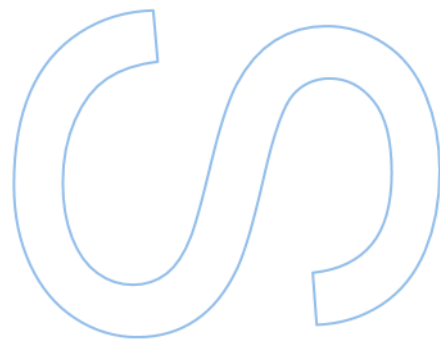
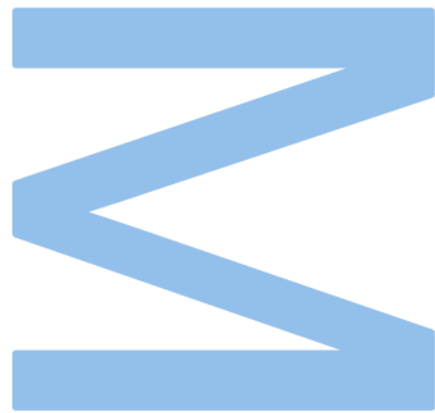


Structural Phase Transitions of Quasi-2D Crystalline Materials

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Master in Astronomy and Astrophysics
Department of Physics and Astronomy
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Resumo

A descoberta de exoplanetas intensificou o interesse no comportamento de materiais sob condições extremas e não-terrestres. Nesta dissertação, recorremos a métodos de primeiros princípios — Teoria do Funcional da Densidade (DFT), Teoria da Perturbação do Funcional da Densidade (DFPT) e o Método de Deslocamento Especial — para investigar as propriedades estruturais, vibracionais e electrónicas de três compostos quasi-2D, naturalmente estruturados por camadas, nomeadamente as perovskitas halogenadas da família Ruddlesden-Popper: K_2CaF_4 , $\text{K}_2\text{CaCl}_2\text{F}_2$ e $\text{K}_2\text{CdCl}_2\text{F}_2$. A partir da fase tetragonal de alta simetria $I4/mmm$, todos os três sistemas relaxam para um estado fundamental ortorrômbico $Cmce$ a 0 K, sempre que os modos instáveis dos fónons são seguidos. As diferenças de energia total indicam que estas fases permanecem praticamente degeneradas (K_2CaF_4 : ≈ 140 meV; $\text{K}_2\text{CaCl}_2\text{F}_2$: 33.36 meV; $\text{K}_2\text{CdCl}_2\text{F}_2$: 39.96 meV), mas apenas as fases $Cmce$ são dinamicamente estáveis.

A análise dos tilts de Glazer revela padrões distintos de distorção octaédrica: K_2CaF_4 apresenta um tilt $a^-a^-c^0$ (associado ao modo de distorção X_3^+) com rotações anti-fase dos octaedros CaF_6 ($a = c = 6,2785 \text{ \AA}$, $b = 13,611 \text{ \AA}$) e gaps electrónicos de 5,9161 eV ($I4/mmm$) $\rightarrow$ 6,0749 eV ($Cmce$). Em contraste, $\text{K}_2\text{CaCl}_2\text{F}_2$ ($a = c = 6,3084 \text{ \AA}$, $b = 16,646 \text{ \AA}$) e $\text{K}_2\text{CdCl}_2\text{F}_2$ ($a = c = 6,3129 \text{ \AA}$, $b = 15,644 \text{ \AA}$) adoptam padrões de tilt $a^0a^0c^+$ (modo X_2^+) com rotações em fase dos octaedros BX_6 ; os respectivos gaps electrónicos aumentam apenas de forma marginal (por exemplo, 3,7674 eV $\rightarrow$ 3,8802 eV para $\text{K}_2\text{CdCl}_2\text{F}_2$). A densidade de estados projectada revela bandas de valência dominadas por orbitais p dos halogéneos e bandas de condução por orbitais s do ião B ou do K, o que indica um carácter iónico robusto preservado através das distorções.

Estes resultados elucidam de que forma a escolha do ião B e a substituição de halogéneos controlam os mecanismos de tilt octaédrico e a estabilização dinâmica de perovskitas de baixa dimensionalidade, mantendo simultaneamente um comportamento isolador eléctrico com gap electrónico largo. As conclusões fornecem uma base sólida para a modelação deste tipo de materiais sob condições exoplanetárias. Trabalhos futuros explorarão a dinâmica da rede em função da temperatura e a eventual ocorrência de expansão térmica negativa nestes análogos de Ruddlesden–Popper.

Palavras-chave: física, astrofísica, astromineralogia, matéria condensada, perovskites, poeiras cósmicas, exoplanetas

Abstract

The discovery of exoplanets has intensified interest in the behavior of materials under extreme, non-terrestrial conditions. In this dissertation, we employ first-principles methods—Density Functional Theory (DFT), Density Functional Perturbation Theory (DFPT), and the Special Displacement Method — to investigate the structural, vibrational, and electronic properties of three layered halide perovskite-related compounds of the Ruddlesden-Popper family: K_2CaF_4 , $\text{K}_2\text{CaCl}_2\text{F}_2$, and $\text{K}_2\text{CdCl}_2\text{F}_2$. Starting from a high-symmetry tetragonal $I4/mmm$ parent, all three systems relax into an orthorhombic $Cmce$ ground state at 0K whenever unstable phonon modes are followed. The total energy differences show that these phases remain nearly degenerate (K_2CaF_4 : ≈ 140 meV; $\text{K}_2\text{CaCl}_2\text{F}_2$: 33.36 meV; $\text{K}_2\text{CdCl}_2\text{F}_2$: 39.96 meV), but only the $Cmce$ phases are dynamically stable.

Glazer tilt analysis reveals distinct octahedral distortion patterns: K_2CaF_4 exhibits an $a^-a^-c^0$ tilt (X_3^+ mode) with out-of-phase CaF_6 rotations ($a = c = 6.2785 \text{ \AA}$, $b = 13.611 \text{ \AA}$) and band gaps of 5.9161 eV ($I4/mmm$) $\rightarrow$ 6.0749 eV ($Cmce$). In contrast, $\text{K}_2\text{CaCl}_2\text{F}_2$ ($a = c = 6.3084 \text{ \AA}$, $b = 16.646 \text{ \AA}$) and $\text{K}_2\text{CdCl}_2\text{F}_2$ ($a = c = 6.3129 \text{ \AA}$, $b = 15.644 \text{ \AA}$) adopt an $a^0a^0c^+$ tilt (X_2^+ mode) with in-phase BX_6 rotations; their band gaps increase only marginally (e.g. 3.7674 eV $\rightarrow$ 3.8802 eV for $\text{K}_2\text{CdCl}_2\text{F}_2$). Projected density of states shows valence bands dominated by halogen p -orbitals and conduction bands by B-site or K s -orbitals, indicating robust ionic character preserved across distortions.

These results elucidate how B-site cation choice and halide substitution govern octahedral tilt mechanisms and dynamic stabilization of low-dimensional perovskites, while maintaining wide-gap insulating behavior. The findings provide a foundation for modeling such materials under exoplanetary conditions. Future work will explore temperature-dependent lattice dynamics and potential negative thermal expansion in these Ruddlesden-Popper analogues.

Keywords: physics, astrophysics, astromineralogy, condensed matter, perovskites, cosmic dust, exoplanets

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1. Introduction

Since ancient times, humanity has looked to the skies to understand nature and our place in the universe. As early as 1000 BCE, the Assyro-Babylonians recorded the periodic motion of stars to keep track of time [1]. Their observations were not just for curiosity purposes—they played a vital role in agriculture, religious rituals, and navigation on both land and sea.

The ancient Greeks advanced this pursuit by trying to measure stellar and planetary distances and explain the mechanics of the universe. Although the geocentric model dominated at the time, astronomers were already moving towards more accurate understandings. Notably, Aristarchus of Samos proposed a heliocentric model and attempted to estimate the distances between the Sun, Earth, and Moon using geometry and early trigonometry [1].

By reaching the Renaissance period, astronomy had already transitioned from a practical tool for timekeeping to a rich scientific field, however still full of unanswered questions. Nicolaus Copernicus revived the heliocentric model in 1543, challenging the long-standing Earth-centered view, and a few decades later, Galileo Galilei's telescopic observations—such as the phases of Venus and the moons of Jupiter—provided us a glimpse into the complexity of our universe [2, 3].

By the 1930s, mineralogy had become an interdisciplinary part of astrophysics [4], especially in the study of interstellar dust. Early research relied mainly on photometry, the measurement of a star's light intensity across broad wavelength regions, to study the brightness and color of stars. This helped estimate properties like albedo (reflected stellar light) of solar system bodies and extinction (the dimming and reddening of starlight caused by dust and gas). However, these measurements couldn't reveal the dust composition.

This changed with the development of spectroscopy. From the 1950s onwards, Infrared (IR) and Ultraviolet (UV) detectors on telescopes allowed researchers to identify the composition of gas clouds, mostly composed of Molecular Hydrogen (H_2), dust grains, minerals, and molecules such as Carbon Monoxide (CO), and Polycyclic Aromatic Hydrocarbons (PAH). Such a breakthrough offered insights, not only into distant molecular clouds, but also of minerals found in comets and asteroids in our own Solar System [5, 6].

Spectroscopy played a key role in identifying dust grain components in the Milky Way. By the 1960s, researchers began studying materials like graphite and meteoritic silicates—both valuable due to their distinct spectral fingerprints. Graphite, for example, shows a clear extinction bump at 217 nm (UV region) [5, 7]. Silicates, on the other hand, are recognized by their Si–O stretching and bending modes in the mid-infrared (e.g. with well-defined absorption lines around $9.7\ \mu\text{m}$, $18\ \mu\text{m}$ wavelengths). A major discovery came with the detection of a broad $10\ \mu\text{m}$ absorption feature in the spectra of late-type giant stars [8], as shown in Fig. 1.1. These are evolved, cool stars (spectral types K and M) that have exhausted their core hydrogen. The feature was traced to Si–O vibrations in circumstellar silicate grains, offering the first strong evidence that minerals could form in the outer atmospheres of dying stars [5, 9, 10]. Even so, these tools alone weren’t always enough to pinpoint specific minerals.

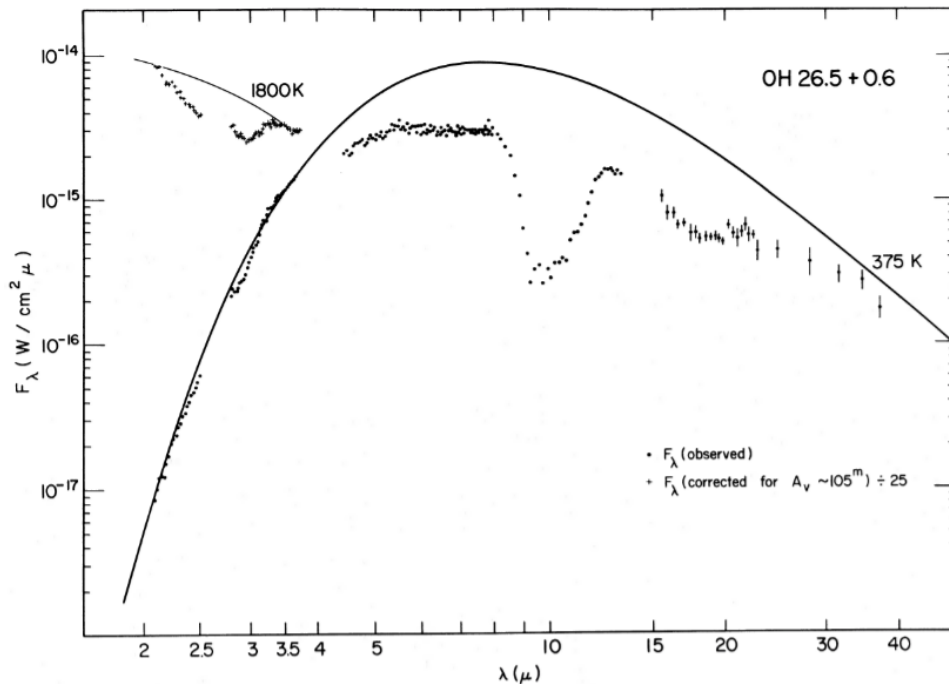


Figure 1.1: A major discovery in the infrared spectra of late-type giant stars was the detection of a broad $10\ \mu\text{m}$ absorption feature, within the $9.7 - 18\ \mu\text{m}$ wavelength range, attributed to Si–O vibrational modes in circumstellar silicate grains. Spectrum of OH 26.5 + 0.6 obtained in 1976 May-June. The solid line represents a 375 K blackbody fit to the $2 - 4\ \mu\text{m}$ data only. The pluses in the upper portion of the figure are the $2 - 4\ \mu\text{m}$ data, corrected for an amount of reddening corresponding to $A_v = 105\ \text{mag}$. The thin line represents a blackbody fit through the corrected 2.0 and $4.0\ \mu\text{m}$ points. Adapted from Ref. [11].

In the 1970s, astrophysics expanded research into the laboratory. Researchers began simulating space-like conditions — low temperatures, high vacuum, and intense radiation—to grow and study cosmic dust analogues. This marked the birth of laboratory astrophysics, a new approach that enables scientists to test how dust grains form and interact

with light, then compare these results with telescope data [5, 12].

At the same time, advances in IR spectroscopy allowed more accurate modeling of dust grain properties. Combining laboratory experiments with astronomical observations, provided researchers with a more complete and accurate description of what cosmic dust is composed of [5]. These works led to the identification of key mineral species, such as silicates, whose mid-infrared features, already observed astronomically, could now be replicated and studied under controlled laboratory conditions. Figure 1.2 presents a comparison of the mass absorption coefficients of natural and synthetic silicate minerals, demonstrating their spectral similarity and supporting their use in identifying dust components in the circumstellar environments of late-type giant stars.

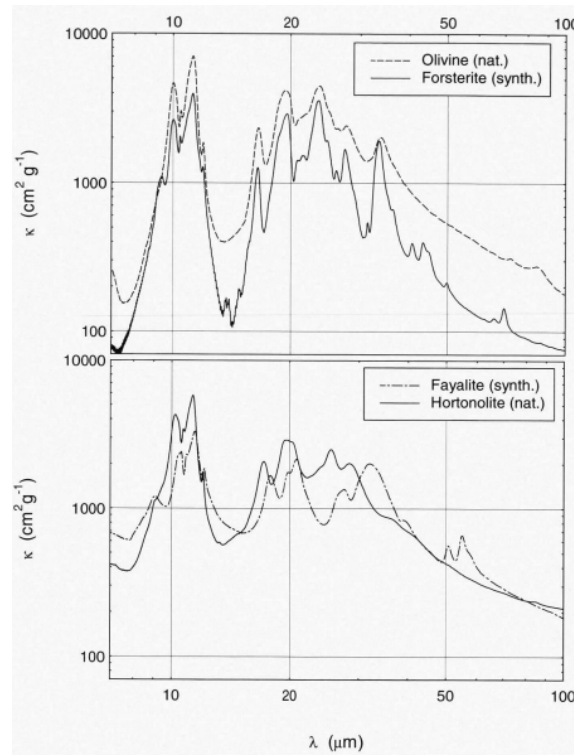


Figure 1.2: Mass absorption coefficients (κ) of olivine-type silicate minerals as a function of wavelength (λ) in the infrared range. The top panel compares natural olivine with synthetic forsterite, while the bottom panel shows synthetic fayalite and natural hortonolite. Distinct spectral features between 10 – 100 μm correspond to Si–O vibrational modes, highlighting compositional differences among the samples. Adapted from Ref. [13]

A major milestone occurred between 1996 and 1998, when the Infrared Space Observatory (ISO) carried out detailed studies of crystalline silicate bands in interstellar and circumstellar dust [14, 15]. These observations provided compelling evidence of mineralogical diversity in space. It was during this period that the term “astromineralogy”

was coined [4], reflecting a growing synthesis between observational astronomy, spectroscopy, and solid-state mineral physics. With these observations, Jäger et al. provided laboratory measurements of mass absorption coefficients for olivines and pyroxenes with varying magnesium-to-iron ratios. These data were crucial for interpreting ISO's spectral observations of crystalline silicates [16].

1.1. Detection of Molecular Clouds in Deep Space

Molecular clouds are the coldest components of the interstellar medium (ISM), typically with temperatures below 30 K and hydrogen number densities ranging from 10^2 to 10^6 cm^{-3} . These clouds are the principal sites of star formation and play a crucial role in galactic evolution. Detecting and characterizing these requires specialized observational techniques, as their low temperatures and high extinction coefficients result in these clouds being 'invisible' at optical wavelengths.

The primary method for detecting molecular clouds relies on radio and millimeter-wave observations of rotational transitions of trace molecules. The most commonly used tracer is carbon monoxide (CO), particularly the $J = 1 \rightarrow 0$ transition at 115 GHz. Despite CO being less abundant than molecular hydrogen (H_2), it is easily detectable due to its permanent electric dipole moment and relatively strong emission lines. Since H_2 lacks a permanent dipole moment and its quadrupole transitions occur at far-infrared wavelengths with low probabilities, detecting it directly in the cold clouds proves to be a challenge and requires very demanding observations [17]. Therefore, CO is used as a proxy, with a CO-to- H_2 conversion factor (X_{CO}) applied to estimate the total molecular gas mass [18].

Large-scale surveys using single-dish telescopes, such as the Institut de Radioastronomie Millimétrique 30-meter telescope (IRAM 30m), Nobeyama 45m, and Atacama Pathfinder Experiment (APEX), have provided valuable maps of CO emission across the Milky Way and nearby galaxies [19–22]. These instruments offer good sensitivity and large sky coverage but are limited in angular resolution. For higher spatial resolution, interferometric arrays like the Atacama Large Millimeter/submillimeter Array (ALMA) and the Submillimeter Array (SMA) combine signals from multiple antennas to produce detailed maps of molecular line emission [23–26]. These allow us to resolve substructures within molecular clouds, such as filaments and dense cores, and to study kinematics, turbulence, and cloud fragmentation processes.

IR observational results offer a complementary approach by tracing thermal emission from dust grains that are well mixed with molecular gas. Space-based observatories such as Spitzer Space Telescope (Spitzer), Herschel Space Observatory (Herschel), and the James Webb Space Telescope (JWST) detect mid- to far-infrared radiation from cosmic dust, which absorbs starlight and re-emits it thermally. Spectral Energy Distribution (SED) fitting of multi-wavelength photometry yields estimates of dust temperature, column density, and cloud mass [27, 28]. Infrared Dark Cloud (IRDC), which appear as absorption features against bright mid-infrared backgrounds, also signal the presence of particularly dense and cold molecular structures.

UV spectroscopy provides a means of directly detecting H_2 via its electronic transitions in the Far Ultraviolet (FUV), typically between 91–112 nm, which correspond to the Lyman (B-X) and Werner (C-X) bands. Instruments like the Hubble Space Telescope's Cosmic Origins Spectrograph (COS) and the Far Ultraviolet Spectroscopic Explorer (FUSE) have been used to study H_2 absorption lines in the spectra of bright background sources such as OB stars and quasars. These measurements allow for the determination of H_2 column densities, excitation temperatures, and the distribution of molecular gas in diffuse and translucent clouds [29]. However, this method is limited to low-extinction sightlines, as dust attenuation quickly suppresses FUV signals in denser regions.

Beyond the commonly used methods, molecular tracers such as HCN, HCO^+ , N_2H^+ , and CS are employed to investigate a range of density and chemical environments within molecular clouds. Alongside these, deuterated molecules like DCO^+ and N_2D^+ serve as important indicators of chemical evolution in such regions [30, 31].

As these molecules are not typically found in warmer environments, their presence signals a cold and chemically evolved environment.

Additionally, isotopologues, such as ^{13}CO , $C^{18}O$, provide us with further information about the depletion processes in cold cores. Such a process refers to the gas-phase molecules sticking to surfaces of cold dust grains and freezing out the gas, reducing their detectability [32]. Spectral line surveys across a range of frequencies enable the construction of detailed chemical inventories. Observing these specific molecules aids the researchers to identify where star formation is likely to begin and provides insights into the physical and chemical conditions that exist during the earliest stages of this process.

Together, multi-wavelength observations across the radio, infrared, and UV regimes, all

form a coherent picture of the structure, composition, and physical conditions of molecular clouds, and enable a deeper understanding of the processes that lead to star and planet formation.

1.2. Quasi 2D-Perovskites structures - potential constituents of Exoplanets and Planetary Interiors

Today, advances in observational technologies have not only enabled the detection of exoplanets in distant star systems, but also the characterization of their atmospheres, yielding insights into their chemical compositions. The next frontier is directing planetary studies to exoplanetary surfaces—that is currently in its infancy, however expected to develop during the upcoming decades.

Theoretical approaches offer a powerful bridge to this future. First-principle calculations, or classical molecular dynamics, when assumed pressure–temperature regimes of environments under interest, may predict plausible stable mantle mineral assemblages and even uncover deep-interior catalytic reactions (e.g. formation of diamond from methane [33]). Moreover, detailed geological and geochemical analyses of planetary surfaces—when paired with interior models—provide essential clues to the formation history, sharpening our overall understanding of planetary structure and evolution. In particular, the identification of specific mineral phases on planetary surfaces—such as high-pressure polymorphs like perovskites—can serve as geodynamic fingerprints, offering indirect evidence of interior conditions. These perovskite type minerals are known to form only under extreme pressures and temperatures, such as those found at Core-Mantle Boundary (CMB) [34] - i.e. oxide-silicates.

On Earth, perovskite structures are believed to form under the extreme conditions of the CMB, where temperatures range from approximately 3000 K to 4500 K, and pressures reach up to 135 GPa. Under this environment, minerals such as olivine, a dominant upper mantle phase with the formula $(\text{Mg,Fe})_2\text{SiO}_4$, undergo a series of high-pressure phase transitions, as detailed in Fig. 1.3. Initially, olivine transforms into wadsleyite and then into ringwoodite in the mantle transition zone, and below depths of 410–520 km [35, 36]. At pressures around 23 GPa (depth 660 km), ringwoodite decomposes into bridgmanite (MgSiO_3 perovskite) and ferropericlase $(\text{Mg,Fe})\text{O}$ [37]. Among these, MgSiO_3 perovskite is now considered the most abundant mineral in Earth’s lower mantle [38].

The presence of different polymorphs (or that of related transition phases) on the surface of exoplanets could imply past or present high-pressure environments, allowing us to

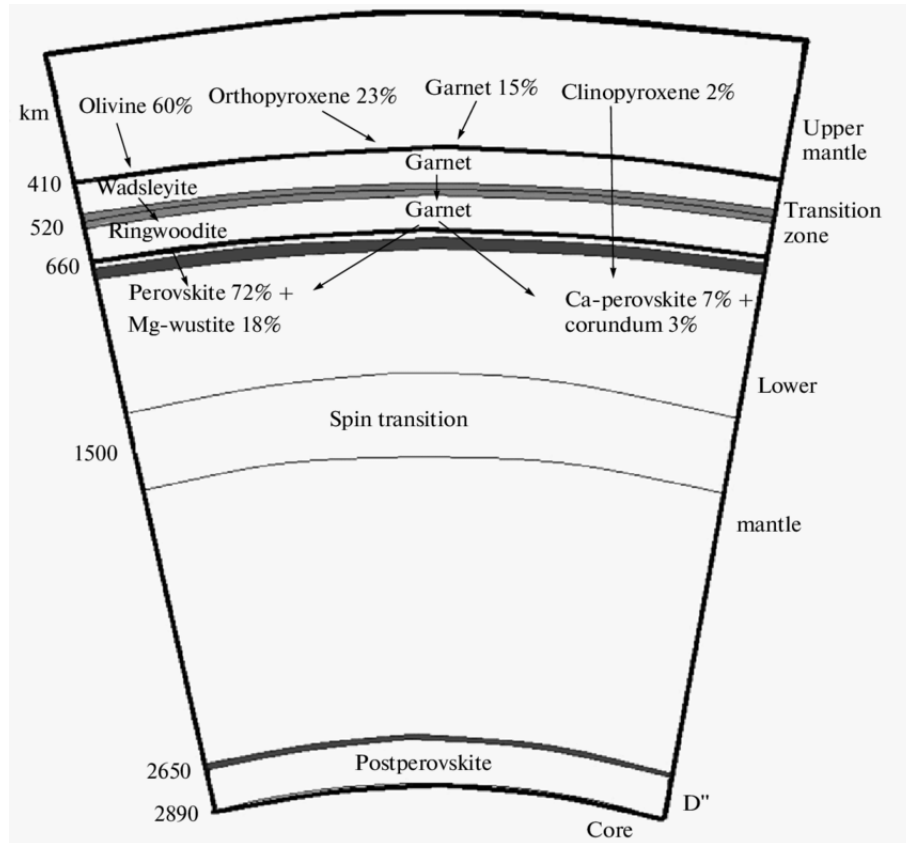


Figure 1.3: Schematic diagram of olivine and its high-pressure polymorphs in the Earth's mantle. At depths close to 410km, olivine ($(\text{Mg,Fe})_2\text{SiO}_4$) transforms into wadsleyite; when reaching 520 km it further transitions to ringwoodite with a spinel structure; and at the 660 km, there is a discontinuity, and the compound breaks down into MgSiO_3 perovskite and ferropericlase. These phase changes correspond to major seismic discontinuities in the mantle. Adapted from Ringwood [39], and summarized in *Olivine* (Wikipedia) [40].

approximate internal temperature–pressure regimes. Studying these phase transitions provides a powerful tool to reverse-engineer the geodynamic activity of distant worlds, even in the absence of direct seismic or gravitational data [41].

In the literature, case studies have been carried out to computationally analyze two types of exoplanets: a rocky world with 7 Earth masses and a gas giant with 67 Earth masses [42]. The study investigates the formation of perovskites on these planets, examining how pressure and temperature influence the mineral compositions in the interior of the mantle, how these decompose, and how new structural phases may be induced, thus revealing deeper insights regarding the atmosphere and surface and internal compositions of these planets.

1.2.1 Study of Halide Analogues in Perovskite Structures

In Fig. 1.4, we may observe the abundance of elements on the Earth's crust relative to Si. Note that the elements used on this dissertation, namely K, and Ca, are considered rock-forming and moderately abundant. Their availability and similar structural roles make these useful analogues to MgSi-based perovskites, which are the most common forms of these structures. In addition, the compositions used in the present work have lower melting points, which enables an easier means to synthesize experimentally and study these under standard laboratory conditions, making these excellent candidates for experimental and theoretical studies.

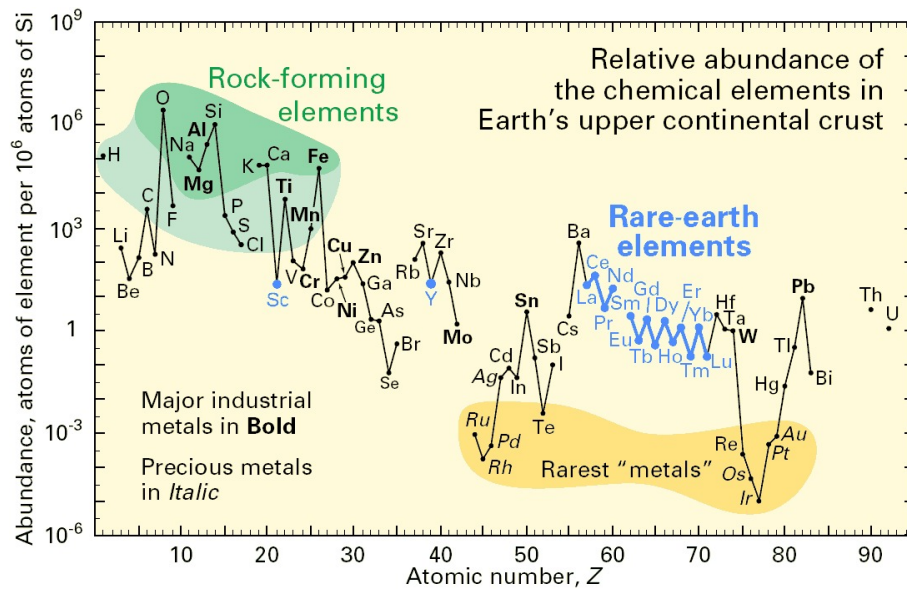


Figure 1.4: Abundance (atom fraction) of chemical elements in Earth's upper continental crust as a function of atomic number. The relative concentrations of various element groups are highlighted. Image taken from Ref. [43]

Fluoroperovskites also serve as chemically accessible and structurally simpler analogues, when compared to silicate perovskites, which are prevalent in planetary interiors, particularly in super-Earths and rocky exoplanets. Studying their behavior under high-pressure conditions, provides valuable insights into the thermodynamic stability and lattice behavior of analogous silicate systems.

In 2017, Jakymiw et al. studied the phase transitions of three-dimensional fluoroperovskites by constructing the structural phase diagrams of KCaF_3 and NaMgF_3 , by resorting to first-principles calculations. These compounds were analyzed under varying pressures to determine stable polymorphs. The study revealed distinct phase transition

sequences for each compound, with KCaF_3 exhibiting metastability and a tendency toward decomposition above 2.6 GPa; while NaMgF_3 transitioned from the perovskite to post-perovskite CaIrO_3 -type structure at higher pressures. Beyond phase stabilities, investigating the optical and vibrational properties of these materials is also relevant for interpreting remote spectroscopic data. Their characteristic signatures may aid in identifying related compounds in meteoritic samples, cometary material, and even in the atmospheres or surfaces of exoplanets, thereby contributing to planetary science and astromineralogy.

Natural occurrences of fluoroperovskites further reinforce the relevance of these compounds as Earth and planetary analogues. The mineral parascandolaite, KMgF_3 , was identified in volcanic ejecta from Vesuvius, confirming that perovskite-type fluorides, with compositions analogous to those studied in the present work, can naturally form under such extreme geologic conditions [45]. Despite the B-site cation being Mg in this case, its alkaline earth-like character and comparable ionic radius to Ca, suggest strong structural compatibility, supporting its substitution within the same perovskite phase. This shows that such fluoride systems are not only synthetically accessible, but may also exist as stable or metastable phases in the Earth's crust, highlighting their value as both theoretical models and natural analogues. Combined with their moderate abundance, ease of synthesis, and relevance to planetary interiors, these materials offer a promising platform for simulating processes relevant to meteoritic, exoplanetary, and cometary environments, particularly when considering spectral and optical characterization for remote detection.

1.2.2 Naturally Layered Perovskites

Comparatively to the study of the MgSiO_3 perovskite phase, relative to its olivine counterpart, Mg_2SiO_4 usually found in Earth's Mantle, the investigation of the perovskite-type KCaF_3 and its corresponding variants is also of interest. In particular, the formation and structural stability of the K_2CaF_4 and $\text{K}_3\text{Ca}_2\text{F}_7$ analogues remains insufficiently explored in the existing state-of-art literature.

Perovskites can be classified into 3D parent systems (ABX_3) and quasi-2D perovskites, which is where the Ruddlesden-Popper (RP) phases ($\text{A}_{n+1}\text{B}_n\text{X}_{3n+1}$) fit in. Typically, A refers to alkali, alkali earth, or rare earth elements; B to the transition metals; and X can be oxygen or a halogen element. For the latter, they are more commonly known as metal halide perovskites.

This dissertation focuses on RP perovskites (RPPs), which are quasi-2D materials, with naturally stacked primitive-cell layers form of thin-sheet, giving these unique structural, electronic and optical properties.

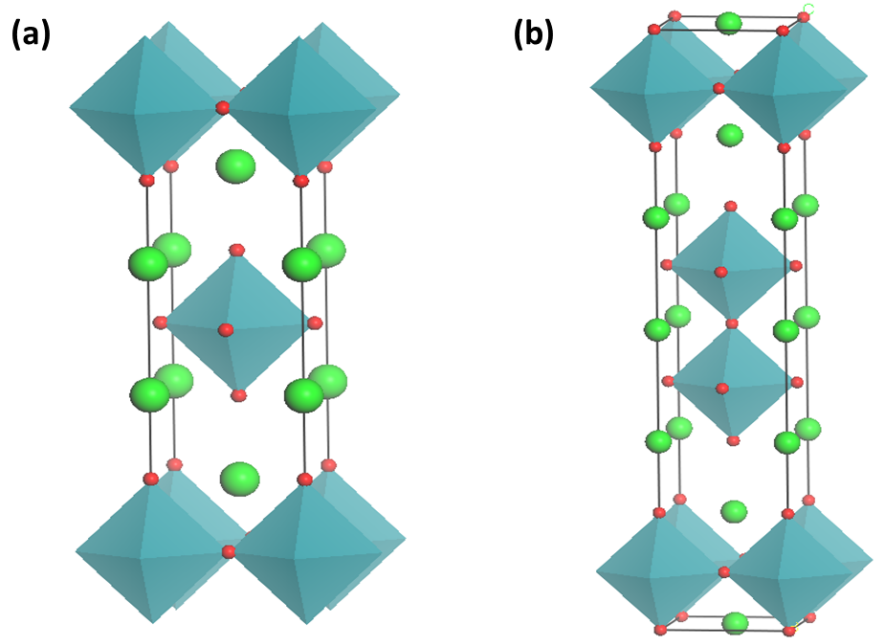


Figure 1.5: Illustration of RPP structures ($A_{n+1}B_nX_{3n+1}$) for the (a) $n = 1$ and (b) $n = 2$ phases. The structures consist of corner-sharing BX_6 octahedra, where the B-site cation resides at the center of the octahedra and X represents the halide anions (shown in red). A-site cations (green) are located within and around the perovskite layers (ABX_3), forming rock-salt-like AX spacing layers. Adapted from Ref. [46].

While most studies, found in literature, focus on RP systems synthesized in the laboratory, naturally occurring RP phases have also been reported. Notably, Rafał Juroszek (2024) documented the natural occurrence of a RP structure, identifying the mineral karlleuite (Ca_2MnO_4) in xenoliths from the Bellerberg volcano in Germany [47].

Due to their formation under extreme temperature and pressure conditions, RPs serve as valuable indicators for investigating planetary interiors. The rare natural occurrences of these phases provide insight into the mineralogical composition and thermodynamic conditions of the deep Earth, particularly near the CMB. By studying the phase transitions, potential transition and dissociation pathways of RPs, as these migrate toward the surface, we can infer about several key aspects of planetary geology, including mantle dynamics and the chemical stratification of Earth's interior, as well as for other planets.

1.2.3 Structural stability in perovskite systems

For RP-type structures there are three main types of distortions which are based on cooperative octahedra rotations, cation displacements, and octahedra deformations [48–50].

The second and third type of distortions are typically associated with the size effects arising from ionic-radius mismatches [48, 51], while the prior relates to phenomena like the Jahn-Teller effect [52].

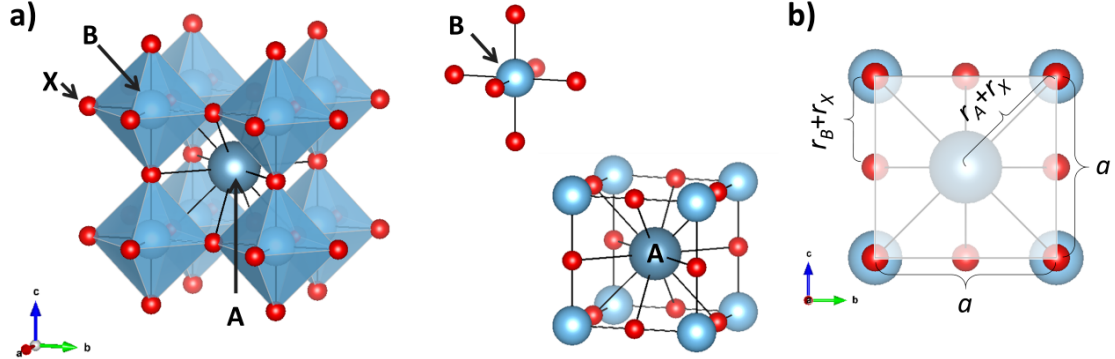


Figure 1.6: (a) Structural representation of the ABX₃ aristotype with cubic $Pm\bar{3}m$ symmetry, depicting the three-dimensional network of corner-sharing BO₆ octahedra. The A cations occupy the center of a cube defined by eight corner-sharing octahedra and are surrounded by 12 X anions in a dodecahedral environment, while the B cations are located at the center of an octahedral environment formed by six X anions. (b) Relation between the ionic radii of each ion (r_A , r_B , r_X) and the lattice parameter a of the ABX₃ cubic unit cell. Image taken from Ref. [53]

In 1926, Goldschmidt [51] developed a mathematical relation for the atomic arrangement in a perovskite structure in order to consistently find a stable structure. In Fig. 1.6 we have the representation of a cubic system with the equation relating to the lattice parameter a , of the cubic unit cell:

$$a = \sqrt{2}(r_A + r_X) = 2(r_B + r_X) \quad (1.1)$$

Goldschmidt [51] defined the tolerance factor t as the quantification of the mismatch of the ionic radii of the perovskite constituents with respect to the cubic structure as:

$$t = \frac{(r_A + r_X)}{\sqrt{2}(r_B + r_X)} \quad (1.2)$$

For tolerance factors between the range $0.7 < t < 1$, significant tension develops on the B–X bonds, accompanied by compression of the A–X bonds. A cooperative series of lattice distortions, comprising BX₆ octahedra rotation modes and A cation displacement modes, enables the reduction of internal strain and maximizes the number of short A–O interactions [48]. This is followed by symmetry reduction from the cubic to orthorhombic/rhombohedral structures. Table 1.1 presents examples of perovskite structures that follow these distortions.

For $t \approx 1$, perovskite structures tend to stabilize in the cubic phase without octahedral rotations. When $t > 1$, the perovskite adopts a hexagonal or tetragonal structure [54].

Table 1.1: Tolerance factor data for reference and halide perovskite variants.

Compound	A cation	B cation	X anion	t
CaTiO ₃	Ca ²⁺	Ti ⁴⁺	O ²⁻	0.97
KCaF ₃	K ⁺	Ca ²⁺	F ⁻	0.90
KCaCl ₃	K ⁺	Ca ²⁺	Cl ⁻	0.87
KCaBr ₃	K ⁺	Ca ²⁺	Br ⁻	0.86

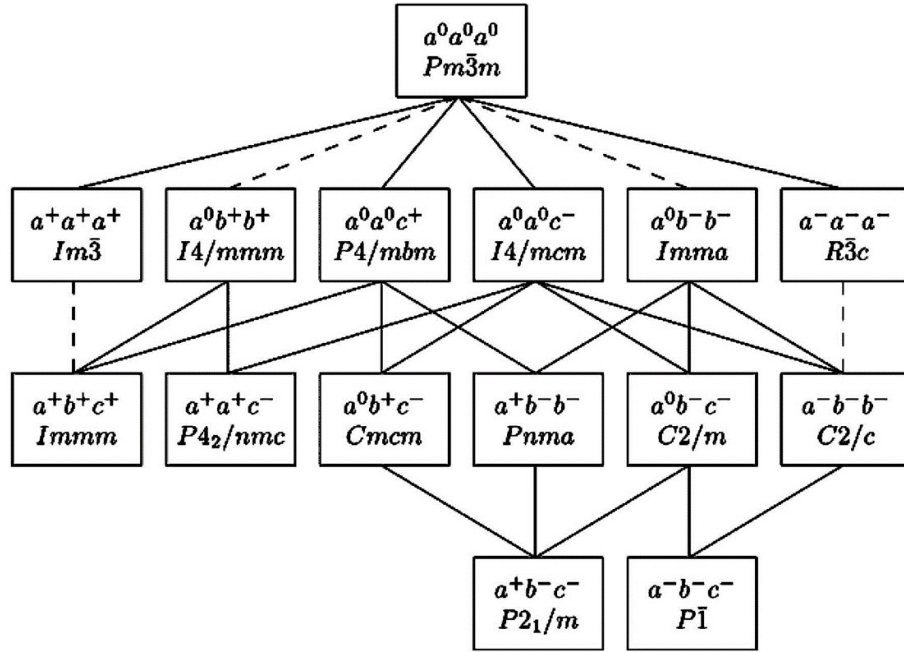


Figure 1.7: Schematic representation of group-subgroup relationships among 15 space groups derived from distinct cooperative BX₆ octahedral tilt systems. Solid lines denote second-order phase transitions (as predicted by Landau theory), while dashed lines indicate first-order transitions. Additionally, it shows the decomposition of the rotational modes that lead to a possible structural phase transition from the cubic phase $Pm\bar{3}m$ to the orthorhombic $Pnma$ ($a^- a^- c^0$ and $a^0 a^0 c^+$). Illustration taken from Ref. [53].

In the present work, we also complemented calculations with mixed halogen perovskites, which take a different approach, when one tries to calculate the tolerance factor. For these specific compounds, the halogen atomic radii takes into account their weighted average as [55]:

$$r_X^{avg} = x \cdot r_{X_1} + (1 - x) \cdot r_{X_2} \quad (1.3)$$

where, x is the mole fraction of the halogen X_1 and r_X represents the ionic radius of the X -th ion.

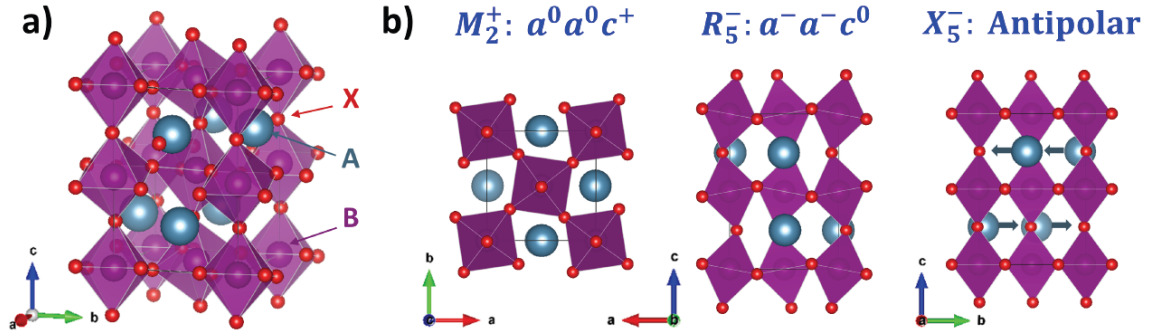


Figure 1.8: **a)** Structural representation of the ABX_3 $Pbnm$ orthorhombic structure. **b)** Illustration of the tilting patterns of the BX_6 octahedra, featuring rotation modes described by the irreducible representations M_2^+ and R_5^- relative to the cubic $Pm\bar{3}m$ phase, along with the coupled antipolar displacement of A-site ions associated with the X_5^- mode. Illustration adapted from Ref. [53].

In Figure 1.7, the different space groups for the various octahedral tilt patterns are shown, which can be easily described using Glazer notation. In Figure 1.8 **b)**, an illustrative example is shown of the decomposition of the rotational modes that lead to a possible structural phase transition from the cubic phase $Pm\bar{3}m$ to the orthorhombic $Pnma$ ($a^- a^- c^0$ and $a^0 a^0 c^+$).

The types of distortions observed in perovskite systems—such as octahedral rotations, cation displacements, and Jahn-Teller distortions—can also be inherent in layered perovskite structures, such as those found in the RP family. Recently, these distortions have attracted significant interest for the development of novel functional materials, such as next-generation systems that evidence spontaneous polarization (ferroelectrics) or materials that present negative thermal expansion [56–59].

However, halide RP materials exhibiting ferroelectricity or negative thermal expansion, following the parent $AA'X_3$ perovskite composition ($A = \text{Na, K, Rb, Cs}$; $A' = \text{Mg, Ca}$), remain largely unexplored. Fluoride-based RP structures, such as Rb_2MgF_4 , Cs_2CaF_4 , Rb_2CdF_4 , K_2CdF_4 , K_2CuF_4 , $\text{K}_3\text{Cu}_2\text{F}_7$, have been reported, showing that the RP structure can be stabilized in these Fluoride-based compositions [60–62].

In the RP family, the tolerance factor, t , value becomes more limited. This is primarily due to the anisotropic nature of RP structures and the separation of perovskite slabs by interlayer cations, which introduces additional degrees of geometric freedom. However, there is still a correlation between the two systems. For instance, if the parent perovskite is cubic, the corresponding RP phases typically adopts the aristotype $I4/mmm$ structure, as seen in the case of SrTiO_3 and its RP counterparts Sr_2TiO_4 and $\text{Sr}_3\text{Ti}_2\text{O}_7$. [63]

A common descriptor used to assess the feasibility of octahedral coordination is the octahedral factor μ , defined as:

$$\mu = \frac{r_B}{r_X} \quad (1.4)$$

where r_B and r_X are the ionic radii of the B-site cation and the coordinating anion, respectively. This criterion originates from Pauling's rules for ionic solids [64], and reflects the radius ratio required for stable octahedral packing. The empirically accepted stable range lies between 0.442 and 0.895 [65], consistent with close-packed ionic geometries in perovskite systems. This ratio quantifies the size compatibility necessary for the formation of stable BX_6 octahedra, which constitute the fundamental building blocks of both 3D and layered perovskites, making it a useful first screening tool even in the context of layered systems, where octahedral connectivity within the perovskite slabs remains essential.

Due to the limitations of the conventional Goldschmidt tolerance factor and the anisotropic nature of RP perovskites, several alternative descriptors have been developed to better capture the structural complexity of these systems.

For low-dimensional perovskites, a modified geometric descriptor known as the *dimensional tolerance factor* can be introduced:

$$t_{\text{dim}} = \frac{r_{A'} + r_X}{\sqrt{2}(r_B + r_X)} \quad (1.5)$$

Here, $r_{A'}$ represents the interlayer spacer (rather than the traditional A-site), acknowledging that the A' cation resides between the layers, rather than within the perovskite slabs.

For the inorganic RP phases studied in this dissertation, the interlayer spacer will follow the ionic radius of the A cation.

Table 1.2: RP perovskites studied with their octahedral factors $\mu = \frac{r_B}{r_X}$ and Goldschmidt tolerance factors t . Mixed halide systems use the averaged halide radius.

System	RP Phase	μ	t
K_2CaF_4	$n = 1$	0.75	0.95
K_2CdF_4	$n = 1$	0.71	0.94
$K_2CdF_2Cl_2$	$n = 1$	0.62	0.91
$K_2CdCl_2Br_2$	$n = 1$	0.51	0.88
$K_2CdBr_2I_2$	$n = 1$	0.46	0.86
$K_2CaF_2Cl_2$	$n = 1$	0.66	0.92
$K_2CaCl_2Br_2$	$n = 1$	0.54	0.89
$K_2CaBr_2I_2$	$n = 1$	0.48	0.87

1.3. Computational screening and study of quasi-2D systems

This work focuses on using first-principle computational frameworks and materials science of quasi-two-dimensional (quasi-2D) materials, namely the layered perovskites of the K_2AX_4 family (with $X = F, Cl, Br, I$ and $A = Cd, Ca$). These calculations are based in Density Functional Theory (DFT) to study the electronic and optical properties of the structures; the Density Functional Perturbation Theory (DFPT) to study the phase stability within the harmonic approximation; and the Zacharias-Giustino (ZG) theory, involving finite temperature differences, to study structural phase transitions with the anharmonic approximation [EPW package of the Quantum ESPRESSO (QE) software] [66–68]. Alongside benchmarking previously studied materials, I also delve into novel chemically abundant compounds that, up-to-date, have been experimentally unreported, such as K_2CaF_4 . The favorable tolerance and octahedral factors, as shown in Table 1.2, evidence promising potential thermodynamic stability in the same space groups as our benchmark materials. This predictive approach not only evaluates the formation likelihood of such structures in terrestrial or astrophysical environments, but also contributes to a broader interdisciplinary framework for discovering new materials with promising functional properties.

Using first-principles computational methodologies and condensed matter studies, I seek to explore the evolution and composition of celestial bodies. By analyzing exoplanetary surfaces, I aim to infer their interiors and formation conditions.

2. Computational Methodology

In this chapter, we begin by introducing the many-body problem, which lies at the core of theoretical condensed matter physics and materials science. We then outline the main computational approaches used to tackle this problem in the context of solid-state systems. Starting with DFT, we present its formulation and practical use as an effective mean-field method to study ground-state properties. We then describe DFPT, which extends DFT to account for lattice dynamics and phonon calculations. Lastly, we discuss the ZG, Special Displacement Method (SDM). These frameworks together provide the theoretical basis for the results presented in this dissertation.

2.1. Many-Body Problem

Solving the Schrödinger equation for a many-body quantum system with N interacting fermions in complex structures requires approximations that simplify their interactions, especially in crystalline systems.

The full many-body Schrödinger equation includes both electrons and nuclei:

$$\hat{H}\Psi(\mathbf{R}, \mathbf{r}) = E\Psi(\mathbf{R}, \mathbf{r}), \quad (2.1)$$

with Hamiltonian:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 - \sum_{\alpha=1}^{N_n} \frac{1}{2M_\alpha} \nabla_\alpha^2 + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N_e} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_{i=1}^{N_e} \sum_{\alpha=1}^{N_n} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} + \frac{1}{2} \sum_{\substack{\alpha,\beta=1 \\ \alpha \neq \beta}}^{N_n} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|}. \end{aligned} \quad (2.2)$$

Here, M_α , Z_α , and $\mathbf{R}_\alpha$ are the mass, charge, and position of nucleus α , and $\mathbf{r}_i$ is the position of electron i .

Due to the complexity of solving this many-body equation exactly, approximations are essential. The *Born-Oppenheimer approximation* [69] assumes fixed nuclei, neglecting their kinetic energy and treating the repulsion factor as a constant, can thus be separated in its nuclear wave-function:

$$\Psi(\mathbf{r}, \mathbf{R}) = \psi_{N_e}(\mathbf{r}; \mathbf{R}) \phi_{N_n}(\mathbf{R}), \quad (2.3)$$

allowing the electronic configuration to be solved independently:

$$H_{N_e} \psi_{N_e} = \left[-\frac{1}{2} \sum_{i=1}^{N_e} \nabla_i^2 + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,\alpha} \frac{Z_\alpha}{|\mathbf{r}_i - \mathbf{R}_\alpha|} \right] \psi_{N_e} = E_{N_e}(\mathbf{R}) \psi_{N_e}. \quad (2.4)$$

This energy $E_{N_e}(\mathbf{R})$ is minimized by perturbing the atomic positions by a small displacement around respective minimum.

A second assumption of the Born-Oppenheimer approximation considers now the nuclear dynamics:

$$H_{N_n} \phi_{N_n} = \left[-\sum_{\alpha} \frac{1}{2M_\alpha} \nabla_\alpha^2 + \sum_{\alpha \neq \beta} \frac{Z_\alpha Z_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \right] \phi_{N_n} + E_{N_e}(\mathbf{R}) \phi_{N_n} = E_{\text{tot}} \phi_{N_n}. \quad (2.5)$$

This yields nuclear wave-functions describing vibrations, rotations, and displacements. However, for materials like superconductors, these approximations fall short—electron-phonon coupling must be included [70].

To simplify the Coulomb electron-electron interactions, *Hartree* [71] proposed replacing them with an effective mean-field potential, now known as the Hartree potential:

$$U_{ee}(\mathbf{r}) = \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \quad n(\mathbf{r}) = \sum_j |\psi_j(\mathbf{r})|^2, \quad (2.6)$$

where $\mathbf{r}$ and $\mathbf{r}'$ are position vectors in real space, $n(\mathbf{r})$ is the electronic charge density, and $\psi_j(\mathbf{r})$ are the single-particle wave-functions of the system. This approach treats the electron-electron repulsion in an averaged way, by assuming that each electron moves under the influence of the smooth electrostatic potential generated by the total electron density.

This yields the *Hartree equation*:

$$\left[-\frac{1}{2} \nabla^2 + U_n(\mathbf{r}) + U_{ee}(\mathbf{r}) \right] \psi_l(\mathbf{r}) = \epsilon_l \psi_l(\mathbf{r}), \quad (2.7)$$

where ϵ_l the corresponding energy eigenvalues. The term $U_n(\mathbf{r})$ represents the external potential due to the nuclei (often written as $v_{\text{ext}}(\mathbf{r})$), while $U_{ee}(\mathbf{r})$ is the Hartree potential describing the mean-field electrostatic interaction between electrons. This formulation neglects both the Pauli exclusion principle and electron correlation.

To enforce antisymmetry, *Fock and Slater* introduced the *Slater determinant* [72]:

$$\Psi(\mathbf{r}_1\sigma_1, \dots, \mathbf{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1\sigma_1) & \cdots & \psi_1(\mathbf{r}_N\sigma_N) \\ \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1\sigma_1) & \cdots & \psi_N(\mathbf{r}_N\sigma_N) \end{vmatrix}, \quad (2.8)$$

where $\psi_i(\mathbf{r}_j\sigma_j)$ are single-particle spin-orbitals depending on both the spatial coordinate $\mathbf{r}_j$ and the spin variable σ_j . The spin variable σ_j represents the spin state of the j -th electron, typically taking the values $\uparrow$ or $\downarrow$, which account for the intrinsic angular momentum (spin) of the electrons. This determinant form ensures the total wave-function is antisymmetric under the exchange of any two particles, in compliance with the Pauli exclusion principle.

Thus leading to the *Hartree-Fock equation*:

$$\hat{F}\psi_i = \epsilon_i\psi_i, \quad \hat{F} = \hat{h} + \hat{J} - \hat{K}, \quad (2.9)$$

where $\hat{J}$ and $\hat{K}$ are the Coulomb and exchange operators, respectively.

2.2. Density Functional Theory

DFT is widely used in computational physics and chemistry, and applied to study organic and inorganic, molecules and solids. It enables accurate modeling of geometries, energies, electronic structure, vibrational spectra, and magnetic properties [73].

2.2.1 Kohn-Sham Equations

Hohenberg and Kohn [74] demonstrated that the ground-state properties of a quantum many-body system are uniquely determined by its ground-state electron density $n(\mathbf{r})$, rather than the full many-body wave-function. In this framework, the electron density is defined as

$$n(\mathbf{r}) = \langle \Psi | \hat{n}(\mathbf{r}) | \Psi \rangle, \quad (2.10)$$

where $\hat{n}(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$ is the density operator, where N is the total number of electrons, $\delta(\mathbf{r} - \mathbf{r}_i)$ is the Dirac delta function and $\mathbf{r}_i$ is the position of the i -th electron, and Ψ is the ground-state wave-function. The total energy of the system is expressed as a universal functional of the density:

$$F[n] = \langle \Psi | \hat{T} + \hat{U} | \Psi \rangle, \quad (2.11)$$

where $\hat{T}$ is the kinetic energy operator, and $\hat{U}$ is the electron-electron interaction (Coulomb repulsion) operator.

In DFT, this universal functional $F[n]$ encapsulates all internal electronic interactions and is independent of the external potential. The total energy can then be written as

$$E[n] = F[n] + \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r}, \quad (2.12)$$

where $v_{\text{ext}}(\mathbf{r})$ is the external potential, typically arising from the nuclei. However, because the exact form of $F[n]$ is unknown, Kohn and Sham introduced an approach that maps the interacting system onto a fictitious non-interacting system with the same electron density, allowing for practical calculations using effective single-particle equations.

The total energy becomes:

$$E_v[n] = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + F[n], \quad (2.13)$$

which is minimized by the ground-state density.

Kohn and Sham [75] decomposed $F[n]$ as:

$$F[n] = T_s[n] + E_{xc}[n], \quad (2.14)$$

where $T_s[n]$ is the kinetic energy of a non-interacting reference system:

$$T_s[n] = \sum_i \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) d\mathbf{r}. \quad (2.15)$$

The total energy functional can then be explicitly written as

$$E_v[n] = \int v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r} + \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[n] + T_s[n], \quad (2.16)$$

where the first term, $\int v_{\text{ext}}(\mathbf{r})n(\mathbf{r}) d\mathbf{r}$, corresponds to the interaction energy of the electrons with the external potential, which typically arises from the nuclei. The second term, $\frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$, represents the classical Coulomb repulsion energy between the electron densities and is often referred to as the Hartree energy. Finally, $E_{xc}[n]$ is the exchange-correlation energy functional, which incorporates all many-body effects beyond the classical Hartree approximation, including both exchange and correlation contributions.

The exchange-correlation energy functional is commonly expressed as

$$E_{xc}[n] = \int n(\mathbf{r}) \varepsilon_{xc}(n(\mathbf{r})) d\mathbf{r}, \quad (2.17)$$

where $\epsilon_{xc}(n)$ is the exchange-correlation energy per electron at position $\mathbf{r}$.

Minimizing $E_v[n]$ with respect to $n(\mathbf{r})$ leads to the self-consistent Kohn-Sham equations:

$$\left[-\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}), \quad (2.18)$$

where the effective potential $v_{\text{eff}}(\mathbf{r})$ is given by

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \mu_{xc}(n(\mathbf{r})), \quad (2.19)$$

and

$$\mu_{xc}(n(\mathbf{r})) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} \quad (2.20)$$

is the exchange-correlation potential.

These equations must be solved self-consistently since the effective potential depends on the electron density given by

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.21)$$

The total ground-state energy can be evaluated from the Kohn-Sham eigenvalues ϵ_i as [75]

$$E = \sum_i \epsilon_i - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + \int n(\mathbf{r}) [E_{xc}(\mathbf{r}) - \mu_{xc}(\mathbf{r})] d\mathbf{r}. \quad (2.22)$$

Here, the first term, $\sum_i \epsilon_i$, is the sum of the single-particle Kohn-Sham energies. The second term subtracts the double-counted classical electron-electron repulsion energy, commonly called the Hartree energy. The last integral corrects for exchange and correlation effects that are not accounted for by the single-particle energies or the Hartree term.

2.2.2 The Exchange-Correlation Potential

The exchange-correlation potential Eq. 2.20 is a functional derivative of the exchange-correlation energy which in turn is related to the density. In order to guarantee cohesion in the Kohn-Sham correlation, the exchange energy is defined as:

$$E_{xc}[n] = (T[n(\mathbf{r})] - T_s[n(\mathbf{r})]) + (E_{ee}[n(\mathbf{r})] - E_{\text{Hartree}}[n(\mathbf{r})]) \quad (2.23)$$

where $T[n]$ is the exact kinetic energy of the interacting electron system and $T_s[n(\mathbf{r})] = \sum_{i=1} \int \psi_i^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_i(\mathbf{r}) d\mathbf{r}$ is the kinetic energy of the non-interacting Kohn-Sham reference system [75]. Similarly, $E_{ee}[n(\mathbf{r})]$ represents the full electron-electron interaction energy, while $E_{\text{Hartree}}[n(\mathbf{r})] = \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} d\mathbf{r}d\mathbf{r}'$ corresponds to the classical Coulomb repulsion energy between electrons. This decomposition highlights that the exchange-correlation energy accounts both for the difference in kinetic energy between the interacting and non-interacting systems, as well as all many-body electron-electron interactions beyond the classical mean-field approximation.

This expression highlights that $E_{xc}[n]$ accounts for the difference in kinetic energy between the interacting and non-interacting systems, as well as all many-body electron-electron interactions beyond the classical mean-field approximation.

The terms that relate to the kinetic and electron-electron interactions, and which represent the overall energy of their interaction, independent of the external potential, fall into one expression from Hohenberg-Kohn theory, the universal functional, F_{HK} , written as [74]:

$$F_{HK}[n] = T_s[n(\mathbf{r})] + E_{ee}[n(\mathbf{r})] \quad (2.24)$$

Eq. 2.24 encapsulates the two terms that are not known exactly. This allows us to rewrite 2.23 as:

$$E_{xc}[n(\mathbf{r})] = F_{HK}[n(\mathbf{r})] - (T_s[n(\mathbf{r})] + E_{\text{Hartree}}[n(\mathbf{r})]) \quad (2.25)$$

There are multiple approximations into the exchange-correlation potential which we will explain below.

The first approximation is the Local-Density Approximation (LDA), where one takes the value of the density at a specific point $\mathbf{r}$,

$$E_{xc}^{LDA}[n(\mathbf{r})] = \int \epsilon_{xc}^{HEG}[n(\mathbf{r})] d^3r \quad (2.26)$$

$$v_{xc}^{LDA}[n(\mathbf{r})] = \frac{d}{dn} \epsilon_{xc}^{HEG}[n(\mathbf{r})] \quad (2.27)$$

from [74] referred to the homogeneous electron gas (HEG) we get ϵ_{xc}^{HEG} which is the

energy per unit volume of this gas with a certain density n . Additionally we can also take electron spin into LDA, also known as the Local Spin-Density Approximation (LSDA), is written as,

$$E_{xc}^{LSDA}[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] = \int \epsilon[n_{\uparrow}(\mathbf{r}), n_{\downarrow}(\mathbf{r})] d^3r \quad (2.28)$$

The exchange energy component can be analytically calculated as,

$$E_x^{LDA}[n(\mathbf{r})] = -\frac{3}{4} \left(\frac{3}{\pi} \right)^{\frac{1}{3}} \int n(\mathbf{r})^{\frac{4}{3}} d\mathbf{r} \quad (2.29)$$

A problem arises when one tries to calculate the correlation energy of the HEG, originally it can be obtained by parameterizing the results of multiple densities through a Monte Carlo approach [76]. Currently there are multiple parameterized forms for this functional [77].

Even though this method yields accurate results when compared to experiment, it fails in predicting several properties. These include stability of ions, underestimation of the band gaps of semiconductors and insulators, overestimation of hydrogen bond lengths.

To improve upon the limitations of the LSDA, the generalized-gradient approximation (GGA) was developed. Unlike LSDA, which considers only the local electron density, GGA incorporates the gradient of the electron density, thus taking into account not only the magnitude of the density at each point but also its spatial variation. This refinement allows for a more accurate description of exchange-correlation effects, especially in systems with rapidly varying electron densities.

An improvement in the accuracy with respect to what is obtained from the LSDA, is by including the effects of inhomogeneities into the density, in the form:

$$E_{xc}^{GGA}[n_{\uparrow}, n_{\downarrow}] = \int f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}) d^3r \quad (2.30)$$

This method does correct some difficulties of LSDA/LDA, but still cannot solve the underestimation of the band gap, and fails in the description of long-range interactions (e.g. van-der-Waals interactions).

This method also has the peculiarity to overestimate the equilibrium volume of solids.

Therefore a revised form for solids has been implemented, and known as the Perdew-Burke-Ernzerhof revised for solids (PBEsol) [78, 79].

2.2.3 Expansion of the Kohn-Sham wave-functions

The Kohn-Sham equations can be solved in momentum space by expanding the electronic wave-functions in a plane-wave basis set. This approach is particularly well-suited for periodic systems, as it naturally exploits the translational symmetry of crystalline solids and facilitates efficient numerical implementation.

By Bloch's theorem, the Kohn-Sham wave-functions can take the form of traveling plane-waves modulated so that these encapsulate the translational periodicity of the system [80],

$$\varphi_{\mathbf{k},n}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} \sum_{\mathbf{G}} c_{\mathbf{k},n}(\mathbf{G}) e^{i\mathbf{G}\cdot\mathbf{r}} \quad (2.31)$$

where $\mathbf{k}$ is the crystal wave-vector restricted to the Brillouin zone (BZ), n is the band index and $\mathbf{G}$ are the reciprocal lattice vectors, related to the primitive vectors of reciprocal space, $\mathbf{b}_{i,j,k}$, of the form,

$$\mathbf{G} = m_1 \mathbf{b}_1 + m_2 \mathbf{b}_2 + m_3 \mathbf{b}_3 \quad (2.32)$$

where m_i are three integers, and ,

$$\mathbf{b}_i = 2\pi \frac{\mathbf{a}_j \times \mathbf{a}_k}{|\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)|} \quad (2.33)$$

where $\mathbf{a}_{i,j,k}$ are the unit-cell vectors and the real-space cell volume is expressed by $V = |\mathbf{a}_i \cdot (\mathbf{a}_j \times \mathbf{a}_k)|$.

The electronic density becomes,

$$n(\mathbf{r}) = \sum_{\mathbf{k},n} \sum_{\mathbf{G},\mathbf{G}'} f_{\mathbf{k},n} c_{\mathbf{k},n}^*(\mathbf{G}') c_{\mathbf{k},n}(\mathbf{G}) e^{i(\mathbf{G}-\mathbf{G}')\cdot\mathbf{r}} \quad (2.34)$$

where $f_{\mathbf{k},n}$ are the band occupation numbers. Applying a Fourier transform yields:

$$n(\mathbf{G}) = \sum_{\mathbf{k},n} \sum_{\mathbf{G}'} f_{\mathbf{k},n} c_{\mathbf{k},n}^*(\mathbf{G}' - \mathbf{G}) c_{\mathbf{k},n}(\mathbf{G}'), \quad (2.35)$$

where the summation over $\mathbf{k}$ should, in principle, be carried out over all wave-vectors in the BZ. However, due to the presence of crystal space group symmetries, this sum can be restricted to the irreducible part of the BZ by considering only symmetry-inequivalent $\mathbf{k}$ -points.

For periodic calculations two important convergence parameters have to be considered. Firstly, the summation of the BZ sampling replaces the integration of the periodic functions over the reciprocal space. For evaluating these integrals computationally, a weighted sum over a subset of $\mathbf{k}$ -points is performed, and these are reduced to the irreducible BZ [81], where a finite set of reducible $\mathbf{k}$ -vectors is generated. The second convergence parameter is the cut-off radius, it is set to truncate the sums over the reciprocal lattice vectors. Since the complete set of reciprocal lattice vectors $\mathbf{G}$ is infinite and the orbitals and densities tend to evidence smooth variations at small scales, the plane-wave components are negligible for large $\mathbf{G}$ -vectors.

These vectors can be set to a certain cut-off radius which are defined by the correspondent kinetic energy, $E_{cutoff} = G_{max}^2/2$, where the G_{max} is the radius of the sphere containing the full set of plane waves up until the reciprocal space volume of the sphere, defined by the cut-off, $V_{sphere} = (4\pi/3)G_{max}^3$.

When using plane-wave basis sets, the count of basis states shifts abruptly as the cutoff energy is varied. These jumps occur at different cutoff values whenever the $\mathbf{k}$ -point sampling grid is altered. Even at a fixed cutoff energy, modifying the unit cell's dimensions or geometry will introduce similar discontinuities in the plane-wave basis. Employing a finer $\mathbf{k}$ -point mesh can mitigate this effect by distributing less weight to each individual plane-wave state, yet the issue can still arise even with very dense samplings. To address this, one can apply a correction factor that bridges the gap between the number of states in an ideal basis set with infinitely many $\mathbf{k}$ -points and the actual number of states included in a given calculation [82].

Plane-wave basis sets are inherently complete and orthonormal, free from linear dependencies, and agnostic to atomic positions. They offer a straightforward framework for computing forces, stresses, and force constants.

2.2.4 Pseudopotentials

During 1934, Fermi introduced a concept that approximated the interaction between electrons and nuclei by focusing on the interactions of valence electrons, effectively simplifying

the treatment of the full Coulomb interaction, and thus being a precursor to the pseudopotential method. In 1935, Hans Hellmann [83] presented an effective potential to describe the complicated effects of the core electrons of potassium.

The idea of considering an effective-potential, is that the pseudopotentials substitute the effects of the core electrons and the nucleus of an atom. This way the Schrödinger equation takes the pseudopotential as a fixed value for the the external potential instead of going over the Coulomb interactions of all the core electrons. With the motivation of reducing the number of employed basis sets and the number of electrons, this method has been widely applied for periodic solid state systems.

Only in the late 50's did Phillips and Kleinman [84] apply the concept of pseudopotentials to metals and semiconductors, generalizing this to Hellmann's original idea.

By applying the pseudopotential concept, we can write the wave-function as the sum of a smooth function (pseudo wave-function) plus an oscillating function (see Fig. 2.1) to maintain orthogonality between the valance and core electrons, as:

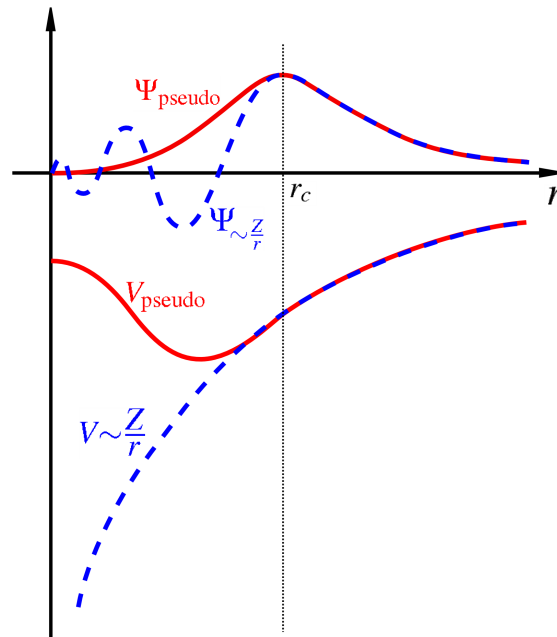


Figure 2.1: A comparison of a wave-function in the Coulomb potential of the nucleus (blue) to the one in the pseudopotential (red) is shown. The real and the pseudo wave-functions and potentials match above a certain cutoff radius r_c . Figure taken from Ref. [85].

$$|\psi_v\rangle = |\varphi_v\rangle + \sum_c \alpha_{cv} |\psi_c\rangle \quad (2.36)$$

where $\alpha_{cv} = -\langle \psi_c | \varphi \rangle$, $|\psi_v\rangle$ and $|\psi_c\rangle$ are the exact solutions of the Schrödinger equation for the valence and the core electrons, respectively, and $|\varphi_v\rangle$ is the pseudo wave-function.

The Schrödinger equation for the smooth orbital, $|\varphi\rangle_v$, is written as,

$$\hat{H} |\varphi_v\rangle = E_v |\varphi_v\rangle + \sum_c (E_c - E_v) |\psi_c\rangle \langle \psi_c | \varphi_v\rangle \quad (2.37)$$

There are three main type of pseudopotentials for plane-wave electronic structure calculations; however, for this dissertation only the projector augmented-wave (PAW) and the norm-conserving were considered.

The norm-conserving pseudopotentials, introduced by Hamann, Schlüter and Chiang [86], require that the pseudo and all-electron valence eigenstates have to ensure the same energies, amplitudes and charge densities outside a pre-defined cutoff radius, r_c (Fig. 2.1). The definition stems from the matching integrated charge inside the cut-off radius for which each wave-function, has to comply with the norm of the true valence wave-function, and the normalized pseudo-orbital have to be exact as the true orbital beyond r_c . This is mathematically expressed as,

$$R_l^{PS}(\mathbf{r}) = R_{nl}^{AE}(\mathbf{r}) \quad (2.38)$$

for $r > r_c$ and,

$$\int_0^{r_c} |R_l^{PS}(\mathbf{r})|^2 r^2 dr = \int_0^{r_c} |R_{nl}^{AE}(\mathbf{r})|^2 r^2 dr \quad (2.39)$$

for $r < r_c$, where $R_l(\mathbf{r})$ is the radial part of the wave-function with the angular momentum l , and the superscript PS and AE are the pseudo and all-electron wave-function, respectively.

The cutoff radius affects both the accuracy of calculations and how well the pseudopotential works in different environments — this is called transferability and it is an important measure of how accurate the pseudopotential is.

The smallest possible value for the cutoff radius is based on where the outermost node of the real wave-function is located. If the cutoff radius, r_c , is close to this minimum, the pseudopotential is more accurate and is called a hard pseudopotential.

If a much larger cutoff radius is considered, the pseudopotential becomes smoother and less dependent on angular momentum. This is called a soft pseudopotential. While soft pseudopotentials allow for faster convergence in plane-wave calculations, these may not work well across very different systems, with strong correlations.

Therefore, choosing the right cutoff radius means finding a good balance between having a small enough basis set and obtaining accurate results.

The ultrasoft pseudopotentials, where norm-conservation is not enforced, are constructed specifically for particular atomic environments making them computationally more efficient at the cost of being more specific, and cannot be applied in a general sense. An example includes 3D transition metals where a large plane-wave basis-set is needed to treat strongly-localized orbitals. The best known approach had been developed by Vanderbilt et al. [87].

Later on Blöchl [88] further developed the ultrasoft pseudopotential concept by generalizing the pseudopotential and linear and augmented plane-wave (LAPW) methods into the PAW method [88, 89]. This method takes the pseudo wave-function to an all-electron wave-function (Kohn-Sham single particle wave) through linear transformation, operating directly on the full valence and core wave-functions. This method can be applied for first-row and transition-metal elements with affordable basis-sets, while providing the full all-electron wave-function, yielding a higher accuracy for a given level of optimization. The PAW potentials typically provide more accurate results due to the lower radial cut-offs and these reconstruct the exact valence wave-function with all nodes in the core region [89].

This potential considers the true wave-functions, $\psi(\mathbf{r})$, onto numerically convenient pseudo wave-functions, $\varphi(\mathbf{r})$, generating smooth wave-functions with rapidly convergent plane-wave expansion. The transformation is done by considering a transformation operator τ which maps the pseudo- onto the all-electron (AE) wave-functions.

$$|\psi(\mathbf{r})\rangle = \tau |\varphi(\mathbf{r})\rangle \quad (2.40)$$

The pseudo wave-functions are identified with the envelope functions of the linear methods or the wave-functions of the pseudopotentials approach, whereas the AE wave-function is a full one-electron Kohn-Sham wave-function.

The total energy is then expressed through a pseudo wave-function,

$$E[\psi(\mathbf{r})] = E[\tau\varphi(\mathbf{r})] \quad (2.41)$$

The transformation operator τ makes the smooth pseudo wave-function for each atomic region, so that the resulting wave-function has the correct nodal structure. Therefore, the operator will be written as the identity with the sum of atomic contributions S_R ,

$$\tau = 1 + \sum_R S_R \quad (2.42)$$

where R is the atomic site. For every atom, S_R will add the difference between the all-electron and the PS wave-function. For each local contribution, S_R , acts only within some augmentation region enclosing the atom, implying that the all-electron and PS wave-functions will coincide outside the augmentation regions. The equivalent of the augmentation region for the linear methods is the muffin-tin or the atomic sphere framework. In the pseudopotential method, the augmentation region will correspond to the core region [88].

$$|\phi_i\rangle = |\varphi\rangle + \sum_i (|\phi_i\rangle - |\tilde{\phi}_i\rangle) \langle \tilde{p}_i | \varphi \rangle \quad (2.43)$$

The AE wave-function can therefore be obtained from the PS wave-function, for each atomic placement R , represented by i . The local terms, S_R , are defined for each augmentation region by specifying a target function $|\phi\rangle$ (AE partial-waves) of the transformation for a set of initial functions $|\tilde{\phi}\rangle$ (PS partial-waves), which are orthogonal to the core states and satisfy the completeness relations in the augmentation region. This is:

$$|\phi_i\rangle = (1 + S_R) |\tilde{\phi}_i\rangle \quad (2.44)$$

The AE partial-waves are hence solutions to the radial Schrödinger equation. The functions $\langle \tilde{p} |$ are the projector functions, which probe the character of the wave-function and, for exactly each PS partial-wave these must satisfy the orthogonality and completeness condition, $\sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i| = 1$, within the augmentation sphere, so that the one-centre expansion is identical to the PS wave-function:

$$\sum_i |\tilde{\phi}_i\rangle \langle \tilde{p}_i | \varphi \rangle \equiv |\varphi\rangle, \quad \langle \tilde{p}_i | \tilde{\phi}_j \rangle = \delta_{ij} \quad (2.45)$$

The partial-waves are functions on a radial grid, multiplied by spherical harmonics, and the PS wave-functions can be expanded into plane-waves [90].

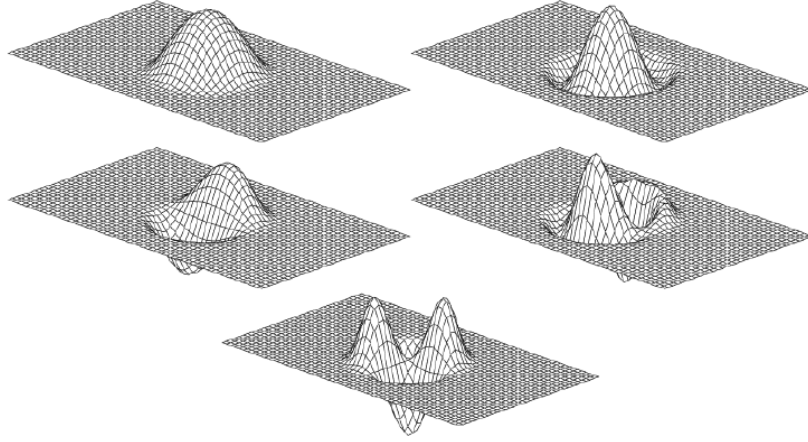


Figure 2.2: Projector functions of the Cl atom for two s-type partial-waves (top), p-type (middle) and d-type (bottom). Obtained from Ref. [90]

2.3. Density Functional Perturbation Theory

DFPT provides a linear-response approximation to compute the phonon properties of crystals explored in subsection Dynamical Matrix and Phonon Frequencies (Harmonic Approximation). Within DFPT, and for small and periodic perturbations (typically represented by the wave-vector $\mathbf{q}$) are evaluated as a first-order perturbation of the electron density and wave-functions. By observing Eq. 2.50, from the second order term, we obtain the force-constant matrix [91].

For periodic solids, the plane-wave atomic displacement, $\mathbf{q}$, is treated through Bloch's theorem. The response of the crystal to a phonon with wave-vector $\mathbf{q}$, is an "incommensurate" perturbation, breaking the periodicity that Bloch's theorem is based on. However, one can take advantage of the fact that the resulting first-order density and potential can be written with the same translational periodicity as the unperturbed lattice, once a Bloch phase factor is factored out [92]. In practice, it is possible to solve the linear-response equations for each $\mathbf{q}$ in the irreducible Brillouin zone (BZ), where the atomic displacements $u_{k\alpha}(\mathbf{q})$ for each atom, k , in direction, α , modulates the potential and induces first-order perturbations to the Kohn–Sham wave-functions.

Since each wave-vector $\mathbf{q}$ is independent, the full response matrix is block-diagonal in $\mathbf{q}$, with each block (or eigenvalue) corresponding to a single $\mathbf{q}$. Consequently, the linear-response equations decouple into independent problems for each wave-vector.

$$\begin{bmatrix} q_1 & 0 & 0 \\ 0 & q_2 & 0 \\ 0 & 0 & q_3 \end{bmatrix}$$

This is the standard DFPT approach as formulated by Baroni et al. (1987, 2001) and [92], which factorizes incommensurate perturbations onto periodic supercells.

2.3.1 Dynamical Matrix and Phonon Frequencies (Harmonic Approximation)

The displacement of atom k in unit cell p , denoted as $\tau(k, p)$, due to lattice vibrations can be expressed in terms of the phonon normal modes as:

$$\tau(k, p) = \frac{1}{\sqrt{N} m_k} \sum_{\mathbf{q}, \nu} e(k, \mathbf{q}, \nu) e^{i \mathbf{q} \cdot \mathbf{r}(k, p)} A(\mathbf{q}, \nu) \quad (2.46)$$

Here:

- N is the number of unit cells in the crystal,
- m_k is the mass of atom k ,
- $\mathbf{r}(k, p)$ is the equilibrium position of atom k in unit cell p ,
- $\mathbf{q}$ is the phonon wavevector,
- ν indexes the phonon branch,
- $e(k, \mathbf{q}, \nu)$ is the phonon eigenvector (polarization vector),
- $A(\mathbf{q}, \nu)$ is the (complex) amplitude determined by the initial conditions.

This is the standard expression used in DFPT, including implementations such as QE. In this framework, the calculation is inherently time-independent, as DFPT evaluates the static linear response of the electronic system to infinitesimal atomic displacements. The phonon frequencies $\omega(\mathbf{q}, \nu)$ and eigenvectors $e(k, \mathbf{q}, \nu)$ are obtained by diagonalizing the dynamical matrix constructed from interatomic force constants.

Although a time dependence does exist in principle for the normal modes, it is not used in DFPT. The full time-dependent displacement field is formally given by:

$$\tau(k, p; t) = \frac{1}{\sqrt{N m_k}} \sum_{\mathbf{q}} v e(k, \mathbf{q}, \nu) e^{i \mathbf{q} \cdot \mathbf{r}(k, p)} A(\mathbf{q}, \nu) e^{-i \omega(\mathbf{q}, \nu) t} \quad (2.47)$$

This expression becomes relevant in contexts where the dynamics of the atomic displacements are explicitly needed, such as in molecular dynamics or quantized phonon field theories. However, for the purposes of DFPT and phonon calculations in QE, only the static (time-independent) form is used, $A(\mathbf{q}, \nu)$, which can be re-written in the following form:

$$A(\mathbf{q}) = \frac{1}{\sqrt{N}} \sum_{k, p} \sqrt{m_k} \exp[-i \mathbf{q} \cdot \mathbf{r}(k, p)] e^*(k, \mathbf{q}) \cdot \mathbf{u}(k, p) \quad (2.48)$$

for each normal mode $e(k, \mathbf{q}, \nu)$ is parallel to $U(k, \mathbf{q}, \nu)$ and follows the orthogonality relation,

$$\sum_k e(k, \mathbf{q}, \nu) \cdot e(k, -\mathbf{q}, \nu') = \delta_{\nu, \nu'} \quad (2.49)$$

As we are talking about vibrational modes of the atoms in a lattice, we have to consider the energy of each atom dependent on their position, having $E(u_{\alpha, k})$ where α is the direction of the displacement, (x, y, z) , for the k -th atom.

By taking into account the Taylor expansion of the mentioned energy,

$$E \approx E_0 + \frac{1}{2} \sum_{k, k'} \sum_{\alpha, \alpha'} \frac{\partial^2 E}{\partial \tau_{\alpha, k} \partial \tau_{\alpha', k'}} \tau_{\alpha, k} \tau_{\alpha', k'} \quad (2.50)$$

where E_0 is the equilibrium energy; the first order term is neglected, as we consider equilibrium positions, and therefore respective forces should be zero or very close to it (residual forces); and the second-order term is the harmonic energy of the system.

The Dynamical Matrix, $D_{k\alpha, k'\beta}$, is constructed as a function of the wave-vector, $\mathbf{q}$, by considering the second order derivatives of the total energy, in reciprocal space:

$$D_{k\alpha, k'\alpha'}(\mathbf{q}) = \frac{1}{M_k M_{k'}} \frac{\partial^2 E}{\partial \tau_{k\alpha}(-\mathbf{q}) \partial \tau_{k'\alpha'}(\mathbf{q})} \quad (2.51)$$

where M represents the atomic masses. For each $\mathbf{q}$, we solve the self-consistent cycle Fig. 2.3 of every symmetry-inequivalent atom-displacement polarization, and from this, all the force-constant elements in $D(\mathbf{q})$ are readily obtained.

Once the Dynamical Matrix is computed, the phonon frequencies, $\omega_\nu(\mathbf{q})$, are readily obtained through:

$$\sum_{k'\alpha'} D_{k\alpha,k'\alpha'}(\mathbf{q}) e_{k'\alpha'}^{(\nu)} = \omega_\nu^2(\mathbf{q}) e_{k\alpha}^{(\nu)} \quad (2.52)$$

where $e^{(\nu)}(\mathbf{q})$ are the polarization vectors. Fourier interpolations are employed to obtain real-space force constants from the Dynamical Matrix $D_{k\alpha,k'\alpha'}(\mathbf{q})$ with a coarse $\mathbf{q}$ -grid. The interatomic force constants (IFC) $C_{k\alpha,k'\alpha'}(R)$, can be reconstructed by any arbitrary wave-vector $\mathbf{q}'$ through the inverse Fourier transformation,

$$D_{k\alpha,k'\alpha'}(\mathbf{q}') = \sum_R \frac{1}{\sqrt{M_k M_{k'}}} C_{k\alpha,k'\alpha'}(R) e^{i\mathbf{q}' \cdot \mathbf{R}}. \quad (2.53)$$

2.3.2 Perturbative Expansion of the Total Energy

The mathematics behind the DFPT calculations, start from expanding the DFT total energy E , Eq. 2.50, as powers representing a small displacement parameter, λ . Revisiting Eq. 2.37 we can write the orbital wave-functions as $\psi_i = \psi_i^{(0)} + \lambda \psi_i^{(1)} + \dots$ and the external potential, $v_{\text{ext}} = v_{\text{ext}}^{(0)} + \lambda v_{\text{ext}}^{(1)} + \dots$, and therefore one obtains the energy as,

$$E = E^{(0)} + \lambda E^{(1)} + \frac{1}{2} \lambda^2 E^{(2)} + \dots \quad (2.54)$$

$E^{(1)}$ will vanish, as stated previously, and we focus on the second order term of the equation which determines the IFC, within the Harmonic Approximation.

A standard perturbation analysis of the Kohn–Sham energy functional, shows that $E^{(2)}$ can be written in terms of the unperturbed orbitals $\psi_i^{(0)}$ and the first-order corrections $\psi_i^{(1)}$. In particular, one finds contributions of the form

$$E^{(2)} = \sum_i^{\text{occ}} \left[\langle \psi_i^{(0)} | H^{(2)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(1)} | H^{(1)} - \epsilon_i^{(0)} | \psi_i^{(0)} \rangle + \langle \psi_i^{(0)} | H^{(1)} - \epsilon_i^{(0)} | \psi_i^{(1)} \rangle \right] \quad (2.55)$$

where,

$\psi_i^{(0)}$: Unperturbed Kohn-Sham orbitals

$\psi_i^{(1)}$: First-order correction to the orbitals

$H^{(1)}, H^{(2)}$: First and second derivatives of the Kohn–Sham Hamiltonian

$\varepsilon_i^{(0)}$: Unperturbed eigenvalue of orbital i

The first term in the summation represents the direct contribution from the second-order change to the Hamiltonian (evaluated on the unperturbed density/orbitals), the second and third terms are complex conjugates which represent the response of the orbitals to the perturbation.

2.3.3 The Sternheimer Equation and wave-function response

Through the Hellmann-Feynman theorem and enforcing the normalization constraints on $\psi_i^{(1)}$, Eq. 2.55 can be expressed through $H^{(1)}$ as:

$$\left(H^{(0)} - \varepsilon_i^{(0)} \right) |\psi_i^{(1)}\rangle = - \left(H^{(1)} - \varepsilon_i^{(1)} \right) |\psi_i^{(0)}\rangle \quad (2.56)$$

The first-order density $n^{(1)}$, where the right-hand side is orthogonalized to the occupied space to maintain orthonormality.

In effect, $E^{(2)}$ will only be expressed through the first-order wave-functions and density, $E^{(2)}(\psi_i^{(1)})$. The Euler-Lagrange equations in this minimization are the self-consistent Sternheimer equations of the perturbations [92, 95].

DFPT finds the solution to compute $E^{(2)}$ by solving a linear-response eigenvalue, instead of applying finite differences of total energy method, yielding similarities as per the Green's functions [93].

Through the “2n+1 theorem”^{*} the $E^{(2)}$ is computed exactly once the first-order wave-functions $\psi_i^{(1)}$ are known [95]. Through this calculation we are able to obtain all the phonon properties. Once $E^{(2)}$ is converged, the first-order electron density $n^{(1)}(\mathbf{q})$ and potential $V_{xc}^{(1)}(\mathbf{q})$ are known, and $E^{(2)}$ and force constants follow from Hellmann–Feynman expressions.

^{*}States that if the wave-function is known up to n-th order, the energy correction can be determined up to (2n+1)th order. It gives higher-order wave-functions to determine the energy to a specific level of accuracy.

The Sternheimer Equation (2.56), together with the orthonormalization constraints, $\langle \psi_i^{(0)} | \psi_j^{(1)} \rangle + \langle \psi_i^{(1)} | \psi_j^{(0)} \rangle = 0$, projects the first order Kohn-Sham equations for each occupied orbital.

In Eq. 2.56, $H^{(1)}$ includes the first-order change to the external potential, as a function of the atomic displacements, and the induced V_{xc} is obtained from the first-order density, $n^{(1)}$. The unknown parameters, $|\psi_i^{(1)}\rangle$ (and the Lagrange multipliers $\varepsilon_i^{(1)}$), are found by solving these coupled linear equations. In practice, one either inverts the operator $(H^{(0)} - \varepsilon_i^{(0)})$ in the orthogonal subspace to $\psi_i^{(0)}$, or one iterates it self-consistently.

In plane-wave frameworks, this is typically done by employing a self-consistent cycle, closely resembling the ground-state DFT cycle:

- Start with an initial guess for $\psi_i^{(1)}$.
- Compute the electron density $n^{(1)}$.
- Update the Hamiltonian $H^{(1)}[n^{(1)}]$.
- Solve the Sternheimer equations again using the updated Hamiltonian.
- Repeat the steps until convergence is achieved (see Fig. 2.3).

Equivalently, one can use the “sum-over-states” (Green’s function) expression for $\psi_i^{(1)}$, however more current software favor the direct Sternheimer solution. Once $\psi_i^{(1)}(\mathbf{q})$ is obtained, the first-order density follows as

$$n^{(1)}(r; \mathbf{q}) = 2 \sum_i^{occ} \left[\psi_i^{(0)*}(r) \psi_i^{(1)}(r; \mathbf{q}) + \psi_i^{(1)*}(r; \mathbf{q}) \psi_i^{(0)}(r) \right] \quad (2.57)$$

and the first-order potential $V_{xc}^{(1)}(n^{(1)})$ is updated accordingly. In the end, a self-consistent solution of the Sternheimer equation yields $\psi^{(1)}$ and $n^{(1)}$ for each $(\mathbf{q}, \kappa, \alpha)$ (displacing atom κ along the Cartesian directions, α , with wave-vector, $\mathbf{q}$, perturbation). These first-order quantities are then used to construct the dynamical matrix.

2.3.4 Quantum Espresso Implementation

The DFPT implementation in QE was developed by Giannozzi et al. [96, 97], where the main implementation of this process is as follows:

Self-Consistent Sternheimer Cycle in DFPT

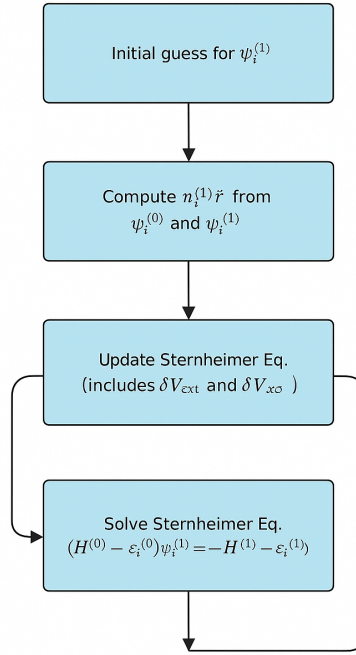


Figure 2.3: Self-Consistent Sternheimer Cycle in DFPT. The diagram illustrates the iterative loop used to solve the Sternheimer equation. Starting from an initial guess for the first-order wave-function $\psi_i^{(1)}$, the procedure computes the induced density $n^{(1)}$, updates the perturbed Hamiltonian $H^{(1)}$, and solves the Sternheimer equation. This cycle repeats until convergence is reached.

- `ph.x` – This is the main DFPT engine. After a ground-state run with `pw.x` (routine to compute the static properties through DFT), `ph.x` specifies the phonon wave-vector(s) $\mathbf{q}$ and atomic perturbations. For each $(\mathbf{q}, \kappa, \alpha)$, the Sternheimer equations are solved and produces the dynamical matrix, $D(\mathbf{q})$, as well as Born effective charges and dielectric constants (when requested).
- `q2r.x` – Performs a discrete inverse Fourier transform of the computed dynamical matrices on a regular $\mathbf{q}$ -grid into real-space interatomic force constants $C(R)$. This enables interpolation of the dynamical matrix at arbitrary $\mathbf{q}$ -points.
- `matdyn.x` – Given the real-space force constants (or directly $D(\mathbf{q})$), this tool computes phonon frequencies on arbitrary $\mathbf{q}$ -paths or meshes. It can produce full phonon dispersions, density of states (DOS).

2.4. Special Displacement Theory

The Special Displacement Theory (SDT) considers the anharmonic approximation and intends to search for dynamically stable structures, by displacing the atomic positions towards a local (metastable) or global (ground-state) minimum.

Several complementary strategies, found in literature, have been developed to tackle anharmonicity and its temperature dependence:

- **Path-Integral and Quantum Monte Carlo (QMC) Methods**

By treating the nuclei via path-integral simulations and the electrons with QMC, one can fully account for nuclear quantum fluctuations and electronic correlations in a nonperturbative way [98, 99].

- **Importance Sampling Monte Carlo (ISMC)**

ISMC employs importance-sampled displacements to efficiently explore the potential-energy surface (PES), offering accurate thermodynamic averages with relatively few configurations [100, 101].

- **Allen-Heine-Cardona (AHC) Perturbation Theory**

In AHC, the electronic self-energy and PES are expanded to second order in the phonon occupation numbers. This yields both the temperature, dependent shifts of electronic bands and the static (Debye–Waller) renormalization of the energy bands [102, 103].

- **Direct Monte Carlo Sampling of the PES**

Rather than relying on Taylor expanding the potentials, one can evaluate the required integrals (Eqs. 2.69-2.71) by averaging the electronic properties over random atomic displacements drawn from the quantum or thermal distribution. This approach typically requires only a modest number of configurations to achieve convergence, since the statistical error decreases as $1/\sqrt{N}$, where N is the number of samples [100, 101].

Each of the above mentioned frameworks balance computational cost, accuracy, and ease of implementation differently: path-integral/QMC methods offer a fully nonperturbative treatment at a higher computational cost, ISMC and direct Monte Carlo reduce sampling noise with judicious importance-sampling, and AHC provides analytical insights via low-order perturbation theory.

The method used to solve some of the problems in this dissertation focuses on the SDT approach, which focuses on the problem of phase transitions and finite temperature deterministically.

Revisiting Eq. 2.50, where we are able to obtain the minimum energy structures, by displacing atoms along the eigenvectors that evidence dynamical instability, we can also apply to the reciprocal space of the normal phonon modes, through the Born-Oppenheimer Non-perturbative methods [104], correlation of the real displacement, τ , to the normal coordinate, x_ν , for a phonon mode ν in reciprocal space. Such can be written as:

$$\Delta\tau_{pk\alpha} = \left(\frac{M_0}{M_k}\right)^{\frac{1}{2}} \sum_{\nu} e_{pk\alpha,\nu} x_{\nu} \quad (2.58)$$

where k , is the atom along the cartesian direction, α , inside the unit-cell, p . This can be represented by the product of the scaling factor of the masses, in which M_0 is the reference or proton mass and M_k considers the mass of the nucleus with the full sum of the phonon polarization vectors, e , multiplied by the normal coordinates.

Therefore we can rewrite Eq. 2.50 in terms of x_ν in the following form:

$$E \approx E_0 + \frac{1}{2} \sum_{\nu,\nu'} \frac{\partial^2 E}{\partial x_{\nu} \partial x_{\nu'}} x_{\nu} x_{\nu'} + \frac{1}{3!} \sum_{\nu,\nu',\nu''} \frac{\partial^3 E}{\partial x_{\nu} \partial x_{\nu'} \partial x_{\nu''}} x_{\nu} x_{\nu'} x_{\nu''} \quad (2.59)$$

when considering some algebraic manipulation by using,

$$\Delta\tau_{k\alpha} = \left(\frac{M_0}{M_k}\right)^{\frac{1}{2}} \sum_{\nu} e_{k\alpha,\nu} x_{\nu} \quad (2.60)$$

$$\sum_{k\alpha} e_{k\alpha,\nu} e_{k\alpha,\nu'} = \delta_{\nu,\nu'} \quad (2.61)$$

$$\frac{\partial}{\partial \tau_{k\alpha}} = \left(\frac{M_k}{M_0}\right)^{\frac{1}{2}} \sum_{\nu} e_{k\alpha,\nu}^{\nu} \frac{\partial}{\partial x_{\nu}} \quad (2.62)$$

taking note that in Eq. (2.59), the energy term can be replaced by a more general quantity, an observable $\mathcal{O}(3)$, which can represent any physical property we want to study.

In non-perturbative approaches, the main goal is to compute the physical behavior associated with this observable $\mathcal{O}$ at a given temperature T . To do so, we calculate its thermal

average, which represents the expected value of $\mathcal{O}$ when the system is in thermal equilibrium at temperature T . This average is expressed as:

$$\langle \mathcal{O} \rangle_T = \frac{1}{Z} [\exp(-\beta_T H) \mathcal{O}] \Rightarrow \Gamma_{\alpha \rightarrow \beta}(\omega, T) = \frac{1}{Z} \sum_n \exp(-E_{\alpha n}/k_B T) \Gamma_{\alpha n \rightarrow \beta}(\omega) \quad (2.63)$$

Here, $\Gamma_{\alpha \rightarrow \beta}(\omega, T)$ denotes the transition rate from state α to β at a finite temperature, T , and frequency, ω . These rates are computed using Fermi's Golden Rule, which provides a framework for evaluating transition probabilities due to a perturbation. A full derivation and discussion of Fermi's Golden Rule will be presented in a later chapter (2.4.1).

This observable can correspond to various physical properties, such as electrical conductivity, atom displacements, among others.

Specifically, for the computation of the SDT, the EPW package provides a dedicated tool known as ZG, named after its developers Marios Zacharias and Feliciano Giustino [67, 68]. Starting from a highly symmetric reference structure, ZG enables the generation of an anharmonic configuration by displacing atoms along selected eigenvectors associated with imaginary phonon frequencies. These displacements capture the effect of anharmonic lattice dynamics, allowing a more accurate representation of thermally induced structural distortions beyond the harmonic approximation.

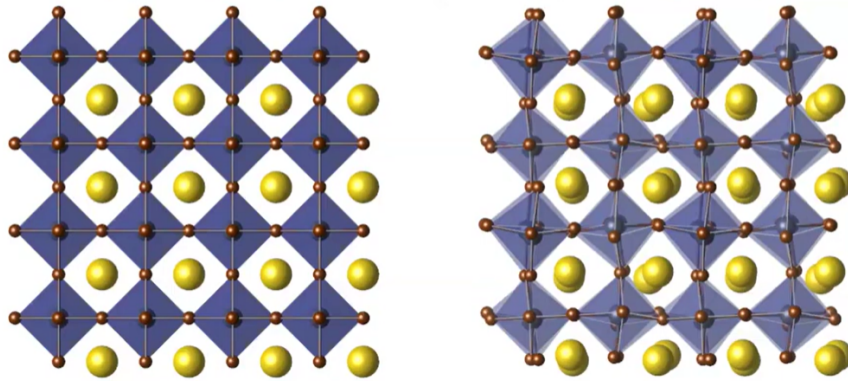


Figure 2.4: Comparison of the high-symmetry perovskite structure in static-equilibrium (left) and anharmonic structure in thermal equilibrium (right). Image taken from Ref. [105].

In perturbative approaches, the theoretical framework can become highly complex and computationally demanding. The absence of an anharmonic PES, the variety of implementation strategies, and the need to account for electron-multiphonon interactions,

among other factors, often make these methods difficult to manage. In contrast, molecular dynamics offers the advantage of not requiring repeated computation of the equilibrium state, although it typically neglects quantum nuclear effects. Finally, the Monte Carlo approximation, while useful, is inherently stochastic and requires a large number of configurations to achieve convergence—often making it feasible only for relatively small systems.

2.4.1 Williams-Lax Theory

The “Williams-Lax Theory” is based on the works by Williams [106] and Lax [107]. The notation for the Born-Oppenheimer quantum states will follow as, $|\alpha n\rangle$, where α relates to the electronic component and n refers to the nuclear part.

The Williams-Lax theory yields a semiclassical approximation for the transitions rate from $|\alpha n\rangle$ to $|\beta m\rangle$ evaluated by considering the Fermi’s golden rule,

$$\Gamma_{\alpha n \rightarrow \beta}(\omega) = \int d\tau |\chi_{\alpha n}(\{\tau\})|^2 \Gamma_{\alpha \rightarrow \beta}^{\{\tau\}}(\omega) \quad (2.64)$$

where ω is the frequency of the external field, and $\chi_{\alpha n}(\{\tau\})$ takes its first steps from the Herzberg-Teller theory [108],

$$\Gamma_{\alpha n \rightarrow \beta}(\omega) = \sum_m \frac{2\pi}{\hbar} |\langle \chi_{\alpha n} | P_{\alpha\beta}^x | \chi_{\beta m} \rangle|^2 \delta(E_{\beta m} - E_{\alpha n} - \hbar\omega) \quad (2.65)$$

The above mentioned expression considers all finite nuclear states, χ , through the optical matrix elements, P , from the starting state α to the final state, β and δ , representing the delta function that takes into account the energy conservation.

This in turn is computationally very demanding, going over every nuclear state for each atom in each primitive cell. Therefore, it is possible to take a semi-classical approach replacing the $E_{\beta m}$ with the adiabatic PES, E_{β}^x :

$$\Gamma_{\alpha n \rightarrow \beta}^{(SC)}(\omega) = \frac{2\pi}{\hbar} \langle \chi_{\alpha n} | |P_{\alpha\beta}^x|^2 \delta(E_{\beta}^x - E_{\alpha}^x - \hbar\omega) | \chi_{\alpha n} \rangle \quad (2.66)$$

Eq. 2.5 is solvable if we assume that the final available transition states have large quantum numbers. In this context, large quantum numbers refer to quantum states where the principal or other relevant quantum numbers (such as angular momentum n, l, m) take on

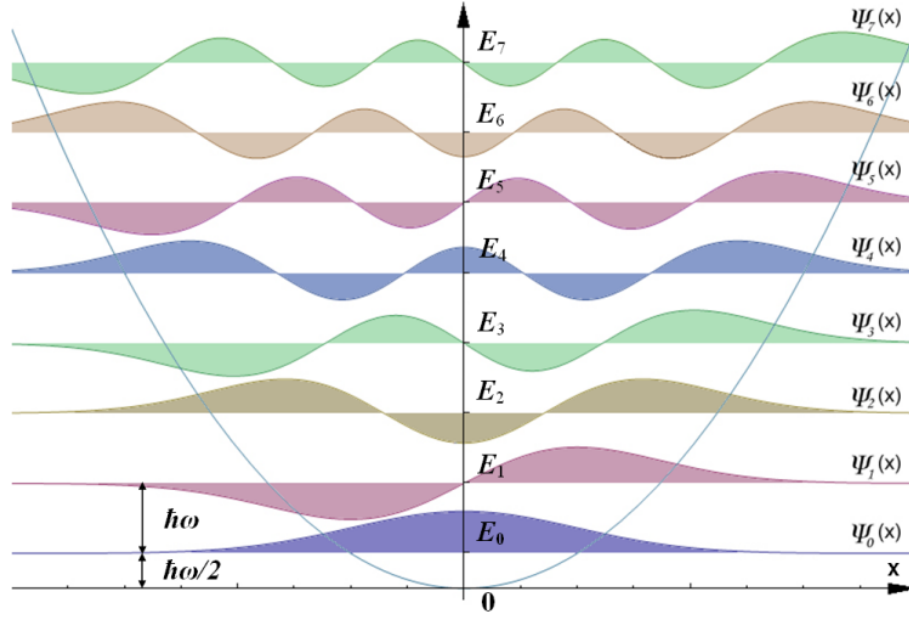


Figure 2.5: Energy levels E_n and wavefunctions $\Psi_n(x)$ of the 1D quantum harmonic oscillator. This representation illustrates the harmonic approximation to the adiabatic PES, used in the Williams-Lax theory to model vibrational states and compute finite-temperature transition rates.

high values, typically much greater than 1 ($n \gg 1$). When these numbers are large, the system begins to behave more classically: the spacing between energy levels becomes very small, and the energy spectrum starts to resemble a continuum. This allows us to treat these energies as if they were continuous variables, in accordance with Bohr's Correspondence Principle, which states that quantum mechanics must agree with classical physics in the limit of large quantum numbers [109].

The next step is to use the Mehler's formula, for which it is possible to convert a discrete sum, into a continuous integral. We will take the quantum Boltzmann distribution to compute the thermal average and thus yield a Temperature T dependent equation. Further more, we can also take the Harmonic Approximation, calculated within the DFPT framework, and introduce it into the Fermi's golden rule, and obtain a finite-temperature transition rate which is averaged over all nuclear configurations weighted by the quantum (Boltzmann) distribution of the phonon modes.

$$\Gamma_{0 \rightarrow \beta}^{(SC)}(\omega; T) = \prod_{\nu} \int dx_{\nu} \frac{\exp(-x_{\nu}^2/2\sigma_{\nu,T}^2)}{\sqrt{2\pi\sigma_{\nu,T}^2}} |P_{0\beta}^x|^2 \delta(E_{\beta}^x - E_0^x - \hbar\omega) \quad (2.67)$$

Under the assumption of the harmonic approximation (independent normal modes), each normal coordinate x_{ν} is Gaussian-distributed with variance $\sigma_{\nu,T}^2 = (2n_{\nu,T} + 1)l_{\nu}^2$, where $n_{\nu,T} = \frac{1}{e^{\hbar\omega_{\nu}/k_B T} - 1}$ is the Bose-Einstein occupancy and l_{ν} is the zero-point length [66]. Thus

the transition probability at temperature T can be written as a multidimensional Gaussian integral over the static transition strengths, $|P_{0\beta}^x|^2$, and the delta function enforces energy conservation (Eq. 2.67) [67].

Additionally, Mehler's formula demonstrates that the summation over the oscillator eigenstates shows that the canonical average is equivalent to integrating over all Gaussian-distributed displacements [66].

Remark 2.1. The formalism developed above by Ref. [67] applies equally well to any Fermi's-golden-rule observable — electronic band structure renormalizations, optical absorption lineshapes, tunneling spectra, *etc.* — and in the infinite-supercell limit it recovers the exact thermodynamic average for any such quantity.

In order to connect to the above described methodology, to the Kohn–Sham DFT framework, one observes that, in the thermodynamic limit $N_e \rightarrow \infty$, the adiabatic PES difference becomes a band-energy difference:

$$\lim_{N_e \rightarrow \infty} [E_\beta^x - E_0^x] = \epsilon_c^x - \epsilon_v^x. \quad (2.68)$$

Replacing Eq. 2.68 into the semiclassical transition rate Eq. 2.67 immediately yields, for the imaginary part of the dielectric function,

$$\epsilon_2^{\text{SC}}(\omega; T) = \prod_v \int dx_v \frac{\exp(-x_v^2/2\sigma_{v,T}^2)}{\sqrt{2\pi}\sigma_{v,T}} \epsilon_2^x(\omega), \quad (2.69)$$

where, in the independent-particle (IP) approximation we have,

$$\epsilon_2^x(\omega) \propto \frac{1}{\omega^2} \sum_{cv} |p_{cv}^x|^2 \delta(\epsilon_c^x - \epsilon_v^x - \hbar\omega). \quad (2.70)$$

Now, expanding $\epsilon_2^x(\omega)$ about $x_v = 0$ shows that all odd powers vanish upon the Gaussian average, leaving

$$\epsilon_2^{\text{WL}}(\omega; T) = \epsilon_2(\omega) + \frac{1}{2} \sum_v \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_v^2} \sigma_{v,T}^2 + \mathcal{O}(\sigma^4). \quad (2.71)$$

Zacharias and Giustino then observe that by choosing a single configuration with

$$x_v = \sigma_{v,T} \quad \text{and} \quad S_v = (-1)^{v-1},$$

the cross terms cancel out:

$$\epsilon_2^{\text{ZG}}(\omega; T) = \epsilon_2(\omega) + \frac{1}{2} \sum_{v\mu} S_v S_\mu \frac{\partial^2 \epsilon_2^x(\omega)}{\partial x_v \partial x_\mu} \sigma_{v,T} \sigma_{\mu,T} + \mathcal{O}(\sigma^4), \quad (2.72)$$

and one can prove

$$\sum_v \frac{\partial^2 \epsilon_2^x}{\partial x_v^2} \sigma_{v,T}^2 = \sum_{v \neq \mu} S_v S_\mu \frac{\partial^2 \epsilon_2^x}{\partial x_v \partial x_\mu} \sigma_{v,T} \sigma_{\mu,T}, \quad (2.73)$$

so that all off-diagonal terms vanish: $\sum_{v \neq \mu} S_v S_\mu \partial^2 \epsilon / \partial x_v \partial x_\mu \sigma_v \sigma_\mu = 0$. Thus the one-shot ZG displacement reproduces the full WL average up to $\mathcal{O}(\sigma^2)$, pushing residual errors to $\mathcal{O}(\sigma^4)$, which for small-to-moderate thermal amplitudes yields highly accurate band-renormalization and spectral broadening without requiring stochastic sampling.

2.4.2 Zacharia Giustino displacement method

Instead of many samples, the SDM employs one optimal configuration of which the displacements reproduce the second-order (and leading higher-order) terms of the Gaussian average [66, 67]. For a supercell of N_p primitive cells and atomic mass M_κ , the ZG displacement is of the form:

$$\Delta \tau_{\kappa\alpha p}^{\text{ZG}} = \sqrt{\frac{M_0}{N_p M_\kappa}} 2 \sum_{\mathbf{q}} S_{\mathbf{q}} \sigma_{\mathbf{q},T} \Re \left[e^{i\mathbf{q} \cdot \mathbf{R}_p} e_{\kappa\alpha, \nu}(\mathbf{q}) \right], \quad (2.74)$$

where the signs $S_{\mathbf{q}} = \pm 1$ enforces the cancellation of the off-diagonal second derivatives and guarantees agreement with the full average up to $\mathcal{O}(\sigma^2)$ [67].

After solving the diagonalization in Eq. 2.52 from DFPT, we can feed into the displacement vector $\Delta \tau^{\text{ZG}}$ the frequencies with the thermal dependent $\sigma_{\mathbf{q},T}$ for each $\mathbf{q}$. Within a physics sense, $\Delta \tau^{\text{ZG}}$ realizes the mean-square displacements of all modes in a single configurations. The atoms of the crystal will hence be displaced accordingly about their high-symmetry positions and the Hellmann-Feynman forces, $F_{p\kappa\alpha} \{ \tau^{\text{ZG}} \}$, will be computed on every atom on the supercell. Such a procedure is computationally cheaper when compared to recalculating all the interatomic force constants (IFC) ($C_{p\kappa\alpha, p'\kappa'\alpha'}$) through the DFPT method.

The finite- T IFC matrix $C^{(j)}(T)$ for the iteration j is obtained by applying the finite-difference method to compute the forces. In practice one uses the linear relation derived in the SDM theory [68].

$$C_{p\kappa\alpha, p'\kappa'\alpha'}(T) \simeq \sum_{p''\kappa''\alpha''} \frac{\sqrt{M_0}}{\sqrt{M_{\kappa'} M_{\kappa''}}} \Delta \tau_{p''\kappa''\alpha''}^{\text{ZG}} F_{p\kappa\alpha}(\{ \tau^{\text{ZG}} \}) \sum_{\nu} e_{\kappa'\alpha', \nu}(0) e_{\kappa''\alpha'', \nu}(0) u_{0\nu}^2 \quad (2.75)$$

where,

- $C_{p\kappa\alpha, p'\kappa'\alpha'}(T)$: Temperature-dependent correlation function.
- M_κ : Atomic mass of atom κ .
- $\Delta\tau_{p''\kappa''\alpha''}^{ZG}$: Special displacement along direction α'' .
- $F_{p\kappa\alpha}(\{\tau^{ZG}\})$: Force component due to the displaced configuration.
- $e_{\kappa\alpha, \nu}(0)$: Polarization vector at the Γ -point.
- $u_{0\nu}$: Zero-point vibrational amplitude.

The summation goes over all phonon modes as well as through all the wave-vectors, and not just $\mathbf{q} = 0$. These displacements and measurement of the forces on each atom. projects the response on each phonon mode, yielding the second derivative $C_{p\kappa\alpha, p'\kappa'\alpha'}(T)$ in one-shot [110].

The IFCs $C_{p\kappa\alpha, p'\kappa'\alpha'}(T)$ obtained from finite differences, contain a certain amount of numerical noise and these must obey the crystal's symmetry and enforce the sum rules. For high-symmetry systems the IFCs should be invariant under symmetry operations $\{\mathbf{S}|\mathbf{v}(S) + \mathbf{R}_m\}$, i.e. for any rotation $\mathbf{S}$, for any translation $\mathbf{v}(S)$. If two atoms (pk) and (PK) are related by these symmetries then their IFC blocks satisfy,

$$C_{PK\alpha, P'K'\alpha'} = \sum_{\beta\beta'} \mathbf{S}_{\alpha\beta} \mathbf{S}_{\alpha'\beta'} C_{pk\beta, p'k'\beta'} \quad (2.76)$$

The enforcement of these relations greatly contributes for the reduction of statistical errors as well as accelerating the convergence of any structure while preserving rotational invariance. One takes the computed $C(T)$ matrix and averages its elements over all symmetry-equivalent indices using Eq. 2.76, this approach automatically deals with two tasks: 1) reducing the noise and 2) applying the sum rule together with the rotational invariance of the dispersion.

After symmetrization, we may also apply minor corrections such as to enforce the translational sum rule (the total force on the unit cell vanishes) and, if needed, averaging degenerate modes to preserve any exact degeneracies. The result is a physically valid IFC matrix $C^{(j)}(T)$ at the current iteration.

2.4.3 Anharmonic Phonon Frequencies and Polarizations

With the updated symmetrized IFC matrix $C^{(j)}(T)$, we are now able to recompute the dynamical matrix and diagonalize it again, as per the last steps in DFPT. From this we are able to obtain new phonon frequencies and eigenvectors for all $\mathbf{q}$,

$$D_{k\alpha,k'\alpha'}(\mathbf{q};T) = \frac{1}{\sqrt{M_k M_{k'}}} \sum_{p'} C_{0k\alpha,p'k'\alpha'}^{(j)}(T) e^{iq \cdot (R_{p'} + \tau_{k'} - \tau_k)} \quad (2.77)$$

after which, one solves the eigenvalue problem (Eq.2.52). This way we are able to obtain the updated phonon spectrum $\omega_{\mathbf{q}\nu}(T)$, as well the the phonon polarization vectors $e_{k\alpha,\nu}(\mathbf{q})$.

At this point the phonon frequencies have been “renormalized” through the anharmonic effects at a defined finite temperature T values. Typically, one may observe softening or stiffening of frequency modes, when compared to the harmonic (0K) spectrum. One may observe the stabilization of anharmonic modes that were unstable (imaginary) in a high-symmetry (high-temperature) structure.

Using the new phonon eigenvectors and frequencies, the special displacement vector $\Delta\tau^{ZG}(T)$ is rebuilt for the next iteration. While the first iteration already provides a good enough approximation; it might not prove to be sufficient, therefore it is possible to compute a new iteration with the ZG displacement vector $\Delta\tau^{ZG}(T)$ from the previous result, recalculating the new displacement as,

$$\Delta\tau_{pk\alpha}^{ZG}(T) = \sqrt{\frac{M_0}{N_p M_k}} \sum_{\nu} S_{\nu} \sigma_{0\nu}(T) \Re [e_{k\alpha,\nu}(0)] \quad (2.78)$$

Here the evaluation of the amplitude mode ν is at Γ . With the new displacements (with an amplitude of $\sqrt{\langle(\Delta Q_{\mathbf{q}\nu})^2\rangle}$), the new atomic configuration is generated and is consistent with the anharmonic phonons.

The updated ZG displacement is subsequently used to calculate new forces and reconstruct the IFC matrix, following the same procedure as stated in Ref. subsection 2.4.2. Since each update to the phonon spectrum modifies the phonon eigenvectors and frequencies, the resulting displacement vector $\Delta\tau^{ZG}$ changes accordingly, requiring an iterative solution. In practice, this displacement is automatically generated from the phonon data using the `ZG.x` module of the EPW code

3. Computational Results: Stability of K_2CaF_4 and related RP ($n = 1$) structures

Studying lattice distortions—such as octahedral rotations and tilts—is essential for understanding the structural, electronic, and optical properties of perovskite materials. DFT provides an effective framework to explore these distortions, offering valuable insights into the energetic stability and potential applications of various compositions.

In this dissertation, we investigate a family of perovskite-analogue systems to K_2CaF_4 , which serve as a particularly relevant case study due to its elemental composition and its relatively low melting points—hence yielding lower phase transition temperatures and pressures, and making it suitable for laboratory-based studies. The choice of elements in our systems is motivated by their status as rock-forming elements with abundances comparable to that of silicon (see Fig. 1.4). Also, such a structural polymorph remains largely unexplored in the literature.

While K_2CaF_4 is the central focus of this work, we also explore structurally similar compounds in which the halide anion (X-site) are partially or fully substituted with Cl, Br, or I chemical elements. This substitution strategy allows us to examine how compositional changes affect both structural stability and optoelectronic behavior. For comparative purposes and benchmarking across computational methods, we additionally include results for K_2CdF_4 and selected halide variants, which have been previously studied [62, 111].

Most previously reported pure-fluoride-based RP structures, crystallize in the high-symmetry tetragonal space group $I4/mmm$ [112–114], as expected for other RP oxide-systems. Therefore, the initial 0 K calculations for the materials, K_2CaF_4 and K_2CdF_4 , were carried out assuming this aristotype symmetry phase (i.e., the undistorted high-symmetry tetragonal structure as shown in Fig.3.1). However, based on the tolerance factor, analyzed for the parent perovskites KCaF_3 and KCdF_3 (0.90 and 0.92, respectively [48]) which provide insights into the bond-length mismatch and potential structural instabilities, it is expected that these systems may exhibit octahedral tilt and rotation modes, that will break the symmetry and therefore lower the overall structural symmetry [111].

As a case study, we investigate Cd-based Ruddlesden–Popper (RP) fluorides, such as K_2CdF_4 , which has been experimentally studied [62, 111] and proposed to crystallize in an orthorhombic phase with a Glazer tilt pattern of $a^-a^-c^0$ [111]. The goal is to assess

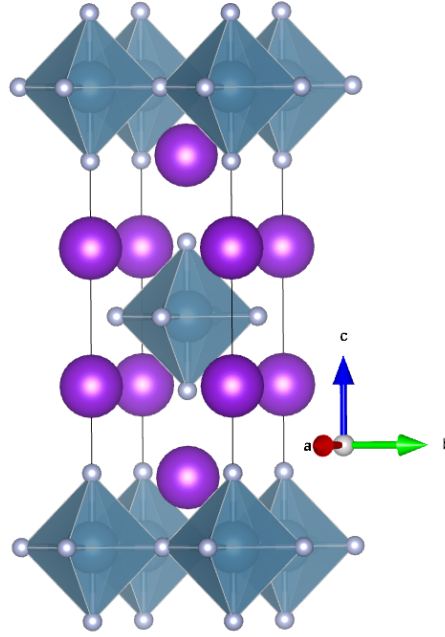


Figure 3.1: Crystal structure of K_2CaF_4 viewed along the $[100]$ direction. The structure consists of layers of corner-sharing CaF_6 octahedra (blue polyhedra), separated by K^+ cations (purple spheres). The Ca^{2+} ions occupy the centers of the octahedra, while F^- ions are located at the vertices. The layered arrangement is characteristic of the Ruddlesden–Popper type structure. The crystallographic axes are shown for reference.

whether analogous of the Ca-based compounds can be stabilized and follow the same phase transition pathways.

Table 3.1: List of studied RP perovskites ($n = 1$).

System	Halide
K_2CaF_4	Pure F
K_2CdF_4	Pure F
$\text{K}_2\text{CaF}_2\text{Cl}_2$	Mixed F:Cl = 1:1
$\text{K}_2\text{CaCl}_2\text{Br}_2$	Mixed Cl:Br = 1:1
$\text{K}_2\text{CaBr}_2\text{I}_2$	Mixed Br:I = 1:1
$\text{K}_2\text{CdF}_2\text{Cl}_2$	Mixed F:Cl = 1:1
$\text{K}_2\text{CdCl}_2\text{Br}_2$	Mixed Cl:Br = 1:1
$\text{K}_2\text{CdBr}_2\text{I}_2$	Mixed Br:I = 1:1

Additionally, through chemical mutation, by mixing the halide elements (e.g., substitution of F with Cl, Br or I), these will influence the lattice parameters, phase stability, and electronic/optical properties [115–117]. In Ref. Mannino et al., it is detailed the compositional arrangement of the halide of $\text{Cs}_2\text{PbCl}_2\text{I}_2$, where in Fig. 3.2, it shows the underlying structure of the most stable PbX_6 octahedra configuration, with the smaller halogen elements being positioned along the octahedra equatorial plane and the larger halogen along the PbX_6 apical sites.

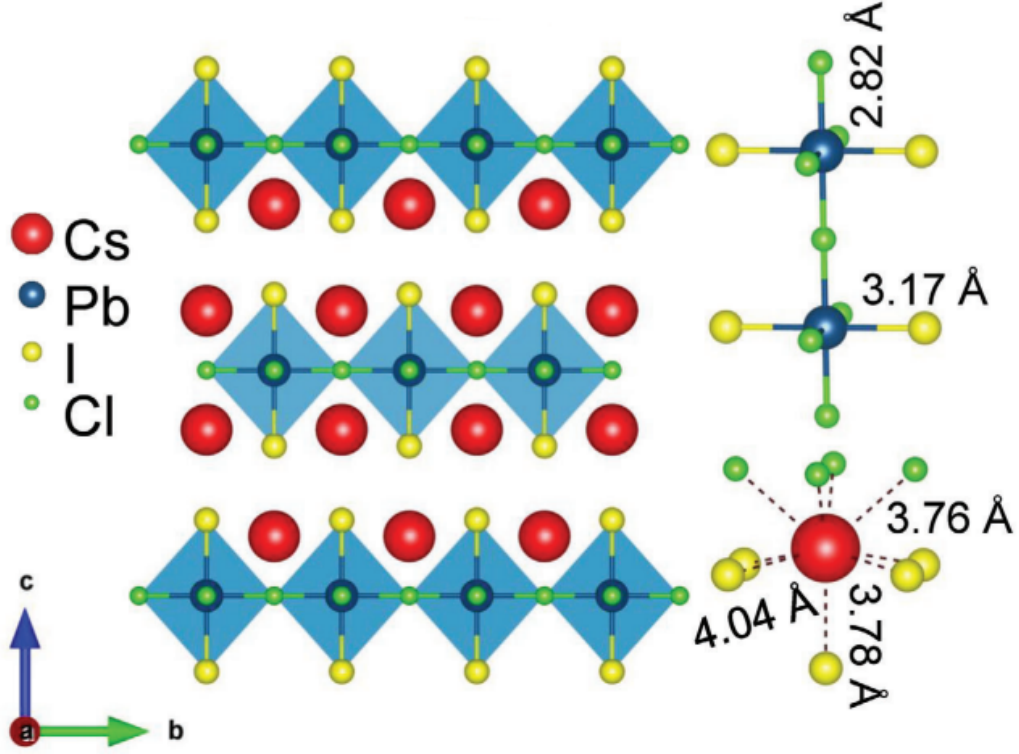


Figure 3.2: Crystal structure of the RP perovskite $\text{Cs}_2\text{PbI}_2\text{Cl}_2$ structure, showing the equatorial Cl^- and apical I^- positions inside the PbX_6 octahedra. Figure taken from Ref. [116].

3.1. Benchmark case study: K_2CdF_4

As previously mentioned, K_2CdF_4 was the first structure to be studied in the present work, serving as a benchmark for the Ca-based compounds of interest. This material is known to adopt a stable tetragonal $I4/mmm$ space group at high temperatures [111], while transitioning to an orthorhombic phase at room temperature. The initial calculations were carried out for the high-symmetry $I4/mmm$ phase, without considering temperature effects.

As expected for a high-symmetry phase at low temperature (since DFT and the harmonic approximation are temperature-independent), the phonon dispersion calculations reveal several unstable modes, thus indicating dynamical instability and the reduction of symmetry as experimentally suggested in Ref. [111], and more recently in Ref. [62].

In Figs. 3.4 and 3.5 we show the electronic properties of K_2CdF_4 in the $I4/mmm$ phase. Although the system is dynamically unstable at room conditions, we analyzed the electronic properties to access potential applications. We obtain an indirect electronic band gap of 3.99 eV, which closely matches the 4.00 eV value listed in the Open Quantum Materials Database [118, 119]. From the partial density of states (PDOS) analysis —Fig. 3.5, we may infer that the valence band maximum (VBM) is composed mainly of F p -states

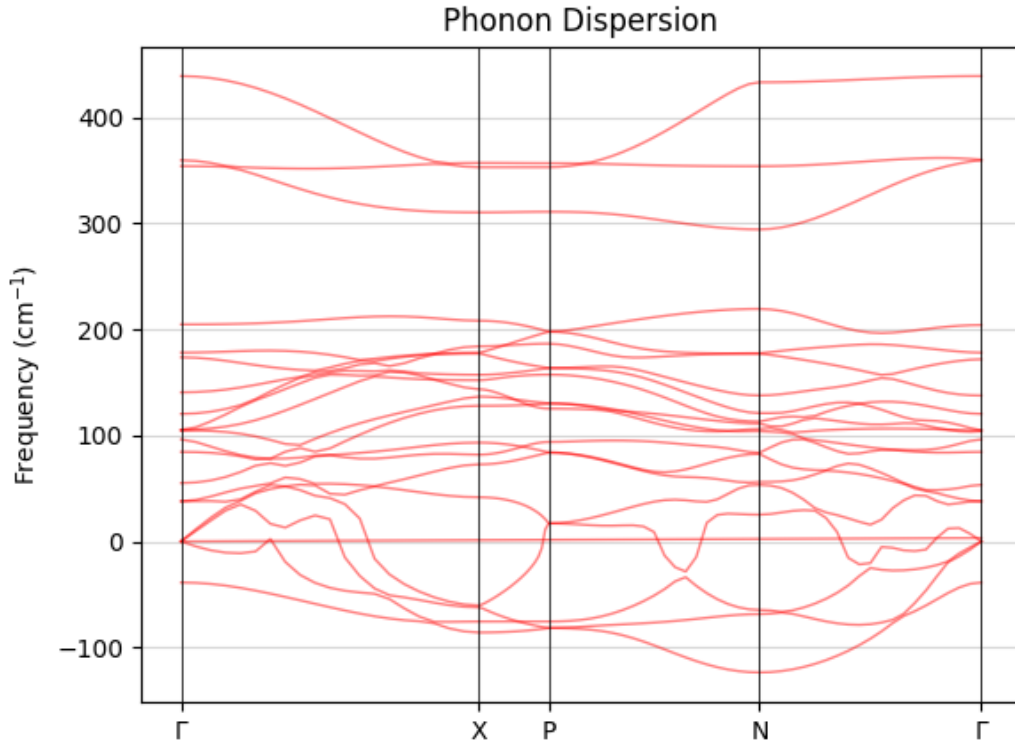


Figure 3.3: Phonon dispersion curves of K_2CdF_4 in the $I4/mmm$ phase within the harmonic approximation at 0K.

and the conduction band minimum (CBM) by a mixture/hybridization of the s -states of F, K and Cd.

Table 3.2 compares the Cd–F bond lengths obtained in this thesis with values reported in the literature [62] at 397K. The relative difference in the analysis is believed to be a result of a non-temperature dependence leading to the results not showing the accurate measurement of these bond lengths. ZG method is still being applied to this structure and at high temperatures it is expected for these results to be similar.

Table 3.2: Quantitative analysis of Cd–F bond lengths in K_2CdF_4 . Literature values taken from Ref. [62]

	Bond type	Bond length (Å)	$\Delta R = R_{eq} - R_{ax} $ (Å)
Results	Axial Cd–F	2.2175	0.0154
	Equatorial Cd–F	2.2021	
Literature	Axial Cd–F	2.1193	0.0613
	Equatorial Cd–F	2.1806	

The respective system calculations have not yet converged, and are still being considered. From the state-of-art, it has been confirmed a ground-state stable system for this material; however, no space group has been confidently determined. Therefore, if being

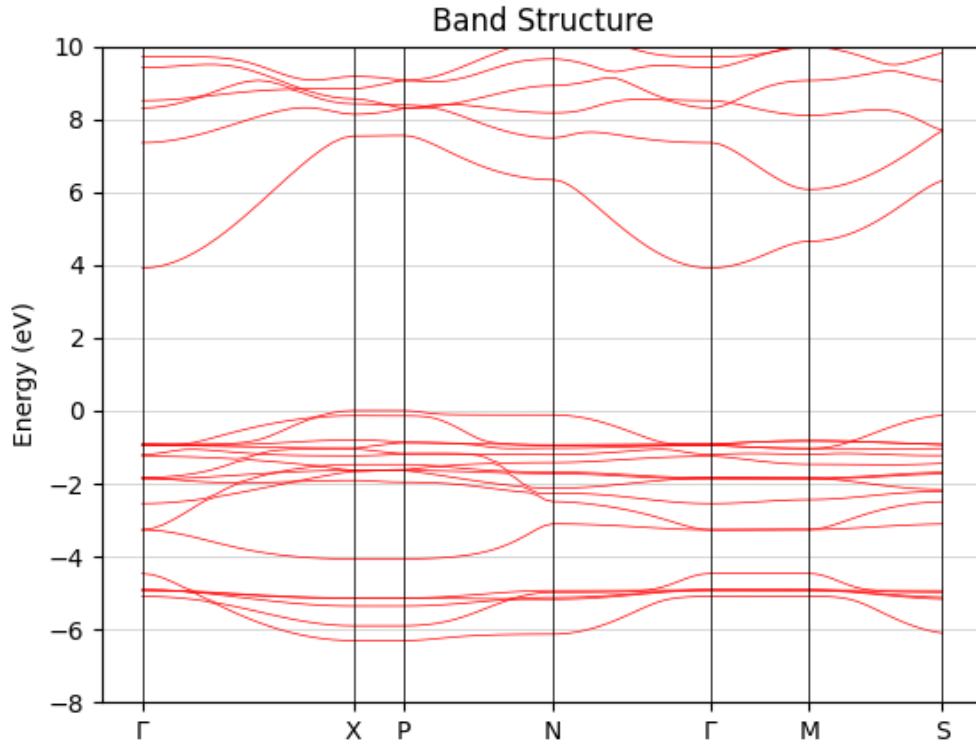


Figure 3.4: Electronic band structure of K_2CdF_4 in the $I4/mmm$ phase at 0 K.

able to converge respective calculations, we may be able to attain, and confirm, for the first time, the ground-state symmetry of this material [62, 111]—experimental analysis only concluded that the system relaxed towards an orthorhombic ground-state phase, possibly with with a Glazer tilt pattern of $a^-a^-c^0$ [111].

Table 3.3: Lattice parameters of K_2CdF_4 for the $I4/mmm$ phase. Literature values were taken from Ref. [120]

Lattice Parameter	Length (Å)	
	Literature	Calculated
a	4.43612	4.0415
b	4.43612	4.0415
c	13.2660	13.2885

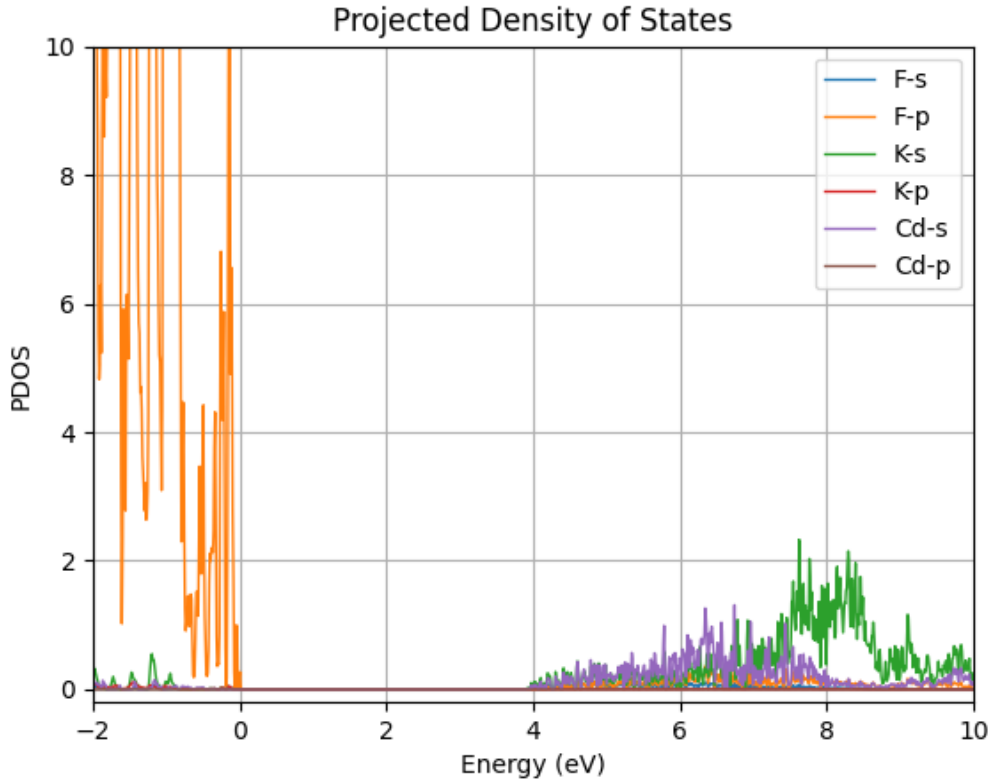


Figure 3.5: Electronic PDOS of K_2CdF_4 in the $I4/mmm$ phase at 0 K.

3.2. K_2CaF_4

In Fig. 3.8 we can observe that the phonon dispersion of the high-symmetry K_2CaF_4 phase is dynamically unstable within the harmonic approximation, where imaginary modes are observed throughout the whole of the BZ. By applying the ZG framework, and after 2 iterations, it was possible to find the stable space group of this structure, which is the $Cmce$, of space group n° 64 (Fig. 3.8).

Figure 3.6 illustrates the structural phases of K_2CaF_4 , highlighting the transition from the high-symmetry tetragonal phase to the distorted, low-symmetry configuration. The first panel corresponds to the high-temperature $I4/mmm$ phase, characterized by its idealized, layered perovskite structure without any octahedral tilting. In contrast, the middle and right panels show the top and side views, respectively, of the relaxed $Cmce$ structure, obtained after full structural optimization (relaxation of the lattice parameters and atomic positions). The $Cmce$ phase, which is dynamically stable at room conditions, exhibits pronounced octahedral tilting that breaks the symmetry and reduces the total energy. The resulting tilt pattern is consistent with common distortions found for other RP compounds and reflects the structural preferences of the K–Ca–F framework under room-temperature conditions.

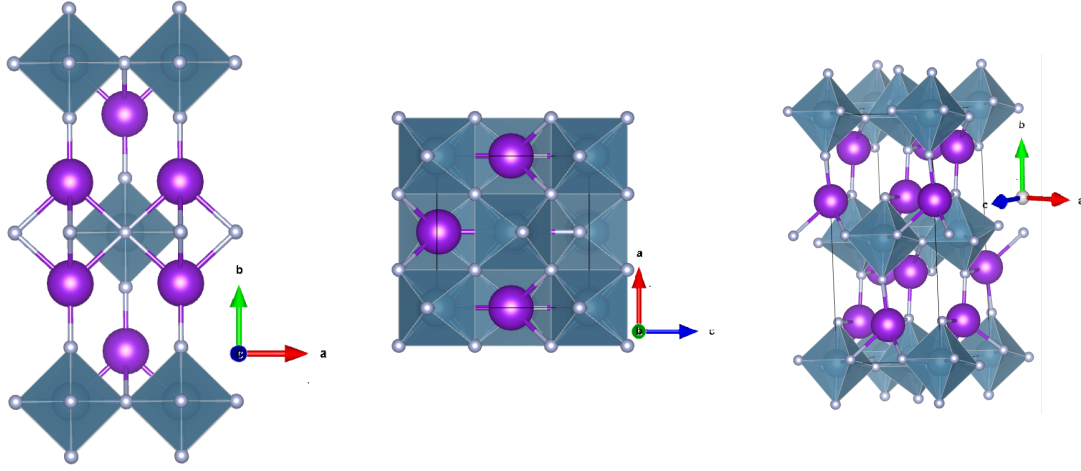


Figure 3.6: Optimized crystal structures of K_2CaF_4 . Initial $I4/mmm$ phase showing instability (left), and the center and right figures show, respectively, the top and side views of the dynamically stable $Cmce$ structure obtained after two ZG iterations.

The rotation of CaX_6 octahedra around the $[110]$ axis of the parent unit cell, characterized by the Glazer tilt pattern $a^-a^-c^0$ (associated with the irreducible representation X_3^+), is highlighted in Fig. 3.7. This tilt pattern is accompanied by a slight antidisplacement of the K ions within the plane of the perovskite layers. Together, these structural distortions contribute to the observed symmetry reduction, in agreement with experimental observations for the previously discussed K_2CdF_4 analogue [111].

The relative energy difference between the two studied phases is around 0.01 Ry (~ 0.14 eV), showing a small energy difference between both polymorphs.

Major differences between the high-symmetry $I4/mmm$ and low-symmetry $Cmce$ phases of K_2CaF_4 , lies in their dynamic stability, with only minor variations observed in the electronic properties. The phonon dispersion of the $I4/mmm$ (Fig. 3.8) evidences imaginary frequencies, indicating that it is dynamically unstable at room conditions; whereas the relaxed $Cmce$ phase exhibits no such instabilities and is therefore the preferred ground state, and being thermodynamically and dynamically stable. Despite the symmetry lowering, the electronic structures remain qualitatively similar, as shown in Fig. 3.9. Both phases display wide band gaps, with values ranging from 5.92 eV for the $I4/mmm$ phase, and 6.07 eV for the $Cmce$ phase, suggesting minimal impact of the structural distortion on the overall electronic character. Likewise, the PDOS show comparable features, indicating that the phase transition mainly serves to stabilize the structure without introducing significant changes in its electronic behavior (Figures 3.9, 3.10). Slight differences are observed mainly on the F s -states, most likely due to the tilting and rotations of the octahedra cages. The obtained band gaps for the RP structure are similar to the values theoretically

reported for the parent perovskite KCaF_3 , where an indirect band gap of ≈ 6.01 eV is observed for both insulating polymorphs [121]. Compared to the K_2CdF_4 counterpart, we may infer that the valence band dispersion is more flat, suggesting that the effective mass of the electrons are heavier. Such effects occur as well for the ground-state system of K_2CaF_4 . The conduction band is more dispersive, when compared to the valence band; although as symmetry breaks towards the orthorhombic ground-state, the higher energy bands become less parabolic-like.

Table 3.4: Lattice parameters of K_2CaF_4 of both polymorphs.

Lattice Parameter	Length (Å)	
	<i>I4/mmm</i>	<i>Cmce</i>
a	4.43957	6.18223
b	4.43957	13.46646
c	13.61105	6.39217

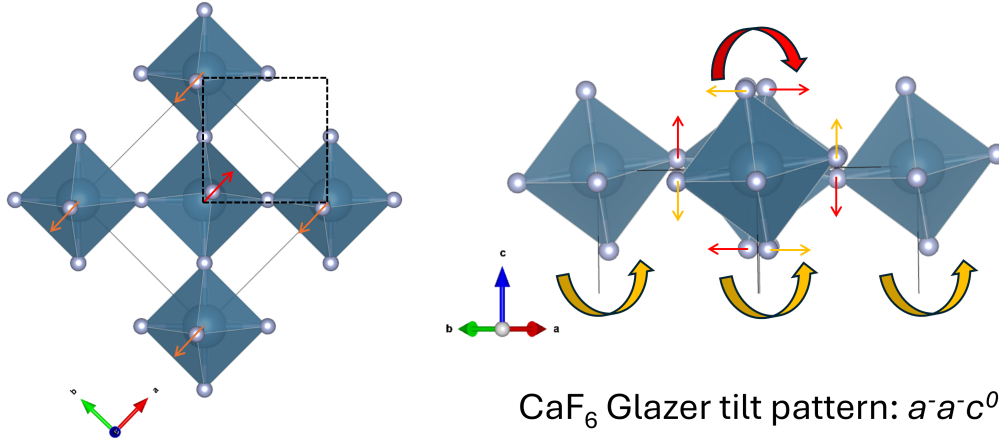


Figure 3.7: Octahedral tilt system in the layered perovskite K_2CaF_4 structure. The CaF_6 octahedra exhibits a $a^-a^-c^0$ tilt pattern (Glazer notation), characterized by out-of-phase rotations about the in-plane axes (a and b), and no rotation about the c -axis. The left panel shows a top-down view of the CaF_6 layer with tilt directions indicated by the orange and red arrows. The right panel illustrates the side view, highlighting the alternating rotations along a and b , and the absence of tilt around c . Coordinate axes are indicated in both views.

Table 3.5 shows the axial and equatorial Ca–F bond lengths in K_2CaF_4 for both the *I4/mmm* and *Cmce* phases. Unlike the mixed-halide compounds, the bond length differences (ΔR) are minimal, with nearly equal axial and equatorial values, especially in the distorted *Cmce* phase where ΔR drops to just 0.001 Å.

Table 3.5: Quantitative analysis of Ca–F bond lengths in K_2CaF_4 .

	Bond type	Bond length (Å)	$\Delta R = R_{eq} - R_{ax} $ (Å)
<i>I4/mmm</i>	Axial Ca–F	2.24925	0.02946
	Equatorial Ca–F	2.21979	
<i>Cmce</i>	Axial Ca–F	2.25065	0.00142
	Equatorial Ca–F	2.25207	

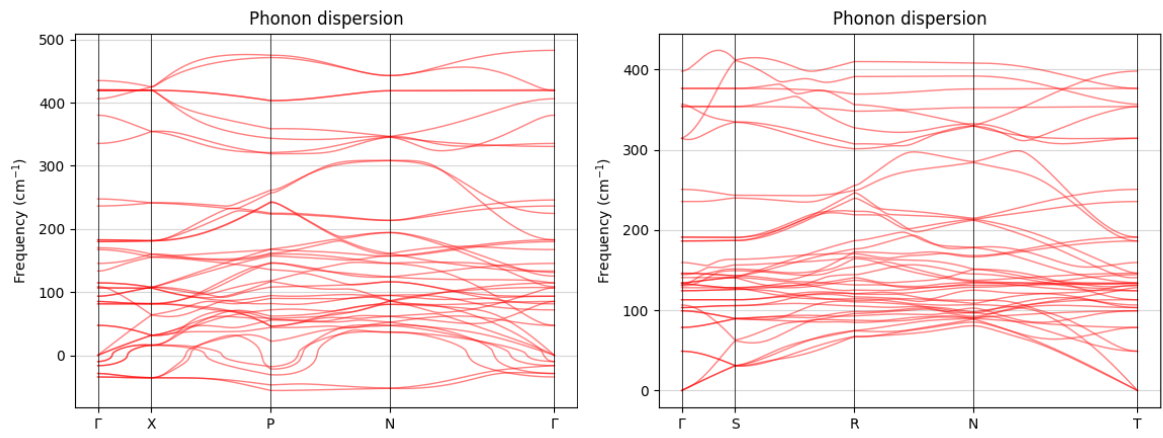


Figure 3.8: Phonon dispersion curves of K_2CaF_4 : (left) the initial unstable *I4/mmm* phase and (right) the final relaxed *Cmce* structure.

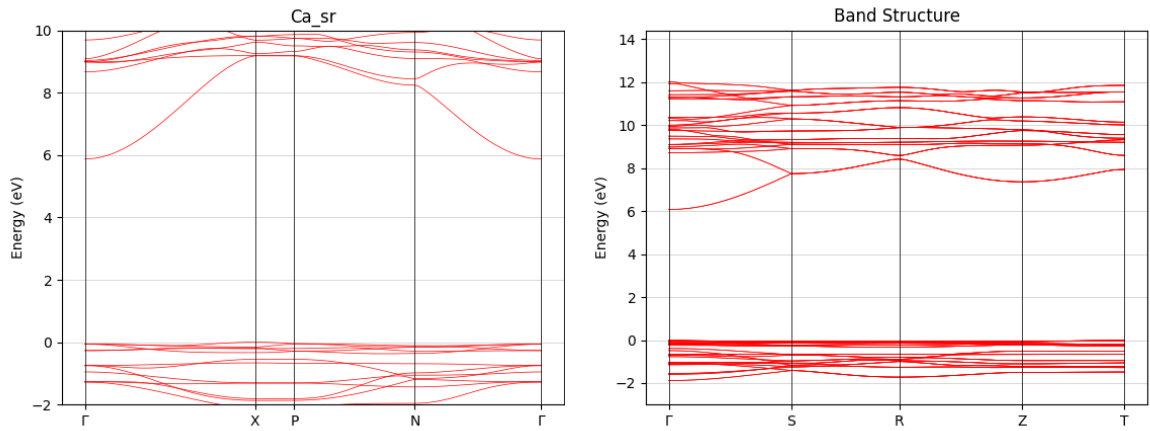


Figure 3.9: Electronic band structures of K_2CaF_4 : (left) initial *I4/mmm* phase and (right) relaxed *Cmce* phase.

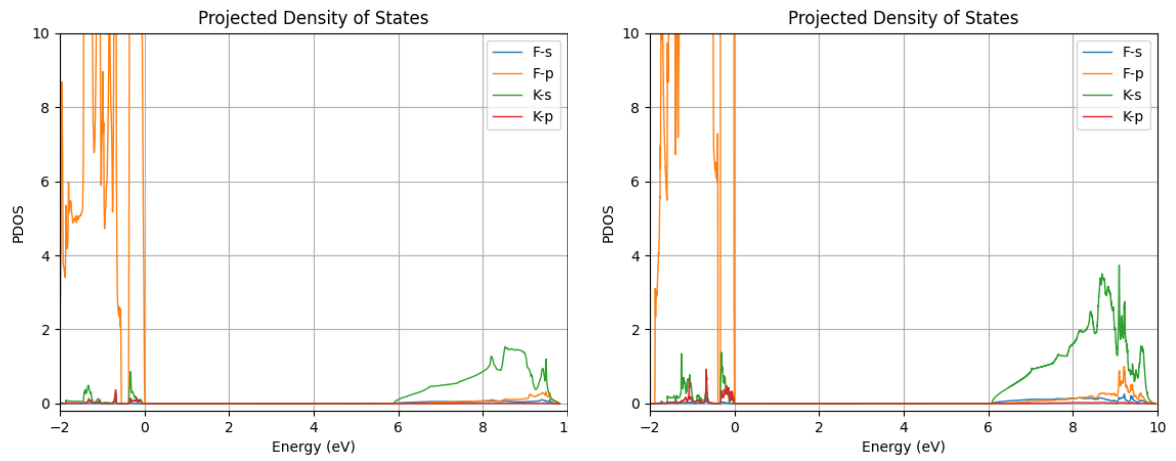


Figure 3.10: PDOS of K_2CaF_4 : (left) initial $I4/mmm$ phase and (right) relaxed $Cmce$ phase. The PDOS provides further insights into the contributions of different atomic orbitals.

3.3. $K_2CdCl_2F_2$

We have also studied structures where mixed cation elements are considered. An example is the $K_2CdCl_2F_2$ system, where half of the F (at apical sites of the octahedra units) are substituted by Cl, as shown in Fig.3.11. The goal is to analyse what differences may occur in the electronic properties, and also to confirm the stabilities of structural phases with considered chemical mutations.

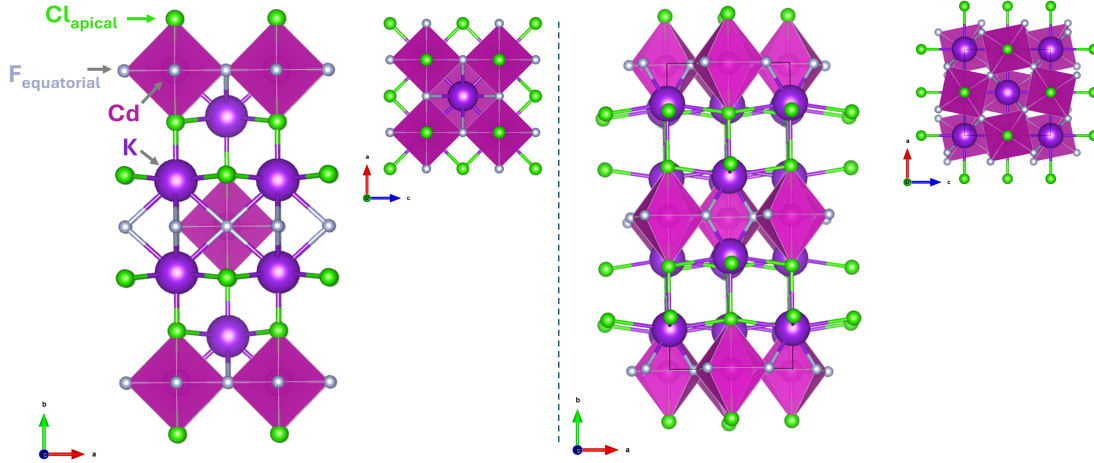


Figure 3.11: Optimized crystal structures of $K_2CdF_2Cl_2$: (left) initial unstable $I4/mmm$ and (right) dynamically stable $Cmce$ phase after one-shot ZG iteration.

From Fig. 3.12 we may observe that the high-symmetry $I4/mmm$ phase evidences localized unstable phonon modes along the X-P BZ directions, a significant improvement compared to the pure fluoride phase, which features multiple imaginary modes along all of the BZ. This hardening of these modes/frequencies is further completed upon displacing the atoms along the unstable eigenvectors, and lowering the symmetry towards the $Cmce$ phase, which shows to be a dynamically stable polymorph.

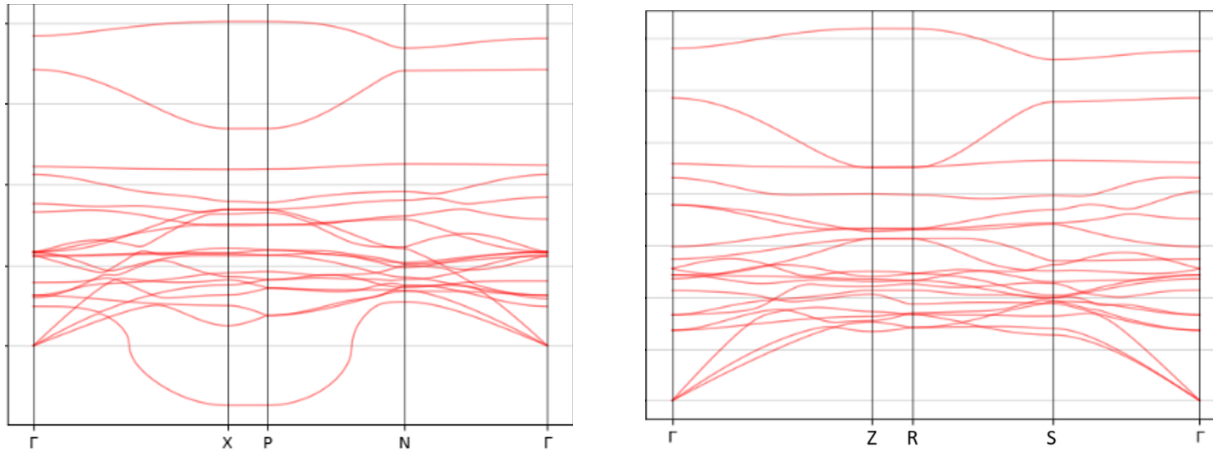


Figure 3.12: Phonon dispersions of $K_2CdF_2Cl_2$: (left) unstable $I4/mmm$ phase and (right) dynamically stable $Cmce$ phase.

As shown in Figure 3.12, the introduction of the Cl ions significantly reduces the soft imaginary phonon modes, for the high-symmetry phase. For the ground-state we obtain a dynamically stable system, as shown as well for the pure structure of F.

The total energy difference between the two $\text{K}_2\text{CdF}_2\text{Cl}_2$ phases were computed to evaluate their energetic stability, giving a total difference of 39.9575 meV

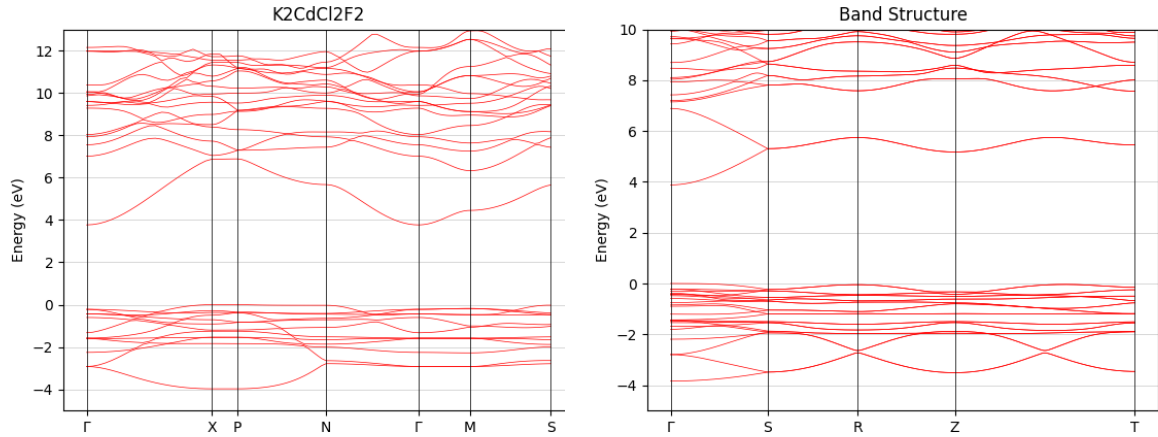


Figure 3.13: Band structures of $\text{K}_2\text{CdF}_2\text{Cl}_2$: (left) high-symmetry $I4/mmm$ phase and (right) room-temperature $Cmce$ phase.

The electronic band structures of both the $I4/mmm$ and relaxed $Cmce$ phases of $\text{K}_2\text{CdCl}_2\text{F}_2$ exhibit a clear band gap, consistent with an insulating character, with the gap width being 3.77 eV and 3.88 eV, respectively. Therefore, the Cl substitution does not have much impact on the band gap width, when compared to the $I4/mmm$ pure F system.

The PDOS shows that the VBM is dominated by the p-orbitals of the apical Cl atoms, while the CBM arises mainly from the Cd s-orbitals. This separation of orbital contributions highlights the role of Cl in the bonding states and Cd in the antibonding conduction states.

The in-phase rotation of CdX_6 octahedra, around the $[001]$ axis of the parent unit cell, is characterized by the Glazer tilt pattern $a^0a^0c^+$ (associated with the irreducible representation X_2^+). The rotational distortion of the octahedra is evident in both the top and side projections of the structure, as detailed in Fig.3.15, indicating a well-defined long-range order of the tilt system. For future work, we aim to investigate the evolution of cell parameters as a function of temperature, particularly in the context of the negative thermal expansion behavior commonly observed in RP phases, such as in the Ca_2MnO_4 system [58]. In fact, the supposed high-temperature $I4/mmm$ phase already exhibits a shorter c -parameter (15.392 Å) compared to the lower-temperature, distorted-symmetry

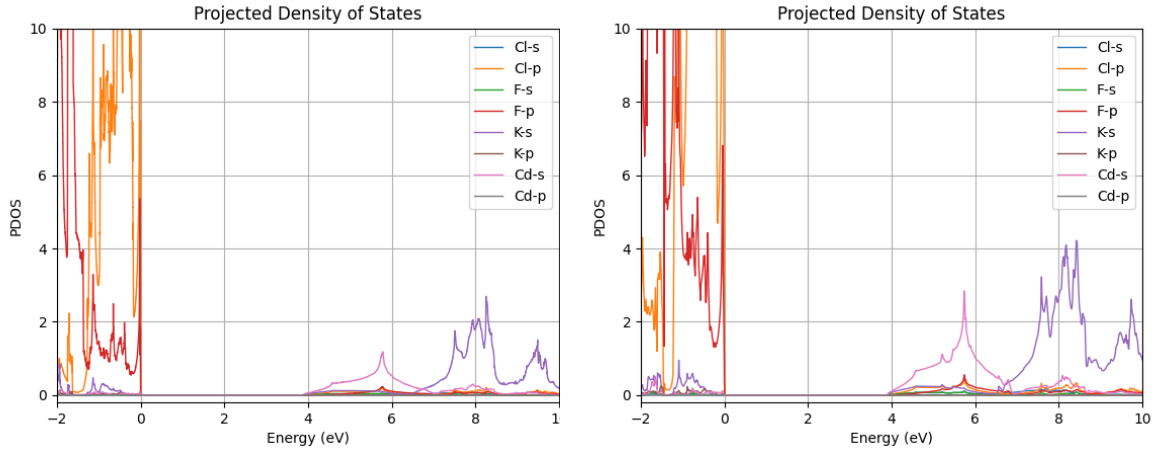


Figure 3.14: Partial density of states for $\text{K}_2\text{CdF}_2\text{Cl}_2$: left – $I4/mmm$ phase and right – relaxed Cmce phase.

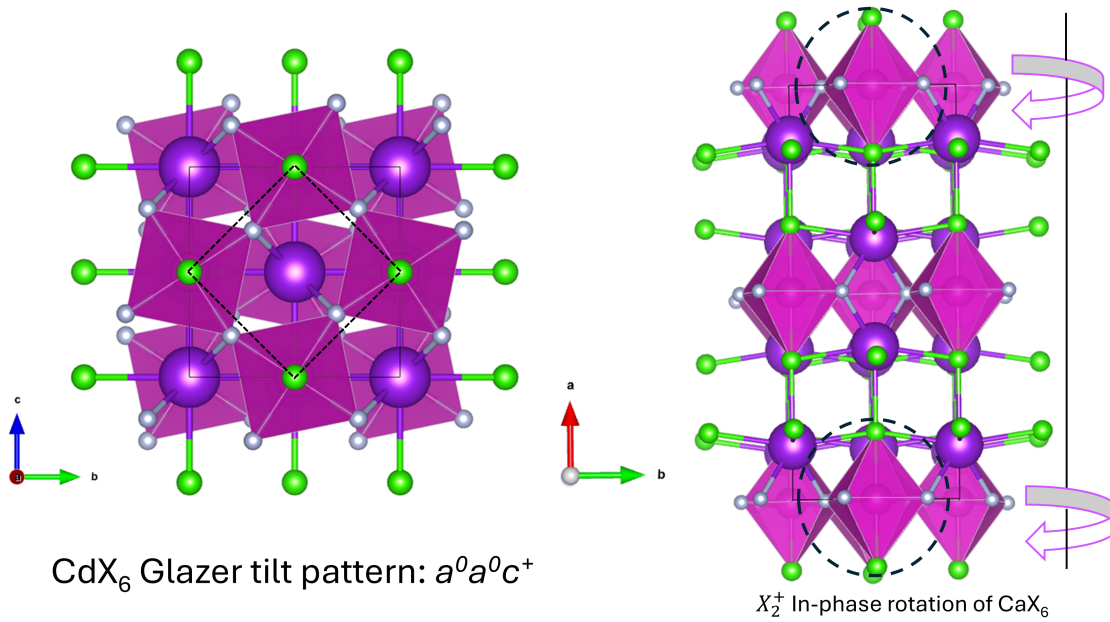


Figure 3.15: Crystal structure of $\text{K}_2\text{CdF}_2\text{Cl}_2$ highlighting the $a^0a^0c^+$ Glazer tilt pattern of the CdX_6 octahedra. Left: View along the [001]. Right: Side view illustrating in-phase rotations of the octahedra around the c -axis. Green, purple, and light grey spheres represent K, Cd, and halide (F/Cl) atoms, respectively. Curved arrows emphasize the rotation directions.

Cmce phase (15.644 Å), suggesting that this system may exhibit uniaxial negative thermal expansion upon heating.

Table 3.6 reports the Cd–Cl (axial) and Cd–F (equatorial) bond lengths in $\text{K}_2\text{CdF}_2\text{Cl}_2$ for both the $I4/mmm$ and Cmce phases. Axial bonds are longer than equatorial ones, with a reduced ΔR in the distorted Cmce phase (0.294 Å) compared to the high-symmetry $I4/mmm$ phase (0.315 Å).

Table 3.6: Quantitative analysis of Cd–F and Cd–Cl bond lengths in $\text{K}_2\text{CdF}_2\text{Cl}_2$.

	Bond type	Bond length (Å)	$\Delta R = R_{\text{eq}} - R_{\text{ax}} $ (Å)
<i>I4/mmm</i>	Axial Cd–Cl	2.56927	0.3146
	Equatorial Cd–F	2.25467	
<i>Cmce</i>	Axial Cd–Cl	2.57690	0.29393
	Equatorial Cd–F	2.28297	

 Table 3.7: Conventional orthorhombic lattice parameters for $\text{K}_2\text{CdF}_2\text{Cl}_2$ (*Cmce*) derived from primitive cell transformation.

Lattice Parameter	Length (Å)	
	<i>I4/mmm</i>	<i>Cmce</i>
a	4.50934	15.64424
b	4.50934	6.31292
c	15.39241	6.31285

3.4. $\text{K}_2\text{CaCl}_2\text{F}_2$

The compound $\text{K}_2\text{CaCl}_2\text{F}_2$ adopts the same $a^0a^0c^+$ tilting pattern of the BX_6 octahedra as described in Figure 3.15, indicating a similar in-phase rotation of the octahedra around the *c*-axis.

The computed total energies for the high-symmetry *I4/mmm* and the relaxed *Cmce* phases of $\text{K}_2\text{CaCl}_2\text{F}_2$ differ by 33.36 meV, with the *Cmce* phase being slightly more favorable. This small energy difference indicates that both phases are nearly thermodynamically competitive within the accuracy of the calculations. However, phonon spectra reveal that only the *Cmce* phase is dynamically stable.

Figure 3.16 compares the phonon dispersions, while Figures 3.17 and 3.18 shows the electronic band structure and PDOS, respectively.

Similar to K_2CaF_4 , the starting point for the calculations of the $\text{K}_2\text{CaF}_2\text{Cl}_2$ structure was set in the high-symmetry *I4/mmm* phase. However, unlike the pure fluoride, the halide mixing induces an improvement in stabilizing several frequency branches. The phonon dispersion for the *I4/mmm* phase already shows a significant reduction in imaginary modes, indicating that halide substitution strongly stabilizes the lattice. We observe a strong localized mode around the high-symmetry P-point. Upon applying the ZG methodology, and by 'following' the unstable eigenvectors the system adopts the low-symmetry *Cmce* phase, which evidences dynamical stability (no imaginary frequencies).

The electronic band structures of both the *I4/mmm* and relaxed *Cmce* phases of $\text{K}_2\text{CaCl}_2\text{F}_2$ reveal clear insulating behavior, with a well-defined band gap in each case. Analysis of

the PDOS show that the top of the valence band is dominated by the p-orbitals of the apical Cl atoms, reflecting their significant contribution to the electronic states close to the VBM. Meanwhile, the CBM is primarily derived from the s-orbitals of the K atoms, indicating a distinct separation of orbital character between the valence and conduction bands - and similar to what occurs to the previously analyzed systems.

Table 3.8: Conventional orthorhombic lattice parameters for $\text{K}_2\text{CaF}_2\text{Cl}_2$ (Cmce) derived from primitive cell transformation.

Lattice Parameter	Length (Å)	
	$I4/mmm$	Cmce
a	4.49648	16.64607
b	4.49648	6.30838
c	16.56494	6.30838

In Table 3.8, the lattice parameters b and c appear equal up to the fifth decimal place, which might suggest a non-orthorhombic structure. However, they differ slightly beyond that precision, with $b = 6.3083825412$ and $c = 6.3083840000$.

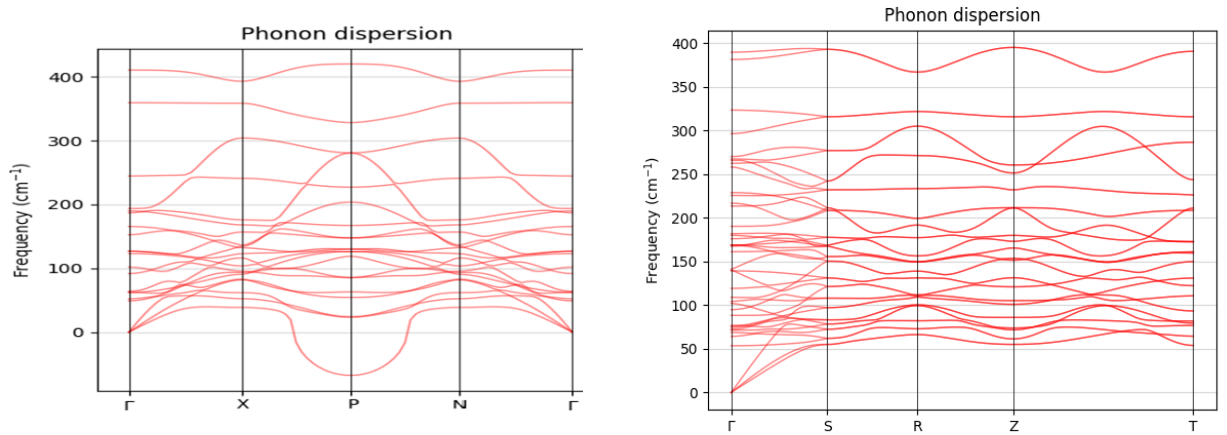


Figure 3.16: Phonon dispersions of $\text{K}_2\text{CaF}_2\text{Cl}_2$: (left) high-symmetry $I4/mmm$ phase, showing one unstable mode; (right) relaxed Cmce phase, which is fully dynamically stable.

Table 3.9 presents a quantitative comparison of Ca–Cl (axial) and Ca–F (equatorial) bond lengths in $\text{K}_2\text{CaF}_2\text{Cl}_2$ for the $I4/mmm$ and Cmce phases. As in the Cd-based counterpart, both structures, the axial Ca–Cl bonds are consistently longer than the equatorial Ca–F bonds, reflecting the anisotropic bonding. The ΔR slightly decreases from 0.514 Å in the $I4/mmm$ phase to 0.485 Å in the Cmce phase.

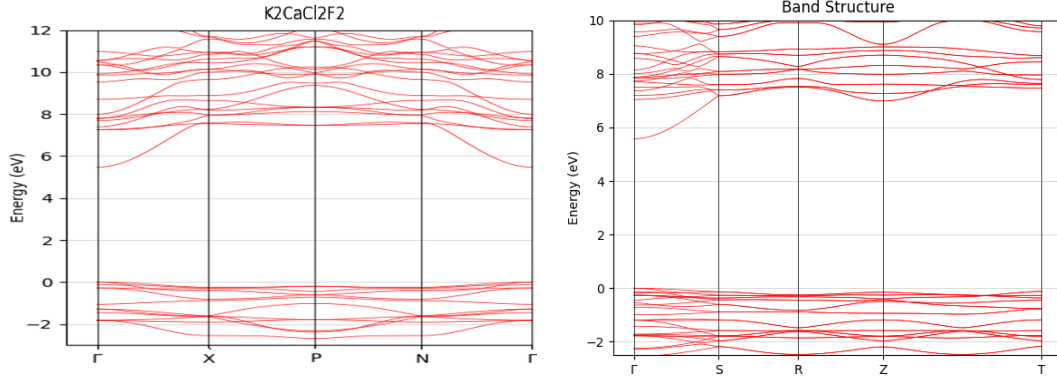


Figure 3.17: Electronic band structures of $\text{K}_2\text{CaF}_2\text{Cl}_2$: (left) $I4/mmm$ phase; (right) relaxed Cmce phase.

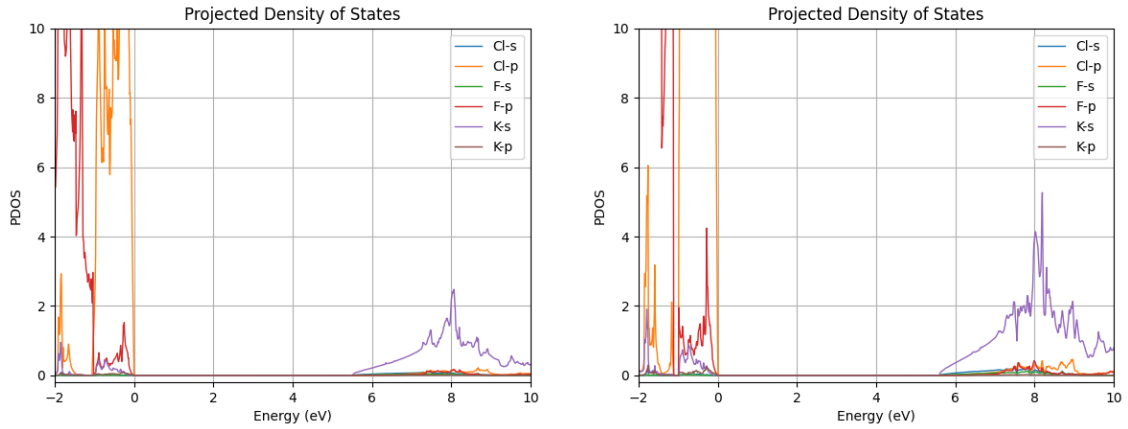


Figure 3.18: PDOS of $\text{K}_2\text{CaF}_2\text{Cl}_2$: (left) $I4/mmm$ phase; (right) relaxed Cmce phase. The orbital character near the Fermi level remains qualitatively similar between both polymorphs.

Table 3.9: Quantitative analysis of Ca–F and Ca–Cl bond lengths in $\text{K}_2\text{CaF}_2\text{Cl}_2$.

	Bond type	Bond length (Å)	$\Delta R = R_{\text{eq}} - R_{\text{ax}} $ (Å)
$I4/mmm$	Axial Ca–Cl	2.76250	0.51426
	Equatorial Ca–F	2.24824	
Cmce	Axial Ca–Cl	2.75920	0.48472
	Equatorial Ca–F	2.27448	

3.5. Analysis of Additional Mixed-Halide Perovskite Compounds

The family of mixed-halide perovskites studied here—comprising $\text{K}_2\text{CdCl}_2\text{Br}_2$, $\text{K}_2\text{CaCl}_2\text{Br}_2$, $\text{K}_2\text{CdI}_2\text{Br}_2$, and $\text{K}_2\text{CaI}_2\text{Br}_2$ —exhibit a consistent trend of enhanced dynamical stability compared to their pure halide counterparts. All compounds were analyzed as starting points in their high-symmetry $I4/mmm$ phase. By computing the phonon dispersions (Figures 3.19, 3.22, 3.25, and 3.28) we may observe a significant decrease of imaginary

phonon modes (hardening of the modes), demonstrating improved dynamical stability induced by the halide mixing at the high-symmetry phase.

3.5.1 $\text{K}_2\text{CdCl}_2\text{Br}_2$

The phonon dispersion of $\text{K}_2\text{CdCl}_2\text{Br}_2$ (Figure 3.19) shows minor remaining instabilities. The band structure and density of states (Figures 3.20, 3.21) remain qualitatively similar to those of the pure compounds, underscoring the stability enhancement without electronic disruption, with a band gap of 2.76 eV.

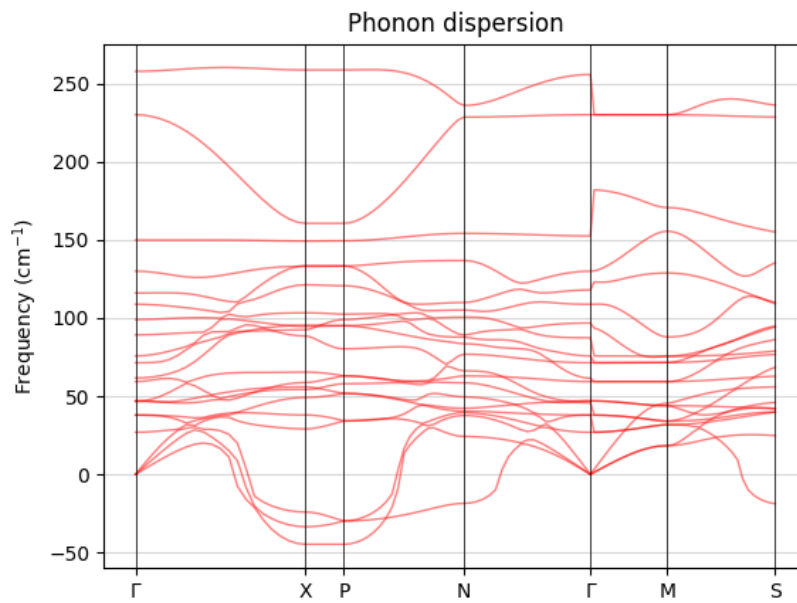


Figure 3.19: Phonon dispersion of $\text{K}_2\text{CdCl}_2\text{Br}_2$ in the $I4/mmm$ phase at 0K.

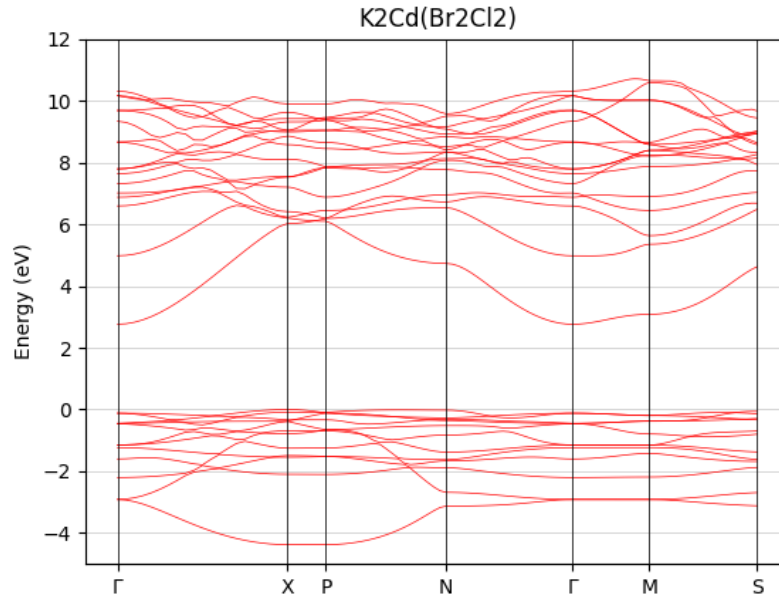


Figure 3.20: Electronic band structure of $K_2CdCl_2Br_2$ in the $I4/mmm$ phase.

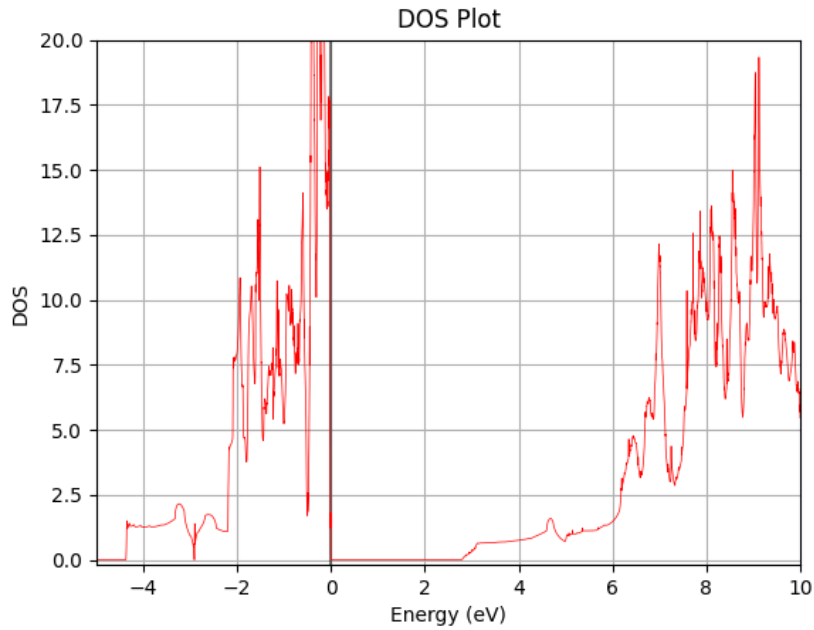


Figure 3.21: Electronic density of states (DOS) of $K_2CdCl_2Br_2$ in the $I4/mmm$ phase.

3.5.2 $K_2CaCl_2Br_2$

$K_2CaCl_2Br_2$ does not exhibit significant changes to the number of negative modes (Figure 3.22), when compared to the F and F-Cl systems at the high-symmetry phase, with a bandgap of 4.31 eV. By changing F to Br we observe a remarkable decrease of gap

width, lowering from 5.47 eV towards 4.31 eV ($\sim 21\%$), when compared to the $\text{K}_2\text{CaF}_2\text{Cl}_2$ system.

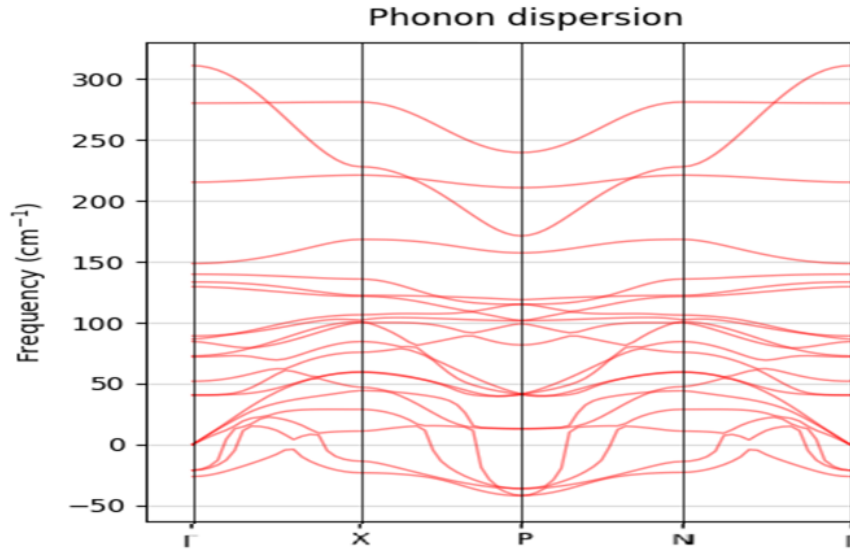


Figure 3.22: Phonon dispersion of $\text{K}_2\text{CaCl}_2\text{Br}_2$ in the $I4/mmm$ phase at 0 K.

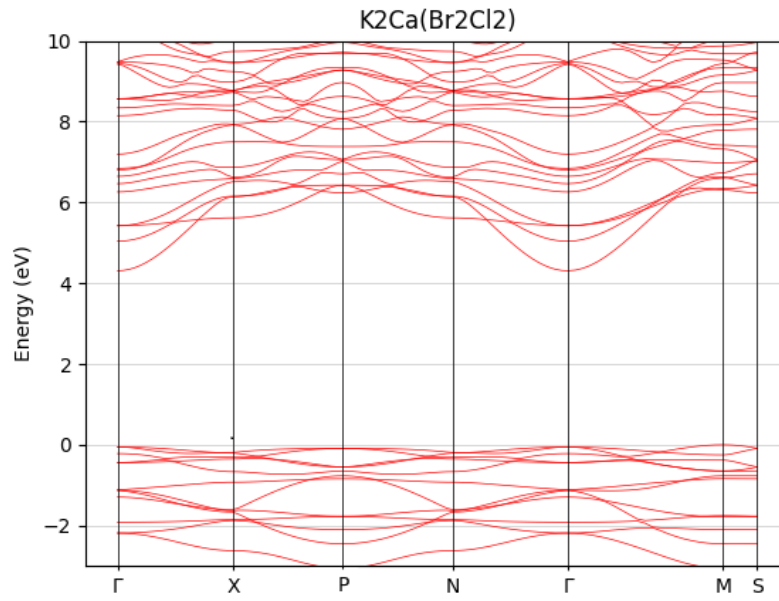


Figure 3.23: Electronic band structure of $\text{K}_2\text{CaCl}_2\text{Br}_2$ in the $I4/mmm$ phase.

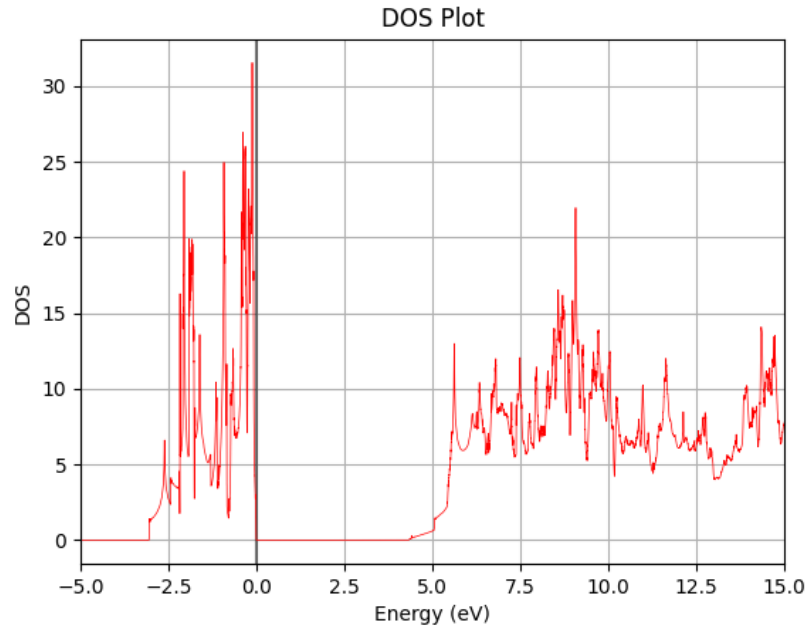


Figure 3.24: Electronic density of states (DOS) of $\text{K}_2\text{CaCl}_2\text{Br}_2$ in the $I4/mmm$ phase.

3.5.3 $\text{K}_2\text{CdI}_2\text{Br}_2$

The $\text{K}_2\text{CdI}_2\text{Br}_2$ structure follows the same trend: phonon calculations confirm strongly improved dynamic stability (Figure 3.25), while the electronic band structure and DOS (Figures 3.26, 3.27) retain features similar to the pure F halide materials. We observe that the band gap is of the order of 3.68 eV, which actually maintains more or less a similar width when compared to $\text{K}_2\text{CdF}_2\text{Cl}_2$ and K_2CdF_4 .

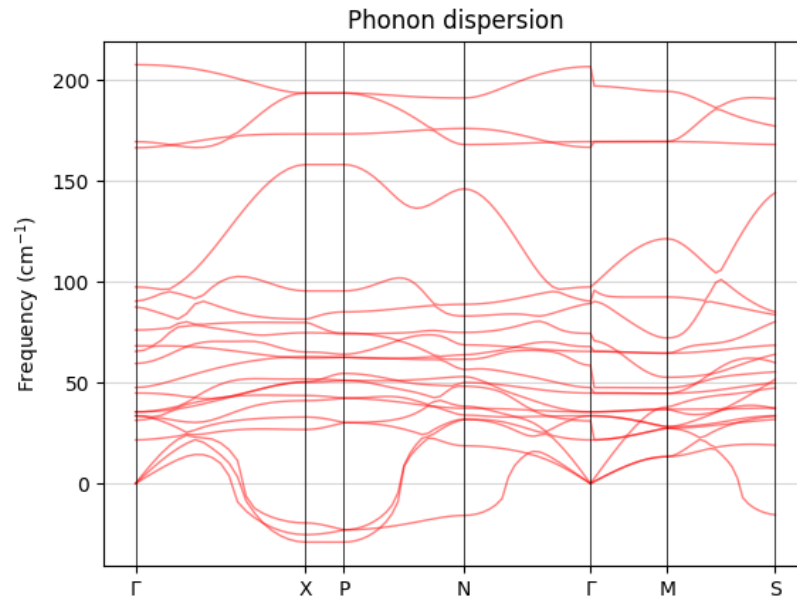


Figure 3.25: Phonon dispersion of $\text{K}_2\text{CdI}_2\text{Br}_2$ in the $I4/mmm$ phase at 0 K.

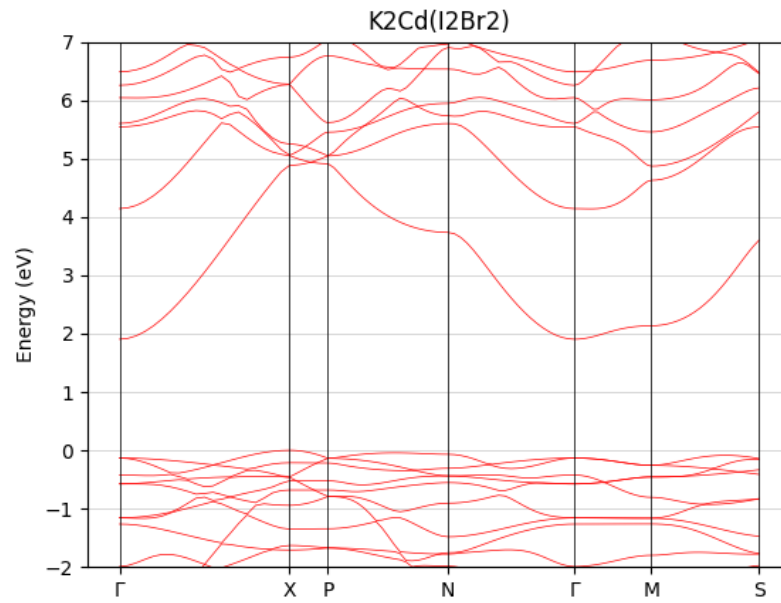


Figure 3.26: Electronic band structure of $\text{K}_2\text{CdI}_2\text{Br}_2$ in the $I4/mmm$ phase.

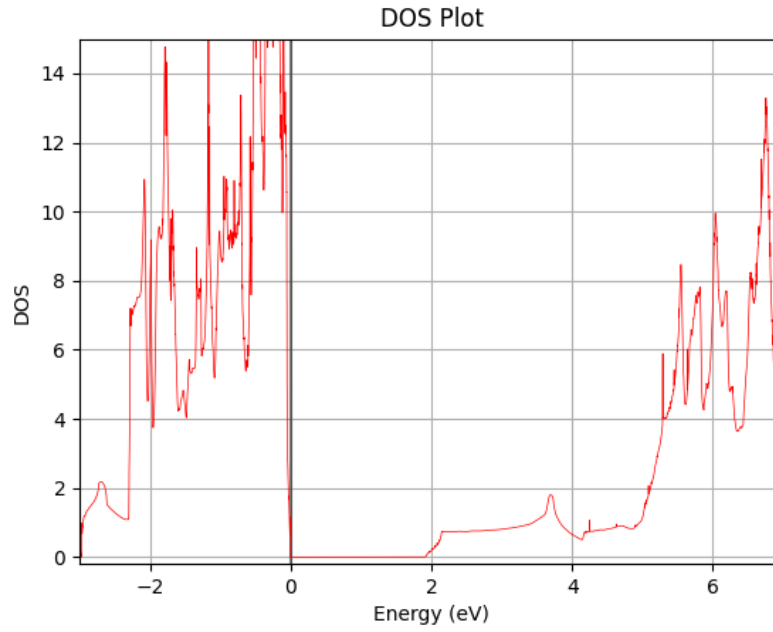


Figure 3.27: Electronic density of states (DOS) of $\text{K}_2\text{CdI}_2\text{Br}_2$ in the $I4/mmm$ phase.

3.5.4 $\text{K}_2\text{CaI}_2\text{Br}_2$

Finally, $\text{K}_2\text{CaI}_2\text{Br}_2$ also exhibits strongly localized imaginary phonon modes (Figure 3.28). Moreover the electronic properties are consistent with the other studied mixed-halide compounds (Figures 3.29,3.30), with a bandgap of 3.71 eV.

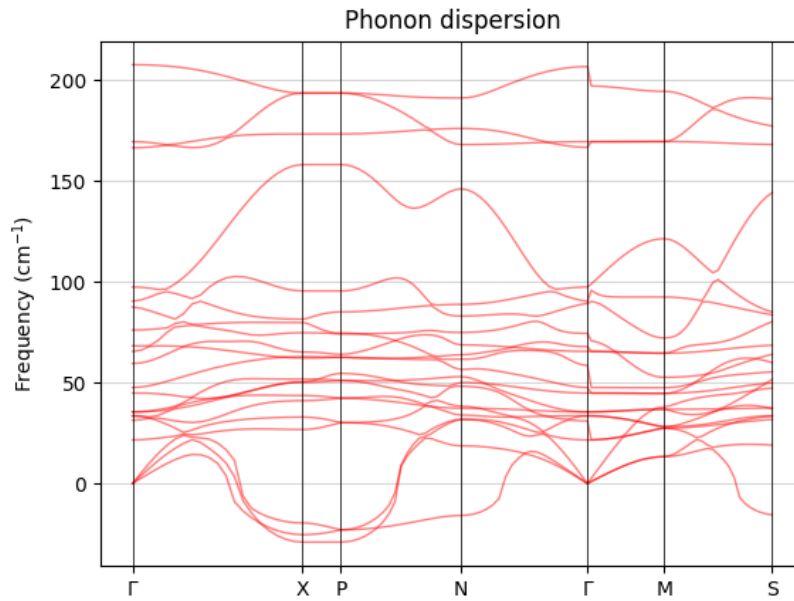


Figure 3.28: Phonon dispersion of $\text{K}_2\text{CaI}_2\text{Br}_2$ in the $I4/mmm$ phase at 0 K.

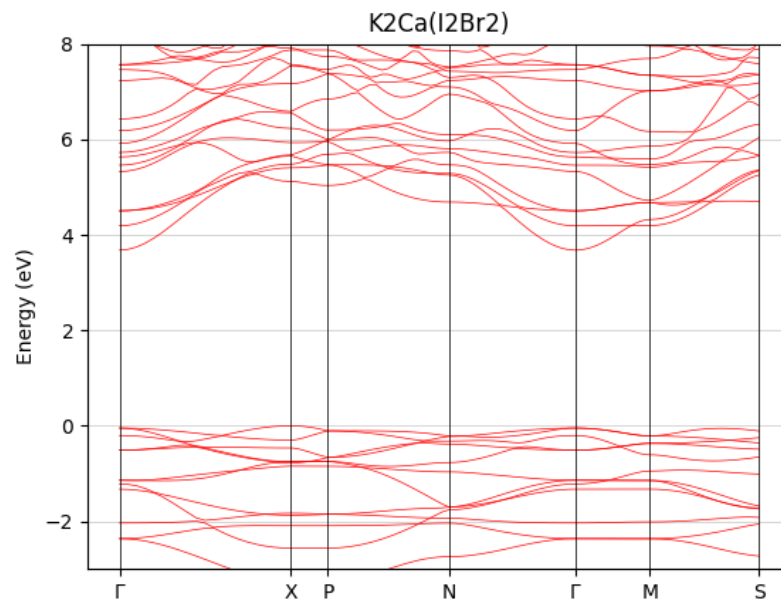


Figure 3.29: Electronic band structure of $\text{K}_2\text{CaI}_2\text{Br}_2$ in the $I4/mmm$ phase.

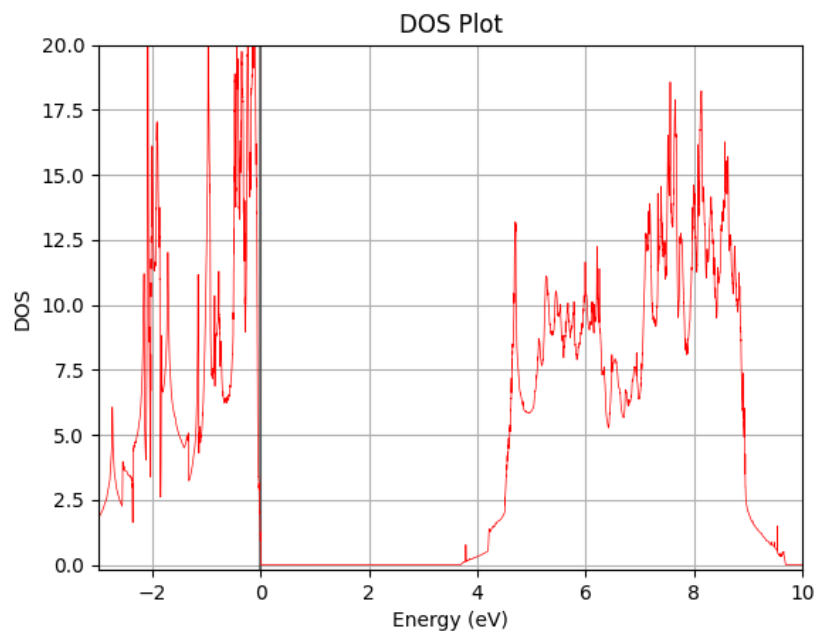


Figure 3.30: Electronic density of states of $\text{K}_2\text{CaI}_2\text{Br}_2$ in the $I4/mmm$ phase.

3.6. Summary of Findings

Table 3.10: Comparison of calculated band gaps for high-symmetry and relaxed phases of various K_2BX_4 compounds at 0K.

Compound	Phase	Band gap (eV)	Band gap type
K_2CaF_4	$I4/mmm$	5.92	Direct
	$Cmce$	6.07	Direct
K_2CdF_4	$I4/mmm$	3.99	Indirect
	$Cmce$	X.XX*	Direct / Indirect
$K_2CdF_2Cl_2$	$I4/mmm$	3.77	Direct
	$Cmce$	3.88	Direct
$K_2CaF_2Cl_2$	$I4/mmm$	5.47	Direct
	$Cmce$	5.55	Direct

1. Dynamical stability and phase transitions:

ZG calculations show that most of the studied fluoride-based RP perovskites stabilize in the orthorhombic $Cmce$ symmetry, even though the pure-halide structures have a different structural path than their mixed-halide counter parts, evidencing only stable phonon modes at 0 K, hence indicating dynamical stability at the considered conditions. However, one of the compounds, (K_2CdF_4), it was not possible to converge, and therefore calculations are still undergoing. This is nevertheless the structure reported in the literature, and thus the one that would supposedly be the easiest to stabilize from the outset. The exact space group is not known in the literature, and only local measurements, from [62], suggest that the structure should undergo a distortion into a supposedly orthorhombic phase. Further investigation into the possible phase transitions and symmetry preferences is required to better understand the behavior of such compounds under pressure and temperature conditions, and thus simulating plausible planetary interior environments.

2. Intrinsic stabilization in mixed-halide phases:

By partially combining halides in the RP $n=1$ phases, we find a systematic reduction of imaginary (negative-frequency) phonon modes. This suggests that mixed-halide RP perovskites more readily sustain higher-symmetry frameworks thus might sustain a higher mechanical rigidity—over a broader range of temperatures.

*Calculations were not converged and further tests are required.

3. Efficiency of ZG/SDM phonon renormalization:

By employing the self-consistent ZG/SDM approach, fully converged phonon spectra for K_2CaF_4 was achieved within two iteration cycles, and for $\text{K}_2\text{CdF}_2\text{Cl}_2$ in only a single-shot iteration. This demonstrates the practical speed and reliability of the method. After identifying the stable space groups through initial ZG calculations, it was not necessary to repeat the ZG routine for $\text{K}_2\text{CaF}_2\text{Cl}_2$, indicating similar phase transitions. Furthermore, substituting Cd into K_2CaF_4 led to an overall improvement in phonon stability, in the *Cmce* phase, though the structure remains unstable. In this case, an additional ZG cycle is likely required to reach full convergence.

4. Conclusions

The findings of the present study may translate into a table-top for laboratory solid-state experiments of tools to aid interpreting the mineralogy and thermal evolution of distant worlds.

- High-pressure mineral phases:** Many rocky exoplanets—including super-Earths and mini-Neptunes—are thought to host high-pressure magnesium and silicate perovskites in their mantles. While fluorides may not occur abundantly in these planets, fluoride Ca-based perovskites provide a convenient low-melting-point analog for laboratory studies. By characterizing the phase transitions and dynamical stability of these fluoride analogs under cryogenic conditions, we can infer the behavior of their high-pressure silicate counterparts deep inside planetary interiors, and thus relate surface measurements to processes in the core–mantle region.
- Atmospheric signatures and spectroscopic implications:** The decomposition and phase transitions of minerals at depth can influence which volatile species are released into the atmosphere during geological activity. Although direct observations of exoplanetary surfaces are currently unfeasible, atmospheric data serve as a valuable window into both surface and interior processes. As remote sensing techniques continue to advance, ab initio models will be vital in linking theoretical predictions with spectroscopic observations.
- Benchmarking computational methods for planetary materials:** The rapid convergence of the ZG/SDM method in our systems demonstrates its suitability for high-throughput screening of candidate exoplanet minerals. Future surveys could incorporate thousands of hypothetical halide and Ca-based compositions, allowing us to map out the stability fields of all plausible mantle phases across a wide range of pressures and temperatures.
- Comparative planetology:** The analog and computational frameworks developed here are equally applicable to Solar System bodies, from Earth’s deep mantle to the interiors of Mars, Venus, and the icy giants. On Earth, phase transitions such as perovskite $\rightarrow$ post-perovskite close to the core–mantle boundary, critically influence seismic anisotropy and mantle convection patterns; fluoride analogs allow

these transformations to be reproduced at much lower pressures and temperatures in the laboratory. For Mars and Venus—where direct seismic data are limited—our approach can predict the stability fields of candidate mantle minerals and guide interpretations of future geophysical missions. By unifying experimental analogs with high-throughput computational surveys, we can build a consistent picture of planetary interiors across diverse compositions and thermal regimes.

By integrating solid-state physics methodologies, such as lattice-dynamics calculations and experimental analog studies, into exoplanetary science, we establish a unified framework that translates atomic-scale insights into models of planetary interiors and observable phenomena. In this approach, phonon-based thermodynamic and stability data obtained under controlled laboratory conditions are mapped onto the extreme pressure–temperature regimes of planetary mantles, enabling predictions of internal structure, phase behavior, and thermal evolution. At the same time, these foundational results can be linked to remote observations, such as transit spectroscopy and thermal emission measurements, thereby connecting fundamental materials physics with the characterization of distant worlds.

4.1. Future Perspectives

The present research is not over, since we have initiated the study of Ca-based type perovskites, which to the best of our knowledge have not yet been experimentally evidenced.

Future work will involve the conclusion of still ongoing calculations, and most importantly, by considering the temperature and pressure effects, we are able to better emulate exoplanetary environments. The computational methodology employed in the present work has demonstrated to be efficient for such studies.

More broadly, the type of study carried out here holds potential to advance our understanding of the composition and evolution of exoplanets. With continued investigation, we may gain deeper insights into the materials and physical processes that shape a variety of cosmological bodies, including molecular clouds, comets and asteroids, and other objects beyond our Solar System. In time, such research can contribute to telling a more complete story about the formation and diversity of not only planetary systems but also other astrophysical environments, a story that continues to unfold with each new discovery.

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