in the BCT_A5 (Sn) phase was found in [5] (approximately 10 wt%), and the system was successfully reassessed.

Using the new Bi–Sn system description, the modification of the Bi–Zn system description and the available thermodynamic and phase equilibrium data, the Bi–Sn–Zn ternary system was also completely reassessed.

The reliability of the assessed parameters obtained for the Bi–Sn–Zn system was verified by calculation of thermodynamic properties and isothermal and vertical sections of the phase diagram. These results were compared with experimental data, both from our work [5] and the literature [43, 45, 47]. The agreement is excellent for a broad set of experimental measurements carried out by different authors. Therefore, the new datasets for the Bi–Sn and Bi–Sn–Zn systems and the modification of the parameter for the Bi–Zn system were included in the “COST531” database [2].

This database, containing 11 elements (Ag, Au, Bi, Cu, In, Ni, Pb, Pd, Sb, Sn and Zn) was created recently in the scope of the COST 531 project [2]. The reliability of the data in this database is validated both by the modeling of thermodynamic properties of the studied systems (e.g. enthalpies of mixing and their comparison with the experimentally measured data) and by the comparison of theoretical and experimental phase equilibrium data, as shown in this paper.

Acknowledgements

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References

THE BEHAVIOUR OF THE LATTICE PARAMETERS IN THE Bi-Sn-Zn SYSTEM

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Abstract

Lattice parameters, coefficients of thermal expansion and mass density were determined by means of X-ray powder diffraction between 30 and 180 °C (or 240 °C - depending on samples' composition). Rietveld refinement was performed in order to obtain phases' lattice parameters at each temperature. The Panalytical X’Pert Pro MPD was used for room temperature X-ray diffraction experiments (RT-XRD) with bulk samples. The aim was to identify the phases that were present in the sample, as well as, their lattice parameters. For some samples, powder high temperature X-ray diffraction measurements (HT-XRD) were also performed, under a vacuum of $10^{-5}$ mbar or an argon atmosphere.

It was found that the lattice parameters of (Bi), (Sn) and (Zn) don't change with the composition, at room temperature, as expected since all samples belong to the three phase region. It was also concluded that (Bi) behaves like an isometric crystalline solid on the contrary of (Zn) that has different expansion coefficients for different crystallographic directions $a (= b)$ and $c$.

Keywords: Bi-Sn-Zn, (RT/HT)-XRD, lattice parameters, expansion coefficients, mass density.

1. Introduction

Health problems (especially neurological and birth malformations) may arise from the excess of lead in human bodies. The excess of lead is due to water contamination. Hence, lead was added to the list of apprehensions with the environment [1]. The objective of COST 531 action "Lead-free Solder Materials" [2] (European
Cooperation in the field of Scientific and Technical Research) was the study of systems that may be used as lead-free solders. The selection of these systems was based on technical and health hazard considerations. The crucial technological properties to be analyzed should be: melting temperature, wettability, surface tension, viscosity of the liquid alloys at different temperatures, oxidation behaviour, thermomechanical fatigue, etc.

The evaluation of experimental phase diagrams, measurement of the thermodynamic properties and consequent optimisation of the corresponding phase diagrams (using CALPHAD method) were some of the aims of the COST 531 action. Bi-Sn-Zn was one of the systems studied in the scope of the above mentioned program.

The coefficient of thermal expansion and mass density are properties that were object of measurements since their knowledge is essential when solders are the issue.

This study complements other previous studies done for the system Bi-Sn-Zn [3, 4].

2. Experimental

Nine samples corresponding to vertical sections with w(Sn) ~ 5 %, 40 % and 59 % were chosen for this study (Fig. 1). They had ~ 20 mm in diameter, ~ 3 mm in high and ~ 2 g in weight. Samples were prepared by mixing pure Bi (> 99.8 %), Sn (> 99.5 %) and Zn (> 99.9 %). The samples were then putted in alumina crucibles and melted in a resistance furnace under an argon atmosphere. The nominal compositions of the samples were confirmed by X-ray Fluorescence (XRF) and Atomic Absorption Spectroscopy (AAS). All samples were homogenized at 120 °C for 60 minutes and slowly cooled down to the room temperature in a rate less than 2 °C/min.

Bulk RT-XRD measurements were performed to identify the present phases. For some samples, powder HT-XRD measurements were also performed, under a vacuum of 10^-5 mbar or an argon atmosphere. The furnace used is an Anton...
Parr Chamber applied to the Panalytical X’Pert Pro MPD. CuKα or primary monochromated CuKα₁ radiations were used. Patterns were collected from 5 to 120º (2θ) with steps of 0.01º and counting time of 10 s.

3. Results

3.1. Room Temperature

RT-XRD data were refined using Rietveld method [5] applied on the Fullprof software [6]. The Rp, Rwp and R_B(Bi), R_B(Sn) and R_B(Zn) are of the order of Rp = 13 %, Rwp = 14 %, R_B(Bi) = 2 %, R_B(Sn) = 1 % and R_B(Zn) = 1 %. (Bi) was refined as rhombohedral (A7), R-3m, (Sn) was refined as tetragonal (A5), I 41/amd (bct) and (Zn) was refined as hexagonal (A3), P 63/mmc (hcp). Results for two of the nine samples measured, with compositions w(Bi) = 23.7 %, w(Sn) = 38.5 %, w(Zn) = 37.8 % and w(Bi) = 53.3 %, w(Sn) = 4.9 %, w(Zn) = 41.8 % can be observed in Figs. 2 and 3, respectively.

By the observation of the phase diagram at room temperature (298 K) and at 393 K (Fig. 1), it can be seen that the only phases that show the possibility of having slightly different lattice parameters than the respective pure element, are (Sn) and (Bi). When comparing our Rietveld refinements data with Sn and Bi pure elements data [7], it can be observed that (Sn) and (Bi) are the phases that present some discrepancy (for (Sn) especially for a = b and for (Bi) especially for c) (if [7] is considered), as expected from the phase diagram.

For (Sn), the difference between the average a = b lattice parameter for (Sn) and for pure Sn is 0.162 % of the value of Sn pure and the difference between the average c lattice parameter for (Sn) and the value for Sn pure is 0.088 % of the value for Sn pure.

![Fig. 2. RT-XRD pattern for a sample with composition w(Bi) = 23.7 %, w(Sn) = 38.5 % and w(Zn) = 37.8 % after Rietveld refinement](image-url)
For (Zn), the difference between the average $a = b$ lattice parameter for (Zn) and the value for Zn pure is $0.038\%$ of the value for Zn pure and the difference between the average $c$ lattice parameter for (Zn) and the value for Zn pure is $0.061\%$ of the value for Sn pure (Fig. 5) considering [7].

For (Bi), the difference between the average $a = b$ lattice parameter for (Bi) and the value for Bi pure is $0.095\%$ of the value for Bi pure and the difference between the average $c$ lattice parameter for (Bi) and the value for Bi pure is $0.238\%$ of the value for Sn pure (Fig. 5) considering [7].

Fig. 3. RT-XRD pattern for a sample with composition $w$(Bi) = 53.3 %, $w$(Sn) = 4.9 % and $w$(Zn) = 41.8 % after Rietveld refinement

Fig. 4. Lattice parameters for (Sn) found after Rietveld refinement. a) $a = b$ (Å) b) $c$ (Å). Inside the circle the value for pure Sn from [7] and inside the square the value for pure Sn from [8].
Bi pure (Fig. 6) considering [7].

As expected the difference between the measured values of the lattice parameters for (Zn) and Zn [7,9] are of the order of the experimental error (Fig. 5). The major differences between the lattice parameter of the pure element and of the respective phase are for a = b in the case of (Sn) and for c in the case of (Bi). For both cases the value of the experimental lattice parameters are higher than those for the pure elements if [7] is considered. That is expected in what concerns (Sn) since it dissolves Bi and Bi as a higher covalent radius than Sn. If Bi occupies Sn sites in the lattice it is expected that the resulting lattice will be expanded when compared with that from pure Sn. For the latter reason, what is not expected is that

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**Fig. 5.** Lattice parameters for (Zn) found after Rietveld refinement. a) a = b (Å) b) c (Å). Inside the circle the value for pure Zn from [7] and inside the square the value for pure Zn from [9].

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**Fig. 6.** Lattice parameters for (Bi) found after Rietveld refinement. a) a = b (Å) b) c (Å). Inside the circle the value for pure Bi from [7] and inside the square the value for pure Bi from [10].
the lattice will be contracted (which is what happens in the case of (Bi) if we take [7] into account) when Sn substitutes Bi. Hence, it may be supposed that the discrepancy found for (Bi), when compared with Bi from [7], is maybe due to two possibilities: the presence of Sn atoms in interstitial spaces (in the c direction) or to experimental inaccuracies. If we take the values for pure Bi from [10], we can consider that the substitution of Bi by Sn results in a contraction of the lattice in the a = b direction.

3.2. High Temperature

If a crystalline solid is isometric (has the same structural configuration throughout), the expansion will be uniform in all dimensions of the crystal. If it is not isometric, there will be different expansion coefficients for different crystallographic directions, and the crystal will change shape as the temperature changes.

The linear expansion coefficient, $\alpha$, is given by equation 1:

$$\alpha_L = \frac{1}{L(T=0^\circ C)} \frac{dL}{dT} \quad (1)$$

$L$ is one of the dimensions of the solid. In this case we've made $L$ has a lattice parameter: $a = b$ or $c$. $dL/dT$ is the obtained by linear regression of the data obtained experimentally.

If a crystalline solid is isometric, the linear expansion coefficient $(Bi)$ seems to be isometric $\alpha_{a=b} \approx c$ (Fig. 7 a) and b)) but not $(Zn)$ (Fig. 8 a) and b)). For polycrystalline Zn $\alpha_L = 3.97E^{-5} K^{-1}$ (for $20^\circ \leq T \leq 250^\circ C$) as it is tabulated in [11]. For a single crystal $\alpha_c = 6.1E^{-5} K^{-1}$ (for $0^\circ \leq T \leq 100^\circ C$) and $\alpha_{a=b} = 1.5E^{-5} K^{-1}$ (for $0^\circ \leq T \leq 100^\circ C$) [11].

Fig. 7. (Bi) lattice parameters as a function of temperature a) $a = b(T)$ b) $c(T)$ obtained with a sample with $w(Bi) = 68.4 \%$, $w(Sn) = 6.0 \%$ and $w(Zn) = 25.6 \%$. Experimental expansion coefficient in comparison with that from [13]. Points surrounded by a circle were not considered for the calculus.

$T \leq 100^\circ C$ [11]. Our results (Fig. 8 a) and b)) are more in agreement with those for a single crystal, indicating thermal anisotropy.

$(Zn)$ has a hexagonal structure in which d (interplanar distance) is related with h, k, l (the Miller indices) and with the lattice parameters $a = b$ and $c$, as follows:
If a reflection corresponds to [002], \( h = 0, \ k = 0 \) and \( l = 2 \), equation 2 becomes: 
\[
\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}
\]  
(2)

In this case, it can be written: \( c = d/2 \).

By analysing the reflection [002] (Fig. 9) we can have a direct measure of the c lattice parameter. We've compared c obtained by the analysis of [002] and by Rietveld refinement in Fig. 10. We've also compared obtained by both ways.

In Fig. 11 it can be observed the volume of the unit cell of (Zn) as a function of the temperature as well as the experimental expansion coefficient.

In Fig. 12 it was plotted the mass density as a function of temperature that was calculated using the equation:

\[
\rho = \frac{nM}{V_{\text{unit cell}}N_A}
\]  
(3)

In which \( n \) is the number of atoms per unit cell, \( M \) the atomic weight, the volume of the unitary cell and \( N_A \) the Avogadro's number.

Using the equation that resulted from the linear fit (Fig. 12), we could calculate the mass density at 250°C as \( \rho_{250\,\text{°C}} = 6.929 \) gcm\(^{-3} \) and compare it with the experimental result from [12], \( \rho_{250\,\text{°C}} = 6.674 \) gcm\(^{-3} \), which corresponds to a difference of 3.8 % (in comparison with the value in [12]). It was also calculated the value at 750 °C, for Zn liquid, \( \rho_{750\,\text{°C}} = 6.423 \) gcm\(^{-3} \) and compared with \( \rho_{750\,\text{°C}} = 6.265 \) gcm\(^{-3} \) from [12]. It corresponds to a difference of 2.5 % (in comparison with the value in [12]). For Zn liquid, the data from [12] was linear fitted and it was obtained: 
\[
\rho(\text{kgm}^{-3}) = 6877 - 0.8199 \cdot T(\text{oC})
\]  
that is comparable with that from Fig. 12.

It was also possible to compare our result, at 20 °C, \( \rho_{20\,\text{°C}} = 7.162 \) gcm\(^{-3} \), with that from [13] \( \rho_{20\,\text{°C}} = 7.140 \) gcm\(^{-3} \), which corresponds to a difference of 0.3 % (in comparison with the value in [13]).

Fig. 8. (Zn) lattice parameters as a function of temperature a) \( a = b(T) \) b) \( c(T) \) obtained with a sample with \( w(\text{Bi}) = 68.4 \% \), \( w(\text{Sn}) = 6.0 \% \) and \( w(\text{Zn}) = 25.6 \% \). Experimental expansion coefficient in comparison with that from [13]. Points surrounded by a circle were not considered for the calculus.
Fig. 9. Zoom of the HT-XRD diffraction patterns as a function of the temperature obtained for a sample with w(Bi) = 68.5 %, w(Sn) = 5.7 % and w(Zn) = 25.8 %. At T > 120 °C, Sn peaks cannot be distinguished anymore. For (Zn) the reflection corresponding to [002] suffers a deflection with the increasing temperature.

Fig. 10. (Zn) c lattice parameter as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6. c parameter was found after Rietveld refinement (squares) and after the analysis of the reflection corresponding to [002] (circles).

Fig. 11. (Zn) unit cell volume as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6 after Rietveld refinement. Experimental calculated expansion coefficient.

Fig. 12. (Zn) mass density as a function of temperature obtained with a sample with w(Bi) = 68.4 %, w(Sn) = 6.0 % and w(Zn) = 25.6 after Rietveld refinement. Mass density of Zn at a temperature near room temperature [13].
4. Conclusions

Both results at room temperature and at high temperature are in good agreement with what was expected by the observation of the phase diagram and by analysis of the available references.

At room temperature, the dissolution of Bi in (Sn) will make the lattice expand. The interpretation of the dissolution of Sn in (Bi) depends on the values considered for Bi pure.

At high temperatures, (Bi) behaves as an isometric solid but (Zn) shows thermal anisotropy, since $\alpha_c(Zn) > \alpha_{a=b}(Zn)$ as it is expected for a single crystal but not for a polycrystalline solid. Nevertheless, the calculated mass density is in agreement with the published data for room temperature, 250°C and 750 °C.

References

Phase field simulations in miscibility gaps

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1. Introduction

There are many systems that present miscibility gaps in the liquid or solid phase. These systems are, for example, Bi–Zn, Li–Zr, Mg–Mn, S–Sb, Sn–P, Ti–W, Cu–Ni–Sn or even glasses, such as Vycor®, that contains approximately 75 wt% SiO₂, 20 wt% B₂O₃ and 5 wt% Na₂O.

In the ternary phase diagram of B₂O₃–SiO₂–Na₂O, Vycor® corresponds to a composition in which at a given temperature, two immiscible liquid phases are formed, one of them rich in SiO₂. When the sample is quenched from the miscibility gap, the two phases corresponding to the immiscible liquids are kept. For industry and for most of the applications only the SiO₂ rich phase is important, and so the other phase will be leach out leaving a porous, high-silica skeleton [1].

In this paper, the dynamics of a thermodynamically unstable solution with respect to composition variations is studied. In such a regime, nucleation of the new phase is not necessary. The phase transformation occurs spontaneously by spinodal decomposition and may result in a multi-phase microstructure in which phases are highly interconnected (for a certain range of compositions and temperatures of the spinodal region). The latter microstructures have numerous applications: one of them already mentioned is Vycor® glass, whose silica structure can be the matrix for other applications such as the study of superfluids [2].

Another very important and up-to-date application concerns the sol–gels for the production of nanoparticles [3] and membranes, with applications in health and in food technology [4].

The spinodal decomposition may also be used to improve the mechanical properties of certain materials since, in general, spinodally decomposed materials can exhibit very fine scale composition modulations, resulting in very high strength materials. The phase field simulations of solid or liquid miscibility gaps may be used to determine how the mechanical properties (local stress, strain fields or Young’s modulus) depend on the composition of the blend. For example, Cu–Ni–Sn alloys can be hardened by spinodal transformation and are used in electrical contact materials that grip by elastic springback, such as in computer connectors [5].

Lead free solder materials are under investigation for environmental reasons. Structural and mechanical properties are also of great importance in what concerns solders. In order to study the mechanical properties of amorphous solders alloys, it is crucial to study the liquid phase.

The phase field method is a subject of interest since a long time ago. Based on the Ginzburg–Landau theory of phase
between different Gibbs energies that give approximately the same equilibrium compositions, in spite of having different corresponding parameters of the excess Gibbs energy.

In this work we have performed phase field simulations for the two liquids separation occurring in the miscibility gap of the Bi–Zn system, for different temperatures and concentrations. We have used the Bi–Zn Gibbs energy previously calculated using the CALPHAD method and found a rich diversity of asymptotic morphologies for different points of the Bi–Zn phase diagram. It was also possible to determine the asymptotic compositions of Liq.#1 and Liq.#2. The latter calculations were performed for two different Gibbs energies representing the liquid phase of the Bi–Zn system obtained by two different authors [14,15] using the CALPHAD method.

2. Theory and calculation

2.1. Determination of the Gibbs energies using the CALPHAD method

The CALPHAD method was used prior to this work to obtain the Gibbs energy of the liquid phase [16].

The method for the calculation of thermodynamic equilibrium is based on modeling the Gibbs energies of all coexisting phases and minimizing the total Gibbs energy of the system. The system Bi–Zn was assessed by Malakhov [14] but some changes were introduced in the first assessment by [16].

The Gibbs energy of mixing of the substitutional solution (liquid phase mixture in this case) is expressed by [17], as:

\[ G_{\text{mix}} = G^\text{id} + G^\text{e} \]

where \( G^\text{id} = RT \sum x_i \ln(x_i) \) is the ideal mixing contribution, \( x_i \) is the molar fraction of the component \( i \) with \( \sum x_i = 1 \) and \( x_i \) is the molar fraction of the component \( i \) with \( \sum x_i = 0 \). \( G^\text{e} \) is the excess Gibbs energy written as:

\[ G^\text{e} = \sum j \sum_i |x_i| T \ln(T) \]

where \( \sum x_i = a_0 + b \cdot T \) and \( c \) where determined using the CALPHAD method and experimental data.

Vizdal et al. [16], after Malakhov [14], and Djallah et al. [15], assessed the liquid phase using the excess Gibbs energy written as:

\[ G^\text{e} = x_{\text{Bi}} x_{\text{Zn}} 0 I_{\text{Bi, Zn}} + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 1 I_{\text{Bi, Zn}} + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 2 I_{\text{Bi, Zn}} + \cdots + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 6 I_{\text{Bi, Zn}} \]

with \( I_{\text{Bi, Zn}} = a_0 + b \cdot T + c \cdot T \) and \( d \) where determined using the CALPHAD method and experimental data.

Djallah et al. [15] assessed the liquid phase using the excess Gibbs energy written as follows:

\[ G^\text{e} = x_{\text{Bi}} x_{\text{Zn}} 0 I_{\text{Bi, Zn}} + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 1 I_{\text{Bi, Zn}} + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 2 I_{\text{Bi, Zn}} + (x_{\text{Zn}} - x_{\text{Bi}}) \cdot 3 I_{\text{Bi, Zn}} \]

with \( I_{\text{Bi, Zn}} = a_0 + b \cdot T + c_2 \cdot T + \cdots + d \) and \( e \) where determined using the CALPHAD method and experimental data.

3. Phase field simulations

During the phase separation occurring at the spinodal region of Bi–Zn system, a mixture of Liq.#1 and Liq.#2 is formed. Because the mixture is incompressible we can characterize the system by one order parameter, \( \phi \), which is defined as \( \phi = x_{\text{Zn}} - x_{\text{Bi}} \). The free energy of the system can be written, phenomenologically, as the Landau functional [6,18],

\[ F[\phi] = \int d\vec{r} \left[ k (\nabla \phi)^2 + G^{\text{ideal}}(\phi) \right] \]
where $G_{\text{liquid}}(\phi)$ is the Gibbs energy $G_{\text{mix}}$, presented in (1) (making $\phi = x_{\text{Zn}} - x_{\text{Bi}}$). The surface tension corresponds to the energy of the flat interface per unit length and is given by $\sigma = k \int \left( \frac{\partial \phi}{\partial n} \right)^2 \, dA$, where the integral is performed across the interface and in the direction normal to it. The functional derivative of $F$ is $\delta F / \delta \phi = k \nabla^2 \phi - \frac{\partial G_{\text{liquid}}}{\partial \phi}$.

The time evolution of the order parameter can be described by Cahn–Hilliard equation for the phase separation in isotropic solids or liquids at the diffusive regime [6,18], which can be written in the form of a continuity equation $\partial \phi / \partial t = - \nabla \cdot \vec{j}$, with current $\vec{j} = - \nabla (\delta F / \delta \phi)$. Since $\phi$ is conserved in the total volume, $\partial \phi / \partial t$ is the divergence of a flux $\vec{j}$.

$$\frac{\partial \phi}{\partial t} = - \nabla \cdot \vec{j} = \nabla^2 \left( \frac{\partial G_{\text{liquid}}}{\partial \phi} - k \nabla^2 \phi \right).$$

(3)

The asymptotic growth regime for phase separation in binary liquids, in the diffuse regime, is given by $L \propto t^{1/3}$, where $L$ is the characteristic length of the phase boundaries. Thus, the asymptotic evolution is very slow leading to almost stationary morphologies for large evolution times. The time that is needed to reach the asymptotic growth regime in a given sample will in general depend on the mobility of the alloy species. In a future work we intend to calibrate the key parameters characterizing the
system by performing a detailed quantitative study of the time evolution of $L$ in the simulations and a subsequent comparison with the observed one in different system samples.

In Eq. (3) changing the time scale can scale out $k$. In fact the same dynamics can be obtained with a different surface tension by changing the size of the simulation box accordingly. Hence, the asymptotic morphology of the system is just a function of the Gibbs energy and not of the value of $k$.

In the alloy system, the atoms of A and B (Bi and Zn in this case) can exchange position only locally (not over large distances), leading then to a diffusive transport of the order parameter.

We have integrated (3) using a standard finite-difference method [19]. In all simulations we have used initial random conditions for $\phi$ and $k = 1$.

4. Results and discussion

In Figs. 1 and 2 both the miscibility gap and spinodal curves, obtained after the assessments of [14,16] and [15] respectively, can be observed. In Fig. 1 the points corresponding to the asymptotic values of $x$(Liq.#1, Zn) and $x$(Liq.#2, Zn), obtained in this work by phase field simulations, can also be observed.

In Fig. 3, the miscibility gap curve of the Bi–Zn system is shown. A good agreement between the equilibrium curve calculated in [16] and the one obtained by the simulations was found as expected. Here, the simulations’ images for different compositions and temperatures represent the asymptotic morphologies of the Bi–Zn system near the equilibrium configuration. It can be seen that the size and shape of the domains change considerably with temperature for the same concentration, and with the concentration, for the same temperature.

In Fig. 4 equivalent results to those of Fig. 3 are shown. It can be observed that the morphologies corresponding to the same temperatures and compositions are considerably different. For instance, interconnected structures may appear in a region of the miscibility gap of Fig. 4 where in Fig. 3 round shaped domains appear.

By the analysis of the asymptotic morphologies shown inside the miscibility gap, it can be seen that for the compositions near each side of the spinodal line (Figs. 1–4), there is a matrix of the more abundant liquid and inside this matrix, isolated round shaped domains of the other liquid phase appear. Concerning the system’ compositions that are more in the middle of the spinodal region, for the same temperature as the previously referred morphologies, interconnected domains can be observed. These interconnected domains have many applications and the identification of the compositions for which they appear is crucial [20,21].

Note for example that, for $x$(Zn) = 0.8 in Fig. 3, interconnected domains appear at least for $T \leq 780$ K. Only round shaped domains can be observed for $x$(Zn) = 0.8 in Fig. 4. If the phase diagrams and spinodal lines are compared, it can be seen that the latter composition in the miscibility gap of Fig. 4 corresponds to the center of the spinodal region and that at $T = 720$ K it is clear...
Fig. 6. 3D diagrams showing the evolution of the two immiscible liquids in the Bi–Zn phase diagram for an alloy with x(Zn) = 0.8 at 700 K and at 800 K. The arrow points the direction of time evolution. The Gibbs energy used was determined by [14,16].

Fig. 7. The Vycor® glass (a) and (b). SEM microphotograph by Vogel [20]. (c) is a simulation obtained for the Bi–Zn system using the Gibbs energy determined by [14,16]. The simulation was obtained for the condition T = 700 K, x(Zn) = 0.8 and the figure was graphically modified to be easily compared with the real one obtained with the glass. The objective is to show that the morphologies obtained using phase field simulations and Gibbs energies, assessed by the CALPHAD method, can be very similar to the real ones for different systems.

that Liq.#1 is more abundant (matrix is Liq.#1). On the contrary, by the observation of Fig. 2, it can be seen that x(Zn) = 0.8 does not correspond to the center of the spinodal and that at T = 720 K it is clear that Liq.#2 is more abundant (matrix is Liq.#2).

The analysis of the morphologies as a function of temperature also reveals that the interconnected domains will change to spheres as the temperature rises to the upper limit of the miscibility gap.
Fig. 8. Schematic phase diagram of the miscibility gap (solid line) and spinodal (broken line) of the sol–gel system (SiO$_2$/others) and SEM micrographs of the dried sol–gels obtained by Nakamura et al. [21]. A – isolated pores – (the base is silica and pores were left by the other phase belonging to the miscibility gap). At the middle the zoom of the real microphotograph and on the right the 2D simulation obtained for Bi–Zn that was treated graphically to be easily compared with real structures. B – interconnected structure – (the base is silica and pores were left by the other phase belonging to the miscibility gap). At the middle the zoom of the real microphotograph and on the right the 2D simulation obtained for Bi–Zn that was treated graphically to be easily compared with real structures. C – aggregates of particles (the particles are from silica and space around them was left by the other phase belonging to the miscibility gap). At the middle the zoom of the real microphotograph and on the right the 3D simulation obtained for Bi–Zn that was treated graphically to be easily compared with real structures. The same type of variation of structure with composition for a given temperature, that can be seen in A, B, and C, can also be observed on the simulations of the Bi–Zn (Figs. 3 and 4) at $T = 700$ K.

The same type of composition and temperature morphologies dependence was found in [20,21].

It can also be seen in Fig. 5 that the dynamics toward equilibrium also differs when different Gibbs energies are considered. We have performed 3D simulations of the phase separation for the Gibbs energy of [14,16], as it can be observed in Fig. 6, where the evolution of the phase boundaries is presented for two different temperatures.

Although Vycor and sol–gel cannot be directly compared with Bi–Zn, it is relevant to show that, in spite of their different Gibbs
energies, similar morphologies can be observed in corresponding relative positions of the miscibility gap and spinodal regions. This fact enhances the possible applications of the method.

Figs. 7 and 8 show comparisons between our Bi–Zn simulated morphologies (obtained with the Gibbs energy [14,16]) and similar ones for observed samples of Vycor® [20] and sol–gel [21], respectively.

5. Conclusions

Using phase field simulations, the dynamics of the two immiscible liquids appearing on the phase diagram of the Bi–Zn system was studied. Good agreement between the miscibility gap curve determined by the simulations and the one obtained by the CALPHAD method was found, as expected.

It was found a rich diversity of asymptotic morphologies for different points of the Bi–Zn phase diagram.

We have compared the morphologies for two different Gibbs energies determined by Calphad method and found very different morphologies for the same times, concentrations and temperatures. Thus, it can be concluded that the different morphologies and the time it takes to reach them is a signature of the calculated excess Gibbs energy parameters for a given system. It could also be verified the similarities between the simulated structures and those observed in different real systems, such as Vycor® glass and sol–gel.

It can be pointed out, that for a given temperature, the morphologies of the Bi–Zn system depend on the composition in a similar way as those observed in the sol–gel system, especially the morphologies obtained with one of the Gibbs energies.

The results obtained in this work show that using the Gibbs energies, obtained for example with the CALPHAD method and phase field simulations, we have a straightforward method to determine the morphologies of the miscibility gap as a function of the concentration, temperature and time. This method may be useful to find the best structures, depending on the applications and purposes; for instance, for the fabrication of nanoparticles.

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References

Chapter 5 - Al-Fe-Ti SYSTEM
Chapter 5.

Al-Fe-Ti SYSTEM

5.1. Introduction

Aluminum-based intermetallic alloys with transition metals are of high interest for their complex crystalline and quasicrystalline structures, formed primarily with late transition metals, and their technologically useful compounds (Mihalkovic & Widom, 2012). Experimental phase diagram determination is difficult because many structures usually exist within small composition ranges; many are intrinsically exhibiting mixed or partial site occupancy.

First principles calculations can help resolve some uncertainties in the phase diagrams but are challenging themselves, for many of the same reasons. Intrinsic disorder requires studying alternative realizations of specific site occupancy. Some of the nearby competing phases may have unknown or poorly known structures. The large unit cells pose computational difficulties. Further complicating the study is the prevalence of magnetism among late transition metals.

The Al-Fe-Ti system was object of our study as one of the goals of the COST 535 EU action, "Thermodynamics of Alloyed Aluminides", 2004-2007. We have performed X-ray diffraction at room (RT-XRD), high temperature (HT-XRD) Differential Scanning Calorimetry (DSC) and Electron Probe Micro Analysis (EPMA) with samples belonging to the system.

In this chapter only the study of the Al-Fe system is going to be described, since this system was studied both experimentally and theoretically. In the nearest future, we will be studying the Al-Fe-Ti by means of first principles theoretical calculations to complement the experimental study we've developed already.
5.2. Al-Fe system

Recently, a paper from (Stein et al., 2010) described the ε phase of the Al-Fe system to have body-centered cubic structure of the Hume-Rothery Cu₅Zn₈-type (space group I-43m), formula Al₈Fe₅, and lattice parameter $a = 0.89757(2)$ nm at 1393K, which is 3.02 times that of cubic AlFe (B2) at the same temperature.

Previously, in 1993, the system was assessed by Kattner & Burton (Fig. 5.1).

![Fe-Al phase diagram](image)

**Fig. 5.1** The Fe-Al system according to the assessment by Kattner & Burton, 1993.

We have performed Differential Scanning Calorimetry (DSC) experiments to define the whole range of stability of the ε phase. The experiments were executed at 10 K/60s and under an Ar flux (Fig. 5.2). We’ve used Alumina crucibles with lids. The samples were prepared from the pure elements, in an arc melting furnace, annealed at 1273 K for 43200s. and cooled down at 0.5 K/60s. The DSC results here presented are in very good agreement with Kattner & Burton, 1993 (Fig. 5.2) and Table 5.1.
At room temperature, the latter samples (that were subsequently submitted to the DSC measurement cited before) presented a two phase region constituted by AlFe and Al\textsubscript{2}Fe, as the Electron Probe Micro Analysis (EPMA) has shown in Fig. 5.3.

**Fig. 5.2** DSC curves obtained in this work (above) were superimposed to the phase diagram in a region centered on the stability range of the \(\varepsilon\) phase of the Fe-Al system (Kattner & Burton, 1993). Dots and dashed lines (below) show the transformation temperatures correspondent to each signalized composition. They were obtained from the DSC curves shown above.

Subsequently to that of Kattner & Burton, 1993, other assessments were performed (e.g. Sundman et al., 2009). In the latter reference, the \(\varepsilon\) phase was modeled recurring to a two sublattice model based on the work of Stein et al., 2010 (Fig. 5.4) that was initially presented in a COST – 535 meeting in 2008. Nonetheless, the experimental data on the phase diagram are not fully described by the assessed \(\text{Al}_{8}\text{Fe}_{5}\cdot\varepsilon\) phase. Furthermore the invariant temperature of the eutectoid reaction \(\text{Al}_{8}\text{Fe}_{5}\cdot\varepsilon \rightarrow \text{AlFe} + \text{Al}_{2}\text{Fe}\), which was found to be 1375 K in (Kattner & Burton, 1993) and that is in agreement with our DSC data (1371 K), was assessed to be 1362 K in (Sundman et al., 2009) (Fig. 5.5).
Table 5.1 Transformation temperatures obtained by means of DSC. In bold, the invariant temperatures.

<table>
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<tr>
<th>x(Al)</th>
<th>$\varepsilon \rightarrow \text{AlFe} + \text{Al}_2\text{Fe}$</th>
<th>$\varepsilon \rightarrow \varepsilon + \text{AlFe}$</th>
<th>$\varepsilon + \text{AlFe} \rightarrow \varepsilon + \text{Al}_2\text{Fe}$</th>
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<td>1500</td>
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Fig. 5.3 EPMA photography and quantitative X-ray analysis of a sample of the Al-Fe system containing x(Al) = 0.62. Results are in agreement with the Al-Fe assessment by Kattner & Burton, 1993.

We have calculated the enthalpies of formation, and the Gibbs energies, as a function of the temperature, as well as the mechanical properties of the AlFe, Al$_2$Fe and of several
compositions and structures that can represent the $\varepsilon$ phase (Fig. 5.6). We have compared our results with the *ab initio* data from Mihalkovic, Widom and coworkers, 2006, with Stein et al., 2010, and Mihalkovic & Widom, 2012.

![High temperature neutron diffraction data](image)

**Fig. 5.4** High temperature neutron diffraction data obtained by Stein et al., 2010. The 1393K was refined including two phases, $\text{Al}_8\text{Fe}_5-\varepsilon$, cubic I-43m and $\text{AlFe}$, cubic, Pm-3m.

![Al-Fe phase diagram](image)

**Fig. 5.5** Sundman et al., 2009, assessed Al-Fe phase diagram. Zoom in the vicinity of the stability range of the $\text{Al}_8\text{Fe}_5-\varepsilon$ phase.
Fig. 5.6 Gibbs energies for several possible compositions and crystal structures of the ε phase and Al$_2$Fe phase.

It can be observed that Al$_4$Fe$_3$, x(Al) = 0.57, cubic, Ia-3d, is the most stable structure for the ε phase and that the tetragonal, I4/mmm, is the most stable for Al$_2$Fe. We haven’t calculated Al$_2$Fe as triclinic, P-1, yet, although this structure was considered by Mihalkovic & Widom, 2012, to be the stable structure of Al$_2$Fe above 380 K. We are in trends of making these calculations. The ε phase should be the most stable in the ε range, however, we still find AlFe to be more stable. The difference between the Gibbs energy of formation of AlFe and the most stable Al$_4$Fe$_3$-ε phase is within the calculation errors, nonetheless, we are still calculating the Gibbs energy of formation of the ε phase with other compositions and structures.

In the nearest future we will compile and publish our results.
5.3. References


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Chapter 6. Final Conclusions and Future work
6. Final Conclusions and Future work

6.1 Final Conclusions

The study performed on the Cu-Sb-S system aims to improve its knowledge by comparing synthetic with natural materials. The compositional variation and thermodynamic properties of the synthetic phases help to establish relations with the natural equivalent composition. The synthetic Tetrahedrite type structure, in its reduced composition \( \text{Cu}_{12}\text{Sb}_4\text{S}_{13} \), and \( \text{Ag}_6\text{Cu}_6\text{Sb}_4\text{S}_{13} \) was studied within the Cu-Sb-S system. Tetrahedrite crystallises in the cubic system space group (I-43m). Moreover in the latter compound Cu can be replaced by other atoms assuming the general \( \text{M}_{12}\text{X}_4\text{S}_{13} \) formula in which \( \text{M} = \text{Cu}, \text{Ag}, \text{Bi}, \text{Hg}, \text{Fe}, \text{Zn}, \text{Pb} \) and \( \text{X} = \text{Sb}, \text{As} \). This phase is very important due to economical reasons. It can carry in its structure precious minor elements. The understanding of the mobility and accommodation of minor elements, like Ag, Bi, Hg, Fe, Zn, Pb, ... that can replace copper positions or form an independent nanostructure in the Tetrahedrite lattice, will allow us to explore the practical applications of this structure.

In this study, we’ve also presented \textit{ab initio} calculations for plain and doped Tetrahedrite, using density functional theory. The selection of a particular doping element/ion is of paramount importance to obtain new and optimized photovoltaic materials from the Tetrahedral type of structures. Using the electronic band structures, density of states and correspondent orbital energies, the probability of certain electrons to be excited from the valence to the conduction band can be inferred. It can also be determined the energy cost of such a jump. Our results for the band structure and density of states for \( \text{Cu}_{12}\text{Sb}_4\text{S}_{13} \) and \( \text{Ag}_6\text{Cu}_6\text{Sb}_4\text{S}_{13} \) show that both compounds have similar band gaps even if the electrons that will jump to the conduction band are from atoms occupying different sites. The energy to overcome the band gap of these semiconductors – Tetrahedrites – falls within the photovoltaic operational range of 1.0 - 2.2 eV and the band gaps can be considered direct, as required.

Concerning the Cu–Li–Mg system, we present some work to respond to the problem of efficient hydrogen storage. This problem remains a major technological obstacle towards the development of a hydrogen-based energy economy.
The fundamental data that supports this work was mainly obtained by neutron diffraction and neutron spectroscopy, differential scanning calorimetry, X-ray diffraction and first-principles calculations.

Based in this data and calculations, it was possible to show that the composition of the ternary compound is CuLi_{x}Mg_{2-x} (x=0.08). By neutron data analysis, especially by pair distribution function fittings and first-principles calculations we were able to determine that Li occupies Mg1 sites (1/2, 0, z).

After analyzing the data obtained by neutron diffraction and neutron spectroscopy, differential scanning calorimetry and first principles calculations we concluded that it is very likely that CuLi_{0.08}Mg_{1.92} will react with hydrogen to form CuLi_{0.08}Mg_{1.92}H_{5}. Nonetheless, according to differential scanning calorimetry results, it is also possible that the stoichiometry of the product is CuLi_{0.08}Mg_{1.92}H_{6}. The structure of the hydride is likely to be monoclinic C2/c which is in agreement with the results obtained both by neutron scattering techniques and first principles calculations. Furthermore, it can be determined the presence of MgH_{2}, formed after hydrogen uptake, even for those samples that did not initially contain CuMg_{2}. We think that CuLi_{0.08}Mg_{1.92}H_{5} will disproportionate to form MgH_{2} and another hydride. In this work it also possible to determine the roll of the Cu-Li-Mg-(H) as a catalyst for both CuMg_{2} and MgH_{2} during absorption and desorption.

Regarding the Bi–Sn–Zn system, the principal results are based on data obtained from differential scanning calorimetry, X-ray diffraction at high and room temperature, scanning electron microscopy and electron microprobe. New values for the liquidus surface of the ternary miscibility gap have also been obtained.

A critical evaluation of the thermodynamic parameters and experimental data available in the literature was carried out for the Bi–Sn, Bi–Zn, Sn–Zn and Bi–Sn–Zn systems. The consistency of the assessed parameters obtained for the Bi–Sn–Zn system was verified by calculation of thermodynamic properties and isothermal and vertical sections of the phase diagram. These results were compared with experimental data, both from our work and the literature. The agreement is excellent for a broad set of experimental measurements carried out by different authors.

Using phase field simulations, the dynamics of the two immiscible liquids appearing on the phase diagram of the Bi–Zn system was studied. Good agreement between the miscibility gap curve determined by the simulations and the one obtained by the Calphad (calculation of phase diagrams) method was found, as expected. It was also found a rich diversity of
asymptotic morphologies for different points of the Bi-Zn phase diagram, and we have compared the morphologies for two different Gibbs energies determined by Calphad method and found very different morphologies for the same times, concentrations and temperatures. Thus, it was concluded that the different morphologies and the time it takes to reach them, is a signature of the calculated excess Gibbs energy parameters for a given system. The latter method may be useful to find the best structures, depending on the applications and purposes; for instance, for the fabrication of nanoparticles.

For the system Al-Fe-Ti, it was observed that Al₄Fe₃, cubic, Ia-3d, is the most stable structure for the ε phase and that the tetragonal, I₄/mmm, is the most stable for Al₂Fe at the ε phase stability range of temperatures. Nonetheless in the ε phase range of stability temperatures, AlFe, Pm-3m, is still more stable than any other calculated structure for the ε phase, including Al₁₄Fe₃. This shows that probably Al₁₄Fe₃ it is not the crystal structure of the ε phase, in spite of the fact that the difference between the Gibbs energy of formation of AlFe and Al₁₄Fe₃-ε is within the calculation errors. We will calculate the Gibbs energies for other possible ε phase’s crystal structures and compare them with that for AlFe, Pm-3m, to obtain the most stable solution.

6.2. Future work

Due to my background in Geology, structures like Chalcopyrite and Tetrahedrite will be object of my interest and will be deeply studied. We will not develop the studies of the Cu-Sb-S system much further, since Sb is toxic. Nonetheless, I will invest future time in the Cu-(Fe,Sn)-S system which will be an interesting system with relation to applications and for which the previous background will be useful.

6.3. Cu-(Fe,Sn)-S system

The Cu-(Fe,Sn)-S system (with Zn, Li, Mn, Ni, In, Ge, Se, Sb... as dopants) with structures of the type Chalcopyrite – Stannite – Kesterite – Tetrahedrite will be the focus of our future work.

We want to synthesize these materials at ambient and at high pressure. High pressure synthesis allows structural changes as those taking place in CuInSe₂, which is tetragonal at
ambient pressure and becomes cubic, NaCl-like, at 7.6 GPa. On further compression, another structural transition is observed at 39 GPa (Pauporté & Lincot, 1995).

Furthermore, we want to synthesize these materials as nanoflakes. Traditionally, multinary Chalcogenides were synthesized by solid-state reaction, which requires high temperature, inert atmosphere protection, and a long time. We want to use a low temperature solution synthesis route, using ethanol, which can produce nanoflakes on a large scale (An, 2003).

The latter nanoflakes will be the basis of an “ink” that we want to develop in order to maximize solar cell absorber areas facilitating the deposition of the photovoltaic material. This will add further possibilities to the thin-films applications.

First principles calculations will allow us, as until now, to choose the best doping elements, by determining as well as controlling the structural and electronic properties. The determination of the mechanical properties will be possible as well. They will provide important information for further mesoscale simulations. To understand the “whole picture”, we will simulate the microstructure from solar irradiation to charge collection using a novel mechanical formalism, which we will develop from scratch using phase field. This study will allow us to visualize and measure the microstructure and develop optimized systems/processes.

The Cu(In,Ga)(Se,S)2 Chalcopyrite type of alloy system provides absorber materials for the most efficient thin-film photovoltaic technology to date (Rau & Schock, 2001). Thin-films based on ZnO/CdS/Chalcopyrite type solar cells are especially outstanding due to their low cost (Dimmler & Schock, 1998), radiation resistance (Dimmler & Schock, 2001), long-term stability (Guillemoles, 2000), and record power conversion efficiencies of over 19% (Contreras et al., 1999).

Traditional solar cell production techniques are usually time consuming and require expensive vacuum systems or toxic chemicals. Depositing chemical compounds such as CIGS on a substrate using vapor phase deposition wastes most of the expensive material in the process (Green, 1982). Chae et al., 2010, have developed a process to create CIGS solar cells based in inkjet printing technology that allows for precise patterning to reduce raw material waste by 90% and significantly lower the cost of producing solar cells with promising, yet expensive compounds.

The work is focused on material based Chalcopyrite type. A layer of this compound with one or two microns thick has the ability to capture the energy from photons about as
efficiently as a 50-micron-thick layer made of silicon (Chae et al., 2010). This is very promising and could be an important new technology to add to the solar energy field, allowing to create working CIGS solar devices with inkjet technology (Chae & al 2010). In particular, they have used the CuGaS₂ compound due to the fact that this material presents a direct band gap in the desirable range.

The copper indium/gallium diselenide Cu(In,Ga)Se₂ (CIGS) thin-film solar cells (Rau, 2001) have emerged as a technology that could challenge the current hegemony of silicon solar panels. This is possible thanks to the peculiar optical and structural properties of CIGS, which possess an extraordinary stability under operating conditions.

However, among ternary Chalcopyrite semiconductors, CuGaS₂ is maybe the most promising material for photovoltaic applications (Chae et al., 2010) due to its bandgap energy (Eg) of 2.43 eV (Siebentritt, 2002) which matches perfectly the solar spectrum for energy conversion and to its large absorption coefficient above Eg. Accurate knowledge of the electronic and optical properties of these materials is very important for many of these applications. In spite of the considerable amount of research devoted to these materials, this knowledge is still incomplete.

The Sulfides can also be mentioned as Chalcogenides, this designation is used when chemical compound containing at least one chalcogen ion (Oxygen, Sulfur, Selenium or Tellurium) and one or more elements with a more electropositive behavior.

Chalcogenide glasses provide a wide range of materials with sufficient stability which transmission of for optical fiber applications at infrared wavelengths (Brady et al., 1998). Some of the earliest demonstrations with Chalcogenide fibers were made with the simple binary glass of arsenic sulfide, AsS, which provided a broad glass formation region and with transmission across the mid infrared (Sanghera & Aggarwal, 1998), and the precedent work involving selenide and telluride glasses provided transmission capabilities at longer wavelengths (Herberholz, et al. 1997). However, even today, the manufacture of Chalcogenide glasses and nanofibers is not straightforward and continues to rely on conventional melting/quenching techniques to produce them.

Recently, Chemical Vapor Deposition (CVD) techniques have been implemented in Chalcogenide fibers fabrication, as it was shown in recent works from (Huang & Hewak, 2004) and (Hewak, 2011). This fabrication has the potential to radically improve the manufacturing process. Hewak, 2011, describes the first phase of a project to adapt the
current fiber manufacture to novel chemical vapor deposition chemistry for application in the next generation of Chalcogenide fibers.

In contrast with silica fibers, which is predominantly a passive material, Chalcogenides exhibit active properties and some are highly nonlinear (Hewak, 2011).

Hewak, 2011, presents the potential applications of the Chalcogenide glasses. These materials can be used in the form of thin-films in the production of highly efficient solar cells and are already used in optical data storage.

Chalcogenide fibers can be used for the transmission of light at wavelengths beyond those possible with silica since glass purity is of the utmost importance for both the scientific study and practical application of Chalcogenides (Huang & Heawak, 2004).

This new process is capable of producing high purity glasses at low cost because it relies on liquid-metal chloride precursors and operates at atmospheric pressure. However, this technique involves a slow growth rate and the required precursors are often impure and expensive.

Some other applications of Chalcogenides are presented by (Harrington, 2004). These compounds are also useful for medical applications such as laser surgery, which requires a wavelength of around 3 μm. Gallium lanthanum sulfide fibers transmit well at this wavelength and their non-toxic components and high melting temperature suits invasive surgery. At similar wavelengths, Chalcogenide fibers have several atmospheric transmission windows (Bureau et al., 2004) and can be applied in spectroscopy and satellites remote sensing (Anne et al., 2009).

6.4. Cu-Li-Mg (H,D) system

The Cu-Li-Mg (H,D) system has been thoroughly studied by the group. At this moment we are studying this system as the base of the negative electrode of a Li battery cell. We expect to have further developments concerning this application soon.

Other ways to explore this system are related with the catalytic effect over other elements and hydrides.
6.5. Al-Fe-Ti system

The Al-Fe system near the ε phase is close to be further understood, both theoretically and experimentally.

We plan to make a bibliography search for being updated with the last studies on the Al-Fe-Ti the system. We will gather all our experimental data and complete it in accordance the publish one.

We want to complement the experimental study with theoretical results for certain phases that compose the system.
6.6. References


