Study of thermodynamic properties of solids through *ab-initio* methods

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Resumen (Español)

El objetivo de este trabajo es estudiar las propiedades de sólidos cristalinos, en particular las propiedades termodinámicas, desde primeros principios - esto es, tomando como punto de partida solo la red cristalina y la naturaleza cuántica de las particulas y construyendo un modelo consistente sobre estos puntos que describan con suficiente precisión las propiedades encontradas por métodos experimentales, e incluso predecir esas misma propiedades en materiales que, por alguna razón, son dificiles de obtener en cantidades suficientes para realizar estudios experimentales, imposibles de analizar con métodos experimentales por tener propiedades que impidan los procesos experimentales o localizados en condiciones imposibles de recrear en laboratorio (como sería, por ejemplo, el núcleo de La Tierra).

Este trabajo se encuentra dividido en dos partes. En la primera parte describiremos, sin entrar en detalle, la teoría que apoya estos métodos - haciendo énfasis en la Teoría del Funcional de la Densidad (DFT) - y el proceso de simulación que, implementado correctamente en un sistema informático, nos permite obtener las propiedades anteriormente mencionadas. Partiendo de las bases de la mecánica cuántica, se modela un sólido cristalino apoyándonos en los dos teoremas de Hohenberg-Kohn, que proporcionan una formulación del operador hamiltoniano para el mismo en la que todas sus propiedades dependen de la densidad de electrones en el estado fundamental del sólido. El potencial externo en este hamiltoniano será entonces aquel que minimice la energía, que es un funcional de la densidad electrónica - de ahí el nombre "Teoría del Funcional de la Densidad" - y por tanto minimizar éste será el objetivo básico de nuestras simulaciones. Para simplificar este cálculo, que en principio es muy complejo, se recurre a varios métodos para reducir el número de cálculos requeridos para obtener un resultado manteniendo una alta precisión en los mismos: se elige una base de ondas planas para expandir las funciones de onda electrónicas, se recurre al teorema de Bloch para reducir los cálculos a la primera zona de Brillouin, se eligen unos puntos especiales de esta zona usando el esquema de Monkhorst-Pack y se corta el desarrollo en ondas planas a una energía de corte, que se verifica que es suficiente para que el desarollo converga dentro de las tolerancias admitidas.

Una vez se obtiene esta densidad del estado fundamental, se puede obtener la estructura cristalina optimizada y de ahí sacar los fonones a través del *método de fonón congelado*, obteniendo la matriz dinámica del cristal y diagonalizando. Por último, se presenta la base teórica para la obtención de las propiedades termodinámicas del sólido a través de la mecánica estadística, considerando los fonones del sólido como un gas ideal de Bose-Einstein extrayendo las funciones termodinámicas de la densidad de estados de fonones ya obtenida.

A partir de entonces nos centraremos en la simulación y análisis de las propiedades de la calcopirita $CdGeP_2$ (en el grupo espacial $I\bar{4}2d$), material con posibles aplicaciones tec-

nológicas, en particular celdas solares. Utilizaremos el método anteriormente mencionado para estudiar sus propiedades estructurales, como las longitudes de los vectores de la red y los coeficientes de compresión, así como el módulo de *bulk* o de compresibilidadde volumen; y las propiedades termodinámicas. Hemos comprobado que los valores obtenidos están en muy acuerdo con los valores experimentales obtenidos por difracción de rayos X o predecidos en la literatura y comprobado que se cumplen en gran medida leyes como la Ley de Dulong-Petit para el calor específico.

El proceso a seguir es conceptualmente simple: empezando con algunos valores de los vectores de la red y las posiciones átomicas en la celda unidad obtenidos en la literatura, simulamos la estructura cristalina usando el software *Vienna Ab-initio Simulation Package* (VASP) a varias presiones y usamos esos datos, junto con el software PHONON, para encontrar las representaciones irreducibles y la frecuencia de los fonones en el punto Γ de Brillouin diagonalizando la matriz dinámica resultante de ligeros desplazamientos de las posiciones de los átomos en la celda unidad. Luego, se simula una supercelda de 2x2x2 para obtener relaciones de dispersión de phonones en toda la zona de Brillouin y la densidad de estados de fonones. Una vez obtenida la densidad de estados de fonones, podemos calcular la entropía, la energía interna, la energía libre y la capacidad calorífica, junto a otras muchas propiedades.

Las propiedades estructurales del cristal las obtendremos de dos maneras: los coeficientes de compresión, ajustando las longitudes de los vectores de la celda unidad como función de la presión y calculando sus derivadas, y el módulo de *bulk,* ajustando la energía frente al volumen a una ecuación de estado apropiada para las condiciones de nuestro sistema - en este caso, emplearemos la ecuación de Murnaghan de segundo orden.

Podemos entonces verificar que, de hecho, los valores obtenidos con este método computacional son muy similares a aquellos obtenidos con métodos experimentales, y sirve como indicador del gran valor de las simulaciones *ab-initio* en el estudio teórico y desarrollo de potencialmente nuevos materiales a la carta, así como en la predicción de propiedades de materiales en condiciones extremas de presión.

Parte del estudio realizado consistió en analizar el cambio en las frecuencias de los fonones cuando el cristal está sometido a altas presiones. Puesto que se ha simulado la estructura optimizada para varias presiones, es posible obtener los fonones en Γ sin recurrir a una supercelda, y estudiar la evolución de la frecuencia de los fonones frente al aumento de la presión aplicada. Como resultado de este estudio detectamos que en este sistema aparece un fonón tipo E activo Raman e infrarrojo con frecuencia imaginaria a partir de aproximadamente 14 GPa. Este resultado predice que la calcopirita CdGeP$_2$no debe ser estable a partir de esa presión y es probable que suceda un cambio de fase, bien a otra estructura estable o bien que se produzca una amorfización del cristal.

En conclusión, en este trabajo mostramos como mediante el uso de simulaciones mecanocuánticas desde primeros principios podemos obtener con gran precisión las propiedades estructurales y dinámicas del sistema estudiado. Además, debido al carácter predictivo del método hemos determinado el rango de estabilidad dinámica del cristal.

Abstract

The purpose of this work is to study the properties, in particular thermodynamic properties, of crystalline solids from first principles - that is, taking into account just the lattice of the crystal and the quantum nature of the particles and building a consistent model on top of those facts that describe with enough precision the properties of the crystal found with experimental methods, and even predict those properties in materials that, for one reason or another, are hard to obtain, impossible to analize with experimental methods, or located in conditions impossible to recreate in a laboratory (as would be, for example, the enormous pressure at the Earth's core).

We will describe, not in extreme detail, the theory that supports these methods - making emphasis in the Density Functional Theory (DTF) - and the simulation procedure that, properly implemented computationally, allows us to obtain the aforementioned properties.

The focus of this work will then shift to simulate and analyze the properties of the $CdGeP_2$ chalcopyrite ($I\bar{4}2d$ space group), a material with several proposed technological applications, especially in solar cells. Using this ab-initio method to find its thermodynamic properties, verifying that the values obtained are within the margins of the experimental values obtained by X-Ray diffraction or predicted in literature.

The procedure followed was conceptually simple: starting from some experimental values obtained from literature, we simulated the structure using the *Vienna Ab-initio Simulation Package* (VASP) at various pressures and used that data, along with the PHONON software, to find the irreducible representations and the phonons' frequency at Brillouin's Γ point diagonalizing the dynamical matrix resultant of slight displacements on the positions of atoms in the primitive cell.

Once obtained, the same software is capable of providing the phonon density of states of the cell, entropy, internal energy, free energy and heat capacity, among many other properties. These values obtained with PHONON were then plotted using Python scripts.

We can then verify that, indeed, the values obtained with this computational method are very similar to those obtained with experimental methods, and serves as a indicator of the value of *ab-initio* simulations in the theoretical study and development of potentially new, a-la-carte materials.

Part of the study realized was to analize the change of the phonons' frequencies when the crystal is subjected to high pressures, resulting in the appearance of an E-type Raman and Infrared-active phonon giving imaginary values at $\approx 14\ GPa$. This indicates that the $CdGeP_2$ chalcopyrite is dynamically unstable above this pressure, and that probably a phase transition to another stable structure or an amorphization would take place.

1 Theory Description

1.1 Overview

Solid is one of the basic states of matter in nature. As all matter is composed by atoms, a solid is the state of matter in which the interatomic forces are strong enough to rigidly tie them together. These same atoms of the solid can organized themselves in several ways, but we can distinguish two big groups: not organized at all or with short reach order - amorphous solids - or in a long reach order - crystalline solids. The latter ones have the most interest from the point of condensed matter physics, as many of the properties of the solid are not solely dependent of the atomic species that compose it, but of the way they are organized inside the crystal and the interactions between atoms resultant of this structure. As such, the study of condensed matter is the study of crystals and their properties.

There are several ways to approach this problem, seemingly simple but complex in its execution. The method we are following in this work is a study from first principles - that is, parting from the formalism of quantum mechanics from zero and building a consistent theory from there.

1.2 Density Functional Theory

A crystalline solid is a system consisting of a set of atomic nuclei with electrons interacting via electrostatic forces, and ultimately described by this hamiltionian:

$$
\begin{aligned}
\hat{H} &= -\sum_I \frac{\hbar^2}{2M_I} \nabla_I^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \frac{1}{2} \sum_{I,J(I \neq J)} \frac{Z_I Z_J e^2}{|\boldsymbol{R}_I - \boldsymbol{R}_J|} + \\
&\quad + \frac{1}{2} \sum_{i,j(i \neq j)} \frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_{i,I} \frac{Z_I e^2}{|\boldsymbol{R}_I - \boldsymbol{r}_i|}
\end{aligned}
$$

With this expression, it would only be a matter of solving the stationary Schrödinger equation to solve this problem and find all of the properties of condensed matter from first principles:

$$
\hat{H}\Psi(\boldsymbol{R}_I; \boldsymbol{r}_i) = E\Psi(\boldsymbol{R}_I; \boldsymbol{r}_i)
$$

However, this many-body problem is not trivial and carries severe computational overhead, to the point of not being feasable to solve in a reasonable time span. As such, it is necessary to find another approach from which to solve this problem.

One of such approaches is the adiabatic approximation, that allows the simplification of the hamiltionian considering that, as the atomic cores move slowly in comparison to the electron gas around it, these core are to all effects static, and their influence on the electrons can be aggregated in an effective potential $V_{ext}(\boldsymbol{r})$ as such:

$$\hat{H} = -\frac{\hbar^2}{2m_e}\sum_i \nabla_i^2 + \frac{1}{2}\sum_{i,j(i\neq j)}\frac{e^2}{|\boldsymbol{r}_i - \boldsymbol{r}_j|} - \sum_i V_{ext}(\boldsymbol{r}_i)$$

The other approach we will employ is the Density Functional Theory (DFT), which is based in the two Hohenberg-Kohn theorems [1], described as follows:

1. For any system of particles interacting inside an external potential $V_{ext}(\boldsymbol{r})$, this potential is uniquely determined by the ground state particle density $n_0(\boldsymbol{r})$. From here it follows that since the hamiltionan of the system is determined by this potential, all the properties of the solid are also characterized by this particle density.

2. Any such potential is uniquely determined by a functional $E[n]$ of the particle density $n(\boldsymbol{r})$. By minimizing this functional, one can find the energy and the electron density of the ground state.

In atomic units, this functional is described as:

$$E[n] = \int V_{ext}(\boldsymbol{r})n(\boldsymbol{r})d\boldsymbol{r} + F[n]$$

with the condition that $\int n(\boldsymbol{r})d\boldsymbol{r} = N$ (N being the total number of electrons in the system) and where $F[n]$ is a universal functional, independent of the external potential, that includes the kinetic energy of the system and the electron-electron interactions. This functional, however, has an unknown form, but it has to include the Hartree energy in some manner.

Kohn and Sham [2] noted that in a system of N non-interacting electrons, $F[n]$ is just the kinetic energy functional. With these two premises, the complete functional expression for interacting electrons can be written as:

$$E[n] = \int V_{ext}(\boldsymbol{r})n(\boldsymbol{r}) + \frac{1}{2}\int \frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r} - \boldsymbol{r}'|}d\boldsymbol{r}d\boldsymbol{r}' + T_S[n] + E_{exc}[n]$$

where the second term is the Hartree energy, $T_S[n]$ is the kinetic energy functional, and $E_{exc}[n]$ is the exchange-correlation energy.

To find the ground-state density of this N-electron system, we must then solve the following set of one-particle equations, the Kohn-Sham equations (KS), enforcing self-consistency:

$$\left\{-\frac{1}{2}\nabla^2 + V_{eff}(\boldsymbol{r})\right\}\psi_i(\boldsymbol{r}) = \varepsilon_i\psi_i(\boldsymbol{r}) \quad ; \quad i = 1\dots N$$

In this set of equations, the electron density of the ground-state will be $n(\boldsymbol{r}) = \sum_{i=1}^{N}|\psi_i(\boldsymbol{r})|^2$, and we have introduced an effective potential given by:

$$V_{eff}(\boldsymbol{r}) = V_{ext}(\boldsymbol{r}) + \frac{1}{2}\int\frac{n(\boldsymbol{r})}{|\boldsymbol{r}-\boldsymbol{r'}|}d\boldsymbol{r'} + \mu_{exc}(n(\boldsymbol{r})) \quad ; \quad \mu_{exc}(n(\boldsymbol{r})) = \frac{\partial E_{exc}[n(\boldsymbol{r})]}{\partial n(\boldsymbol{r})}$$

If the exchange-correlation energy functional $E_{exc}[n]$ were known, the solution to the KS equations would give us the electron density of the ground state and the energy of the system. This exact functional is, unfortunately, unknown. However, we can adopt a reasonable approximation if we consider the electron density $n(\boldsymbol{r})$ to vary slowly, hence adopting a *local density approximation* (LDA):

$$E_{exc}[n] = \int n(\boldsymbol{r})\varepsilon_{exc}(n(\boldsymbol{r}))d\boldsymbol{r}$$

In this approximation, the exchange-correlation density at each point is considered the same as that of an homogeneous electron gas of density $\varepsilon_{exc}(n(\boldsymbol{r}))$. While there are some better approximations for solids and molecules and LDA is sufficient in most cases to obtain the properties that we seek with this method, we used instead a more sophisticated approximation, from the family of *generalized gradient approximations* (GGA), which give an expression for the exchange-correlation energy functional not only dependent on the electron density, but also on its gradient.

Now, once we have these expressions, it is time to solve the KS equations and obtain the ground-state electron density, which will allow us to obtain all the thermodynamic properties of macroscopic systems from first principles. The main way to approach this problem is to expand the possible wave functions $\psi_i(\boldsymbol{r})$ in a convenient basis to solve the equations computationally. Three main basis are the most common ones used in this process, each with advantages and disadvantages:

- Plane waves basis: very simple and easy to implement, and it implies the use of the Fourier transform to switch between real and reciprocal spaces, operation with many efficient computational algorithms already developed. It posesses the disadvantage of needing a large number of plane waves to obtain convergence in the results.

- Linear combinations of atomic orbitals (LCAOs): needs a very low amount of orbitals to reach convergency, preferred in chemistry.

- Atomic sphere methods: consists in dividing the space in several regions, where the nuclear regions present atomic-like properties and the inter-atomic regions present a smooth variation of said properties. This approach provides the best elements of both plane waves and LCAOs, but carries a heavy computational cost and algorithmic complexity.

In this work, we used a plane waves basis to solve the KS equations. In order to reduce the computational power required to obtain results, it is often the case to replace the Coulomb potential created by the nucleus and the inner electrons with a pseudopotential, constructed in such a way that it removes the radial nodes in the nucleus region and maintains the same shape as the real potential outside a certain cutoff radious. The analytical expressions of these pseudopotentials are found in literature for each atom and position.

The periodicity of the crystal also comes into effect when we take into account the shape that the electronic wave functions would have. *A priori*, we know that by Bloch's theorem the wave function in a periodic solid must be a product of a plane wave and a function of the periodicity of the crystal, which can be expressed as:

$$\psi_{n,\boldsymbol{k}}(\boldsymbol{r}) = \sum_{\boldsymbol{G}} C_{n,\boldsymbol{k}+\boldsymbol{G}} e^{i(\boldsymbol{k}+\boldsymbol{G})\cdot\boldsymbol{r}}$$

where the sum runs over the reciprocal laticce vectors $\boldsymbol{G}$, n is the band number and $\boldsymbol{k}$ are points in the first Brillouin zone. To simplify the problem of computing these wave functions for every $\boldsymbol{k}$ point in the Brillouin zone, there are several methods to reduce the number of $\boldsymbol{k}$ points to a finite set of "special $\boldsymbol{k}$ points", like the Monkhorst-Pack scheme.

At this point, the series for a certain $\boldsymbol{k}$ point would still be infinite. In practice, this series can be made finite due to the fact that the coefficients $C_{n,\boldsymbol{k}+\boldsymbol{G}}$ are more important at lower kinetic energies $\frac{\hbar^2}{2m_e}|\boldsymbol{k}+\boldsymbol{G}|^2$ than at higher energies, so it is possible to cut the series at a particular cutoff energy E_{cutoff}:

$$\frac{\hbar^2}{2m_e}|\boldsymbol{k}+\boldsymbol{G}|^2 < E_{cutoff}$$

This cutoff energy will have to be adjusted until the convergence of the sum is reached to reduce the error that it produces in the simulations.

From here, the process becomes iterative: using the pseudopotential chosen for our system of study V_{eff}^{pseudo} and an initial guess for the electronic charge density $n_{in}(\boldsymbol{r})$, we solve the KS equations to obtain their eigenstates and a new electronic density $n_{out}(\boldsymbol{r})$, and feed this new electronic density back to the KS equations until self-consistency is reached. Once this process is done, it is necessary to check that we have obtained the optimized relaxed geometry of the structure, considering that for this to be the case, the forces on the atoms must be zero. These forces can be determined by the Hellmann-Feynmann theorem. [3]

1.3 The Dynamical Matrix. Phonons.

From the relaxed structure obtained with DFT, it is possible now to obtain information about the vibrational properties of the solid in study. These vibrational

properties provide with information about all kinds of thermal, electrical and mechanical properties of the solid, and can be modeled as a set of normal vibrational modes that comprise all the possible vibrations in the structure: we call these modes *phonons.*

To obtain these normal modes, let us consider an infinite crystal, periodic, with N (in the order of Avogadro's number) unit cells and n atoms per cell. We can write a small displacement in the atom j in the cell given by the lattice vector $\boldsymbol{L}$ around its equilibrium position $\boldsymbol{r}_0(jL)$ as:

$$\boldsymbol{u}_{jL} = \boldsymbol{r}_{jL} - \boldsymbol{r}_{0,jL}$$

We can expand the energy of the crystal in a Taylor series of the displacements around the equilibrium as:

$$E = E_0 + \frac{1}{2} \sum_{jj'LL'} \boldsymbol{u}_{jL}^T \boldsymbol{D}_{jLj'L'} \boldsymbol{u}_{j'L'} + \dots$$

where E_0 is the static energy at the equilibrium, $\boldsymbol{u}_{jL}^T$ is the transpose of $\boldsymbol{u}_{jL}$, and the 3x3 matrix $\boldsymbol{D}_{jLj'L}$ is the matrix of the second derivatives of the energy with respect to the displacements of the atoms, represented as:

$$(\boldsymbol{D}_{jLj'L'})_{\alpha\beta} = \frac{\partial^2 E}{\partial(\boldsymbol{u}_{jL})_\alpha \partial(\boldsymbol{u}_{j'L'})_\beta}$$

where α and β run over the Cartesian coordinates.

If we truncate this expansion to second order (that is to say, a harmonic approximation), the equation of motion for each atom is given by:

$$m_j \ddot{\boldsymbol{u}_{jL}} = \boldsymbol{F}_{jL} = -\sum_{j'L'} \boldsymbol{D}_{jLj'L'} \boldsymbol{u}_{j'L'}$$

where m_j is the mass of the atom j and $\boldsymbol{F}_{jL}$ the force on the atom at the jL position. There are $3nN$ equations, three for each atom (one per coordinate). The solutions, as any harmonic system should, have the the form of plane waves. Imposing periodic boundary conditions on the crystal, the $\boldsymbol{k}$ index appears, that represents the $\boldsymbol{k}$ vectors of the first Brillouin cell:

$$\boldsymbol{u}_{jL} = \boldsymbol{\varepsilon}_{\boldsymbol{k}\nu j} e^{i(\boldsymbol{k}\cdot\boldsymbol{L} - \omega_{\boldsymbol{k}\nu} t)}$$

The ν index counts the number of solutions for each $\boldsymbol{k}$, and goes from 1 to $3n$. $\omega_{\boldsymbol{k}\nu}$ is the frequency of the wave. If we replace this solutions in the equation of motion in $L = 0$ (origin of unit cell):

$$m_j\omega_{k\nu}^2\boldsymbol{\varepsilon}_{k\nu j} = \sum_{j'}\left(\sum_{L'}\boldsymbol{D}_{j0j'L'}e^{i(\boldsymbol{k}\cdot\boldsymbol{L'})}\right)\boldsymbol{\varepsilon}_{k\nu j'}$$

In order to simplify this equation and remove its mass dependence, we can define $\boldsymbol{\eta}_{k\nu j}$ as:

$$\boldsymbol{\varepsilon}_{k\nu j} = \frac{1}{\sqrt{m_j}}\boldsymbol{\eta}_{kj\nu}$$

and replace the matrix for its discrete Fourier transform as:

$$\boldsymbol{D}_{jj'}(\boldsymbol{k}) = \frac{1}{\sqrt{m_j m_{j'}}}\sum_{L'}\boldsymbol{D}_{j0j'L'}e^{i\boldsymbol{k}\cdot\boldsymbol{L'}}$$

resulting in the following equation:

$$\omega_{k\nu}^2\boldsymbol{\eta}_{k\nu j} = \sum_{j'}\boldsymbol{D}_{jj'}(\boldsymbol{k})\boldsymbol{\eta}_{k\nu j'}$$

All of the 3×3 matrices for the n atoms can be collected in a single $3n\times 3n$ matrix $\boldsymbol{D}(\boldsymbol{k})$, called the *dynamical matrix*. Its Fourier transform to the real space is also a $3n\times 3n$ matrix, similar to the second derivative matrix, but weighted with the atomic masses. In this case, this matrix is called the *force-constant matrix*:

$$\boldsymbol{C}(\boldsymbol{L})_{j\alpha j'\beta} = \frac{1}{\sqrt{m_j m_{j'}}}\frac{\partial^2 E}{\partial(\boldsymbol{u}_{j0})_\alpha\partial(\boldsymbol{u}_{j'L'})_\beta}$$

Merging all the atomic coordinates in the dispacement vector $\boldsymbol{\eta}_{k\nu}$ we obtain an eigenvalue equation:

$$\omega_{k\nu}^2\boldsymbol{\eta}_{k\nu} = \boldsymbol{D}(\boldsymbol{k})\boldsymbol{\eta}_{k\nu},$$

whose diagonalization allows the calculation of the phonon frecuencies at each $\boldsymbol{k}$ point ($\omega_{k\nu}$) and the eigenvectors $\boldsymbol{\eta}_{k\nu}$, called polarization vectors or normal modes.

The method we used to obtain these phonons in practice is called the *frozen-phonon method,* or direct method, and it will be explained in sec. 2.1.

1.4 From Phonons to Thermodynamics.

Once the phonons are obtained, we can obtain the thermodynamic properties of the solid by considering these pseudoparticles as a "gas", specifically a Bose-Einstein

gas. From statistical mechanics we obtain that the partition function of this Bose gas is:

$$Q = \sum_{\{n_i\}} e^{-\beta E\{n_i\}}$$

where $E\{n_i\}$ is the energy of the system for any given set of occupation numbers. For a phonon, this energy can be expressed as the energy of a harmonic oscillator:

$$E\{n_i\} = \sum_{i=1}^{3N} n_i \hbar \omega_i \quad \Rightarrow \quad Q = \prod_{i=1}^{3N} \frac{1}{1 - e^{-\beta \hbar \omega_i}}$$

From here, the internal energy of the system is trivially:

$$U = -\frac{\partial}{\partial \beta} log Q = \sum_{i=1}^{3N} \frac{\hbar \omega_i}{e^{\beta \hbar \omega_i} - 1}$$

On the limit $V \to \infty$, the sum becomes an integral:

$$U = \int_0^\infty d\omega g(\omega) \frac{\hbar \omega}{e^{\beta \hbar \omega} - 1}$$

where $g(\omega)$ is the phonon density of states. In an analytical problem, this function can be approximated in several ways, like in the Einstein's model or Debye's model. However, finding the phonons *ab-initio* has the advantage that the phonon density of states can be computed numerically directly from the dispersion curve.

After the internal energy is obtained, all the thermodynamic properties are simply derivatives or integrals of this one function [4].

2 Procedure and results

2.1 Description of the procedure

The main purpose of this work is to use the techniques described in the previous chapter, supported by specialized software, to obtain the properties of the chalcopyrite $CdGeP_2$, that crystallizes at normal conditions in the $I\bar{4}2d$ space group (shown in Fig. 2.1). The interest on the cadmium chalcopyrites is due to their possible application in the enhancement of solar cells, as they show promise for increasing the efficiency of frequency-conversion procedure in solar power generation [5].

To achieve this goal, the first step is to find the optimized crystalline structure of the unit cell of the material at 0K and 0GPa of pressure. This simulation will be done using the *Vienna Ab-initio Simulation Package (VASP)* [6]. To start, it is required to possess a starting point for the software to perform the iterative relaxation process implemented in its internal algorithms. This starting point is usually, if possible, experimental data of the lattice vectors and atomic positions within the unit cell obtained from literature. However, this method also works giving a rough guess of the structure to start the process, or even using random search methods, genetic algorithms, metadynamics, etc. to provide a starting point. But having experimental data does serve a purpose for this methos: it saves computer time and makes the simulation easier in general.

It is also valuable to simulate the structure at different pressures (or different volumes, as it is equivalent) to find structural properties like the compression coefficients and the bulk modulus of the crystal. The compression coefficients α_i for each of the lattice vectors (a, b, c) are computed fitting the lattice vector lengths to the pressure applied and using the definition:

$$\alpha_i = -\frac{1}{i_0}\left(\frac{\partial i}{\partial P}\right)_T \quad ; \quad i \in \{a, b, c\}$$

where i_0 is the value of the lattice vector length at 0 GPa of pressure.

The bulk modulus $(B_0 > 0)$, defined as the resistance of the material to changing its volume with pressure :
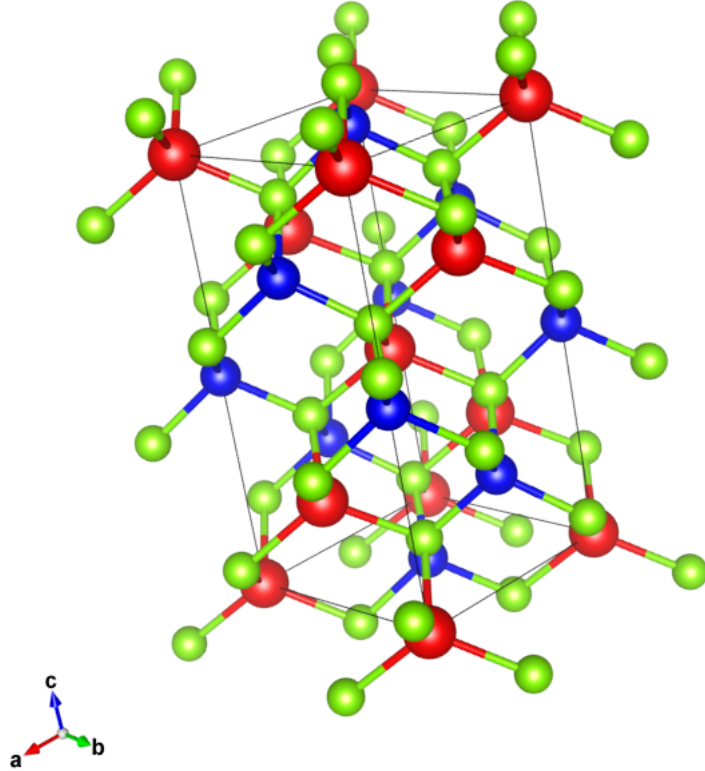
$$B_0 = -V_0\frac{\partial P}{\partial V}$$

Figure 2.1: CdGeP$_2$ chalcopyrite. Red represents cadmium, blue are germanium atoms and green are phosphorus.

is found in a more roundabout manner. From the energy of the ground-state obtained with VASP for different volumes, it is possible to obtain the bulk modulus directly by fitting this expression to a series expansion of the energy against volumen. The most appropiate equation of state in the high-pressure conditions that we are working on is the *Murnaghan equation of state*, applied in a 2nd order expansion [7].

Once the relaxed structure of the unit cell is found, the next step is to find the phonons of the material. To obtain these, we use the frozen-phonon method, which consists in taking snapshots of small displacements of the atoms in the lattice and computing the Hellmann-Feynmann forces on the atoms to finally obtain the interatomic force constants and the dynamic matrix.

Because we want the phonons in all the points of the reciprocal space and not only in the zone center Γ, we need to simulate a larger system[1], so we extend the VASP

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[1]This is because in the unit cell, which is replicated to infinity in all directions, the distances in

simulation of the unit cell at 0K and 0GPa of pressure to a 2x2x2 supercell in the same conditions. Once the relaxed structure of this supercell is found, we need to find the dynamic matrix D_{ijk} of this system instead.

The way to approach this problem is as follows: we displace the atoms of the cell a certain amount, one at a time, and simulate the Hellmann-Feynmann forces with VASP (with no iteration this time, as we do not want a relaxed cell structure in this case). However, this process would take too long if we simulated all of the possible displacements (128 atoms in the 2x2x2 supercell at 3 possible directions per atom implies 700+ simulations, both positive and negative), so we use symmetry properties to reduce the number of simulations required[2].

Once the Hellmann-Feynmann forces are extracted, the results are provided to the PHONON [8] software, that diagonalizes the dynamic matrix and finds the frequency of the phonons and the density of states of ths system. With the phonon density of states $g(\omega)$ we can calculate the internal energy U, the Helmholtz free energy F, the heat capacity C_v and the entropy of the crystal S with the known expressions:

$$U = \frac{N}{2}r \int_0^\infty d\omega g(\omega)(\hbar\omega)coth\left(\frac{\hbar\omega}{2k_BT}\right)$$

$$F = Nrk_BT \int_0^\infty d\omega g(\omega)(\hbar\omega)ln\left[2sinh\left(\frac{\hbar\omega}{2k_BT}\right)\right]$$

$$S = Nrk_B \int_0^\infty d\omega g(\omega)(\hbar\omega)\left\{\left(\frac{\hbar\omega}{2k_BT}\right)\left[coth\left(\frac{\hbar\omega}{2k_BT}\right)-1\right]-ln\left[1-exp\left(-\frac{\hbar\omega}{k_BT}\right)\right]\right\}$$

$$C_v = Nrk_B \int_0^\infty d\omega g(\omega)\left(\frac{\hbar\omega}{2k_BT}\right)^2 \frac{exp\left(\frac{\hbar\omega}{k_BT}\right)}{\left[exp\left(\frac{\hbar\omega}{k_BT}\right)-1\right]^2}$$

where r is the number of degrees of freedom in the crystal, k_B is the Boltzmann constant, N is the number of primitive unit cells, $\hbar$ is the reduced Planck constant and T is the temperature.

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the Brillouin zone, that go by $2\pi/r$, approach 0 for big r values. So in this case, the theory would only be exact in $k = 0$, the Γ point. If we make the simulated lattice bigger, its reciprocal lattice gets smaller, so the points outside Γ are closer to it and the approximations to the values to the phonons in those points becomes more accurate.

[2]Using the symmetry of the crystal, we can reduce the number of atoms to move to one for each Wyckoff position of the space group, as they are equivalent in their surroundings. Furthermore, the geometrical shape of the cell can reduce as well the number of computations in the presence of equivalent directions by only making the displacements in one of those equivalent directions (ex: is $a = b \neq c$, making a displacement in a would be equivalent to making one in b and viceversa).

2.2 Computational details

It is important before presenting our results that we specify the details and parameters used by the performed simulations. Our energy calculations were performed, as previously described, in the *Density Functional Theory (DFT)* [1] framework as implemented in the *Vienna Ab-initio Simulation package (VASP)* [6]. The pseudopotentials used were employed with the *projector augmented wave scheme (PAW)* [9] to take in full account the nodal character of the electron density in the proximities of the atomic core. The energy cutoff required for the set of plane waves to achieve high precision was set to 370 eV. The exchange-correlation energy was described in the *generalized-gradient approximation (GGA)* with the Perdew-Burke-Ernzernhof prescription for solids (PBEsol) [10]. To integrate in the Brillouin zone we used dense meshes of Monkhorst-Pack special $\mathbf{k}$ points [11]: 8x8x4 meshes - obtaining a set of 20 special $\mathbf{k}$ points - ensuring a convergence of the total energy to 1 meV per formula unit.

After the structures were fully optimized with the procedure described in sec. 2.1, the forces on the atoms were less than 0.004 $eV/$Å and the deviation of the stress tensor components from the diagonal hidrostatic pressure form was lower than 0.1 GPa.

2.3 Results

2.3.1 Crystalline structure and compression coefficients.

Provided the experimental data of the lattice vectors and the atomic positions in the unit cell found in literature, the first step of the process is to find the relaxed structure of the crystal at 0 GPa. In this case, we can see that evidently the simulated values do not differ much from the previous data in Tab. 2.1.

	Experimental data[12]	Simulated relaxed structure
Volume (Å^3)	354.434	355.367
a (Å)	5.738	5.723
b (Å)	5.738	5.723
c (Å)	10.765	10.848

Table 2.1: Simulated values against the experimental data for the lattice vectors and volume of the cell.

We simulate the same structure at different pressures and plot its energy against the volume (Fig. 2.2). Pressure, being a direct derivative of energy with respect of volume, pressure-volume will roughly, but not exactly, follow the same minima relationship as energy-volume. In this manner, we also fit this experimental data to Murnaghan's equation of state to find its bulk modulus B_0. We can observe that

the second order Murnaghan fit is very adequate as the equation of state for this system, and that the relaxed structure volume is very close to the energy minimum in this fit.
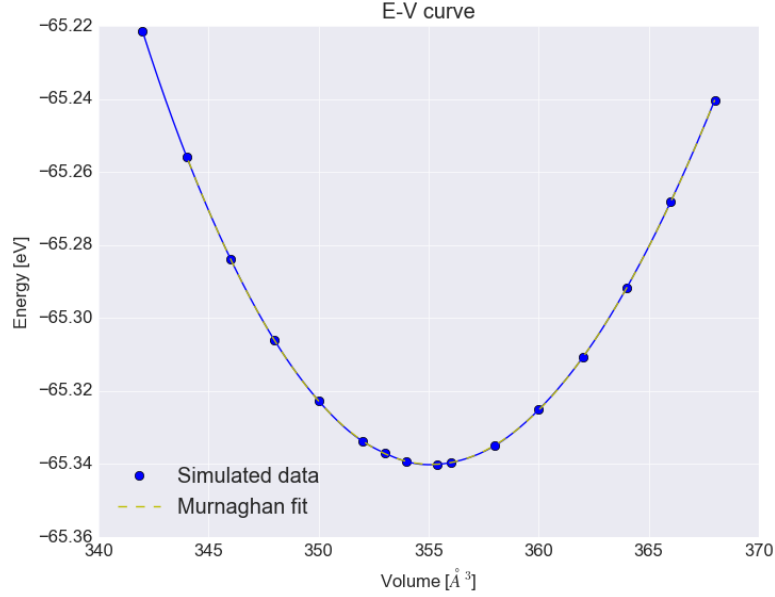

Figure 2.2: Energy of the structure plotted against its volume. .

	Reference data [13]	Simulated relaxed structure
B_0(GPa)	72.0	73.15

Table 2.2: Bulk modulus comparison with reference data.

In this same exercise, we could obtain the length of the lattice vectors (shown in Fig. 2.3) in order to calculate compression coefficients for each of the directions. It is noticeable that the longer axis is more compressible than both of the others. From the data obtained, we fit the values to a second order polynomial and used the expressions in sec. 2.1, obtaining the values in Tab. 2.3. It is clear that the coefficients obtained in this manner are in very good agreement with those on literature.

	Reference data	Simulated relaxed structure
α_a	0.0043	0.00405
α_b	0.0043	0.00405
α_c	0.0045	0.00490

Table 2.3: Compression coefficient comparison with reference data from Gautam et al[13], expressed in GPa^{-1}.
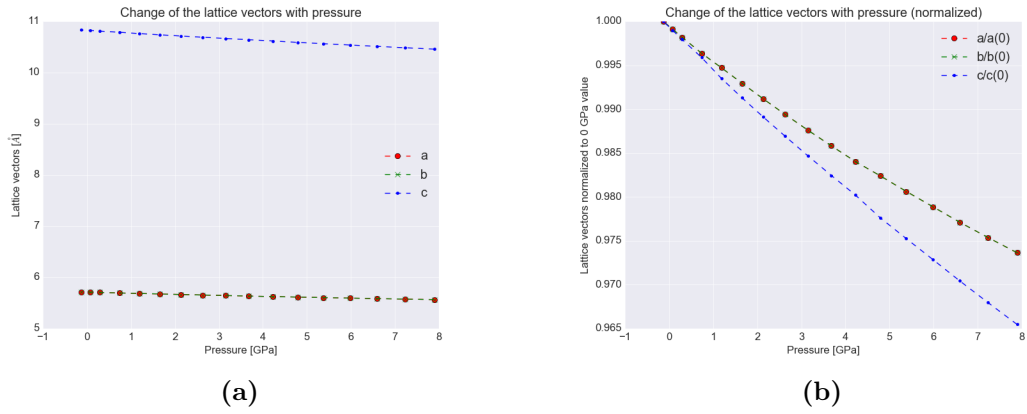
Figure 2.3: (a) Lattice vectors as a function of pressure and (b) normalized to the value at 0 GPa.

From these results we can conclude that the chalcopyrite CdGeP$_2$is a moderately hard material, due to its 75 GPa bulk modulus, that compresses roughly at an equal rate in all directions.

2.3.2 Phonons at 0 GPa

Once the small displacements required to obtain the dynamic matrix of the system are simulated, the corresponding Hellmann-Feynmann forces are used by the PHONON software, that diagonalizes the dynamical matrix and provides the phonons at Γ and also the dispersion curves and density of states, if given the supercell data.

The phonon frecuencies and their irreducible representations are presented at Tab. 2.4, where we can distinguish three regions at Γ: the low frequency zone around $0 \sim 125\ cm^{-1}$, a medium frequency zone at $150 \sim 217\ cm^{-1}$, and a high frequency zone in $280 \sim 380\ cm^{-1}$. This fact is even more evident in Fig. 2.11 and Fig. 2.10.

It is of note that all of the phonons obtained are transversal optical and none are longitudinal. This is due to the frozen-phonon method used to obtain them: it is not capable to distinguish between transversal and longitudinal phonons. The way to find this LO-TO splitting requires the simulation and use of effective Böhr charge in the crystal, implying an extra simulation of the supercell for each displacement, which is beyond the scope of this present work.

The dispersion curves (Fig. 2.4) show how the acoustic phonons (B2, E) go to 0 at Γ. It bears importance to mention that it is not easily distinguishable how the phonons overlap and split in these curves, and while it is possible to distinguish them by analizing the displacement patterns from the eigenvectors obtained by DFT, this is also beyond the scope of ths work.

In the phonon density of states (Fig. 2.5) we observe an interesting detail. If we

Type	Multiplicity	Frecuency ($cm^{-1} \pm 3$)	Irreducible representations
TA	1	0	B2(Raman/Infrared)
TA	2	0.233	E(Raman/Infrared)
TO	2	59.107	E(Raman/Infrared)
TO	1	83.024	B1(Raman)
TO	1	86.026	B2(Raman/Infrared)
TO	2	115.213	E(Raman/Infrared)
TO	2	177.756	E(Raman/Infrared)
TO	1	217.484	B1(Raman)
TO	2	288.433	E(Raman/Infrared)
TO	1	289.300	B2(Raman/Infrared)
TO	1	296.505	A2
TO	1	311.015	A1(Raman)
TO	1	343.404	A2
TO	2	344.171	E(Raman/Infrared)
TO	1	361.183	B1(Raman)
TO	2	367.854	E(Raman/Infrared)
TO	1	379.629	B2(Raman/Infrared)

Table 2.4: Phonons of CdGeP$_2$ at the zone center(Γ). Multiplicity is the number of times this phonon appears in the cell, that is, it is degenerated.

imagined the vibrations in a solid as a set of springs, it would be evident that the springs whose mass is lower would oscillate at higher frecuencies - that is exactly what we observe here, as the lighter atoms (of phosphorus) contibute states at the high frecuencies and the heavier atoms (cadmium) contribute at low frecuencies, with germanium somewhere in between.
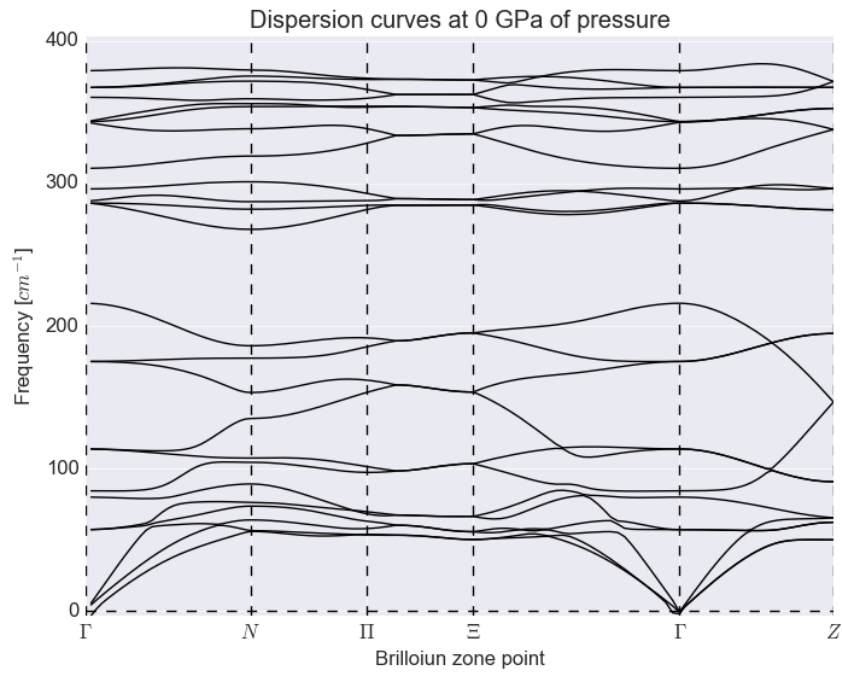
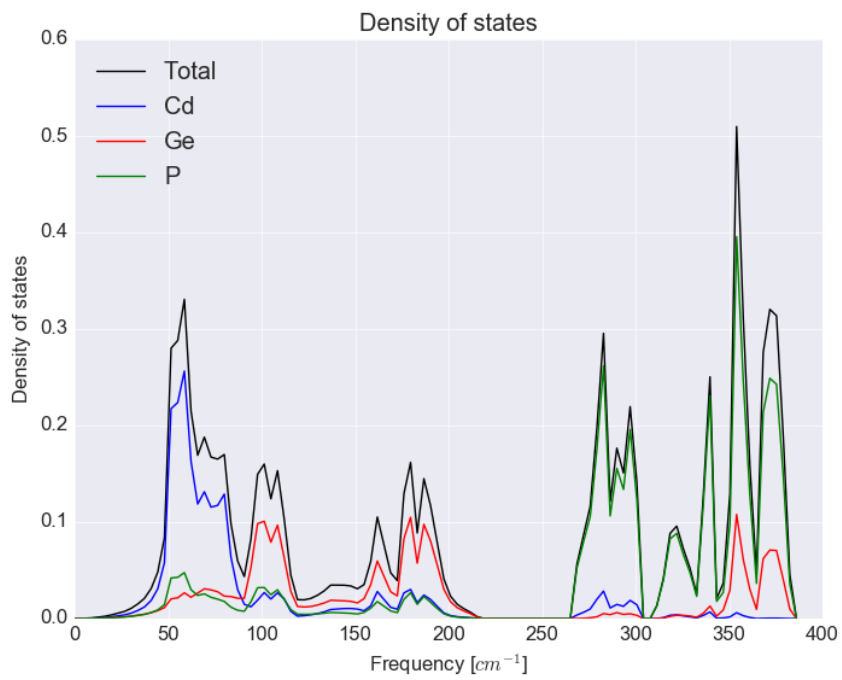**Figure 2.4:** Dispersion relation of CdGeP$_2$.

Figure 2.5: Phonon density of states of CdGeP$_2$, total and split by atom species.

2.3.3 Thermodynamic properties

From the phonons, the thermodynamic properties of the crystal are obtained immediately - entropy (Fig. 2.6), internal energy (Fig. 2.7), free energy (Fig. 2.8) and heat capacity (Fig. 2.9). The most notable fact is the verification of the *Dulong-Petit Law.* a classical thermodynamics law that states that, at high temperatures, heat capacity is constant at $\approx 6\ cal/mol\cdot K$. The small differences in this law are related to anharmonic effects that we have not taken into account for this work.
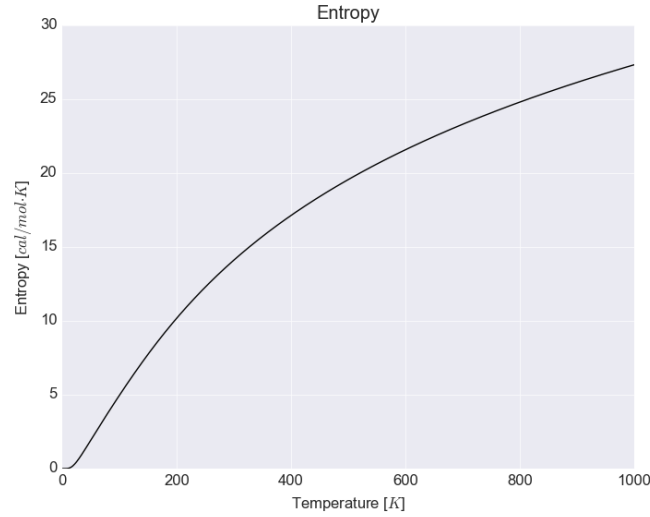
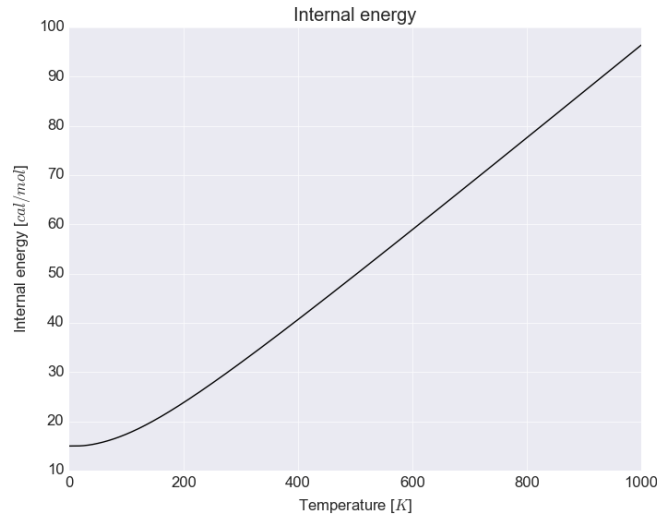**Figure 2.6:** Entropy of the unit cell of $CdGeP_2$ from $\approx 0\ K$ to $1000\ K$.

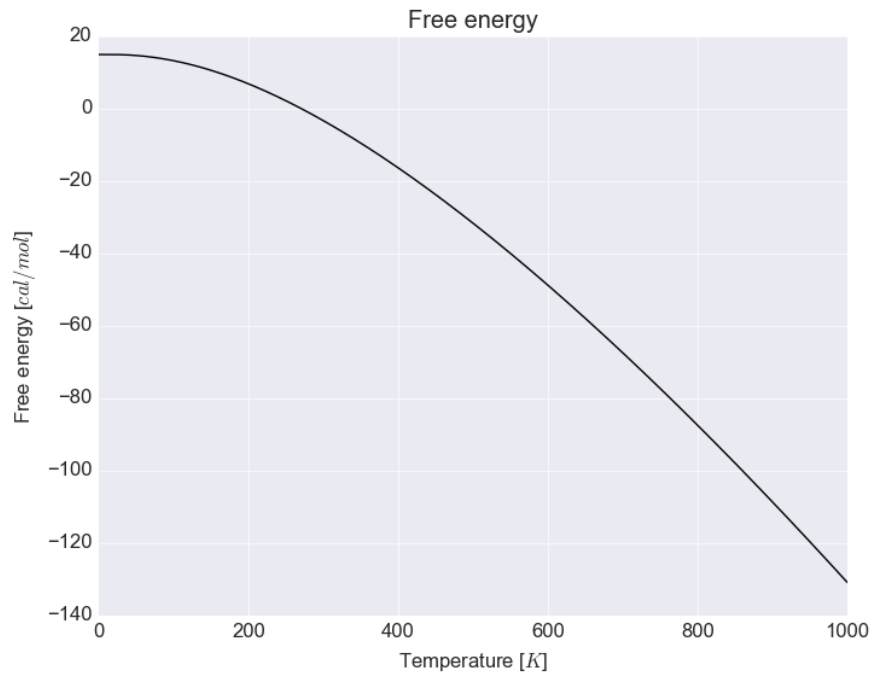**Figure 2.7:** Internal energy of the unit cell of $CdGeP_2$ from $\approx 0\ K$ to $1000\ K$.

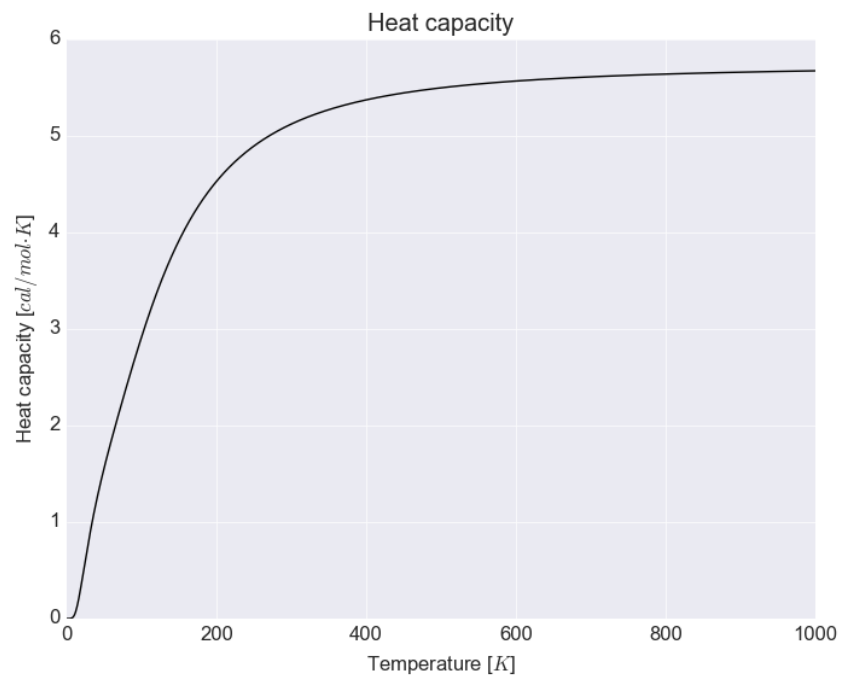**Figure 2.8:** Internal energy of the unit cell of CdGeP$_2$ from ≈ 0 K to 1000 K.

Figure 2.9: Heat capacity of CdGeP$_2$ from ≈ 0 K to 1000 K.

2.3.4 High pressure study

An important part of this work is the study of the material at high pressures. The main purpose of a study of this kind is to characterize the behaviour of substances in extreme conditions not available for direct study in a laboratory. This includes new electrical, thermical or mechanical properties, or crystalline phase changes that may be of interest (i.e., graphite to diamond).

Those phase changes can be observed by obtaining the phonons at the pressure points of interest. One such study in Brillouin's Γ point is represented in Fig. 2.10. In this graph, we can see clearly that one of the phonon frequencies goes into the imaginary numbers at around $\approx 14\ GPa$ of pressure. As phonons are nothing more than the vibrations of the atoms inside the crystalline lattice, this implies a dynamical instability in the structure - that is, this particular structure should not physically exist past this pressure - so a phase change must have taken place.

In Fig. 2.11 we can see clearly that a phonon goes well into imaginary numbers all along a significant area around Γ at $14.9\ GPa$.
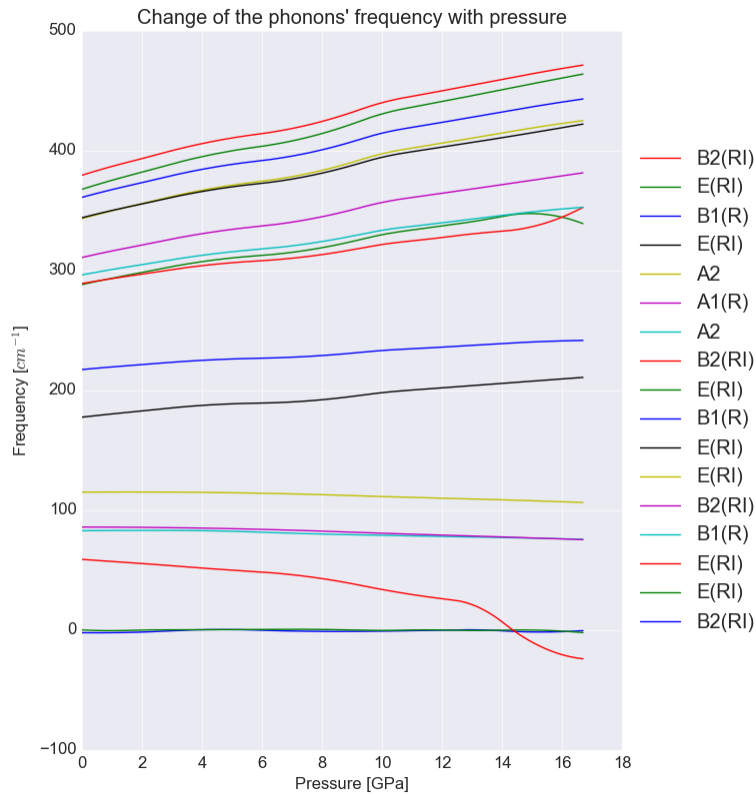

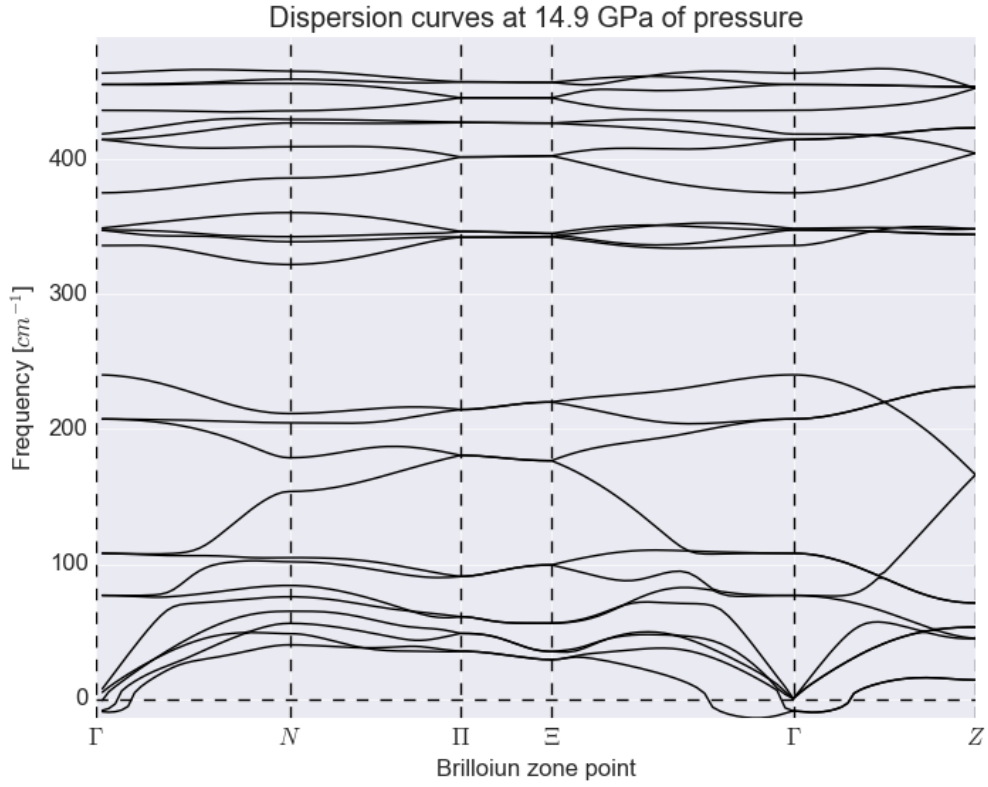**Figure 2.10:** Change of the phonons' frecuencies in Γ from 0 to $\approx 17\ GPa$.

Figure 2.11: Dispersion curves of CdGeP$_2$ at 14.9 GPa.

2.4 Conclusion

Using DFT, an *ab-initio* method to analyze the properties of solids, we studied that the structural parameters obtained in a simulation are in agreement with experimental values of the same compound. We studied as well the thermodynamic properties of this crystal at ambient pressure and verified *Dulong-Petit Law.* Finally, we obtained the phonons and their evolution under pressure, which resulted in the prediction of a phase change or amorphization of the chalcopyrite at high enough pressures.

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