

UNIVERSITÉ DE LIÈGE Faculté des Sciences

First-principles study of the electronic and thermoelectric properties of $Ca_3Co_4O_9$

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 \mathbf{par}

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Chapter 1

Introduction

Transforming energy from one form to another has always been a staple of technology. Using the driving force of water or wind to run the mills, using nuclear energy to produce electricity, it is often necessary to transform energies in order to reach our goals. In the context of environmental issues that become more and more prevalent in today's society, it is necessary to find new, clean and efficient ways to produce energy. Also, using energy more efficiently and identifying new ways to recycle, it is another timely challenge.

As of today, most energy resources are consumed as thermal energy, with an average yield around 30 %. The remaining 70 % are wasted and the major part of this residual energy is rejected in the environment under the form of thermal energy. This wasted thermal energy serves no mean and is difficult to recycle using traditional conversion methods since it is typically associated with temperature ranges below 700 K, presents strong variations of power density and is stored within various environments.

This is why, over the past ten years, there has been a growing interest in thermoelectric materials, which have the peculiar property to convert heat into electricity, and *vice-versa*. Such a conversion is very interesting since electricity can be stored and used for many different applications. Moreover thermoelectric conversion presents also numerous advantages, such as the lack of maintenance, the lack of dependence upon the type of heat source, the easy setup or even the longevity of this technology (related to the absence of moving parts). Thermoelectric generators are composed of different modules which contains many couples of p-type and n-type semiconducting materials (as one can see in figure 1.1). The diffused heat goes hand in hand with the diffusion of charge carriers, in the same direction, which produces a voltage.

Due to their actual weak efficiency, thermoelectric generators are not yet widely exploited. There are however good hopes to use them, in combination with other devices, in power plants for recovering waste heat and converting it into additionnal electrical power. They have also been used in space probes, using radioisotopes as heat sources. Some devices are also set up inside the exhaust pipe of automobiles to convert waste heat into electricity. Those device are called *automotive thermoelectric generators*.

Thermoelectrics can also be used for cooling applications. Those thermoelectric

coolers are most widely used and are mostly known as Peltier coolers. They are mainly used to cool down electronic components, but are also used for many consumers products, such as camping/car coolers. They have also proven themselves to be precise temperature regulators (error around 0.01 K) with the necessary electronic feedback.

One can expect that enhancing thermoelectric performances would lead to a greater amount of mainstream applications, that could also be coupled with other energy converters such as photovoltaics, which fail to grasp the thermal part of solar energy. Even without challenging other traditionnal means for converting heat into electricity, using thermoelectrics to convert wastes into usable energy is a sufficient motivation to use them: whatever the amount, energy has always to be gained in the process! These are examples among many others, but basically, thermoelectrics could play an important role in the future.

Nowaday thermoelectric applications use compounds made of Si, Te, Pb or Se, such as Bi_2Te_3 , and they are not adapted for large scale applications for many reasons: the production costs are high, some compounds are toxic, they are not stable at high temperature, *etc.* Research now focus upon alternative materials which circumvence the aforementionned inconveniences, and might yield to the massive production of cheap, non-toxic and less restrictive thermoelectric device for a larger spectrum of applications.



Figure 1.1: A Seebeck power module which generates electrical power [1].

Recently, interest has gathered around various classes of materials including oxides, which were not expected to exhibit large thermoelectric coefficients, but present other advantages.

The aim of this Master Thesis is to model from first-principles calculations the properties of one of the most promising thermoelectric oxide material: calcium cobaltite, also known as $Ca_3Co_4O_9$ or $(Ca_2CoO_3)(CoO_2)_{1.618}$.

In the first half of the present chapter, the basics of thermoelectricity are introduced. The second half is devoted to the state of the art on thermoelectric oxides, focusing mainly on $Ca_3Co_4O_9$.

1.1 Phenomenological approach to thermoelectrics

In this section, following the approach of Ref. [8], we will present a historical introduction to thermoelectricity, from the discovery of the phenomenon to the characterization of the performance of thermoelectric compounds.

1.1.1 The Seebeck effect

Seebeck discovered the first thermoelectric effect in 1821. He observed that when a metallic compass needle is placed in between two different conductors a and b, linked by junctions at their extremities and under a temperature gradient, the needle is deflected 1.2. The deviation was first assigned to a magnetic effect due to the different responses of the conductors. Later, it was discovered that a difference of electric potential appeared at the junction of two materials under a temperature gradient. Thus, thermoelectricity was discovered. The main use of the Seebeck effect is to measure temperature with a thermocouple.

The Seebeck coefficient, or thermoelectric power (thermopower), of a material is the measure of the magnitude of an induced voltage in response to the temperature gradient across that material. It can be written:

$$\mathbf{E} = S_{ab} \,\,\nabla_{\mathbf{r}} T \tag{1.1}$$

where **E** is the electric field induced by the temperature gradient $\nabla_{\mathbf{r}} T$



Figure 1.2: The experimental device used by Seebeck to discover the first thermoelectric effect.

1.1.2 Peltier and Thomson Effects

In 1834, Peltier discovered a second thermoelectric effect: a temperature gradient would appear at the junctions of two different materials a and b in which a voltage is applied. In other words, when a current is flowing throught the junction, one junction absorbs heat while the other generates it.

Thus, another coefficient is defined: the Peltier coefficient, measuring the magnitude of produced and absorbed heat at the junction when a current is applied:

$$Q = \Pi_{ab}I \tag{1.2}$$

with Q being the produced or absorbed heat, I being the electric current and Π_{ab} being the Peltier coefficient for the couple a and b.

In 1851, Lord Kelvin predicted and observed that both Seebeck and Peltier effects are related: a single material under a temperature gradient and which is traversed by an electric current exchanges heat with the environment. Reciprocally, an electric current is generated when a material is under a temperature gradient with heat flowing through. This phenomenon would be called the Thomson effect. The main difference with the Peltier and Seebeck effects is that the Thomson effect involves only one material and no junction is required.

The Thomson effect offers many perspectives. In one way, thermoelectic materials could be used as refrigerators, and be used in many applications which require a highly precise temperature regulation. On the other way, converting heat into electricity would represent a clean energy source, which is particularly interesting as humankind aspires to respect Earth and its environment better than it used to.

1.1.3 Basic principles and thermoelectric coefficients

We will now introduce the different relations involved in thermoelectricity. Let's consider a basic thermoelectric circuit. Two materials a and b a linked together by two junctions, which we should call X and W. In the case of the Seebeck effect, a difference of temperature dT is applied between the two junctions X and W, which generates a voltage dV between the extremities Y and Z (figure 1.3). In a open circuit, the



Figure 1.3: A basic thermoelectric circuit.

Seebeck coefficient is defined for the couple a and b:

$$S_{ab} = \frac{dV}{dT} \tag{1.3}$$

The sign of S_{ab} is such as if the temperature at the junction W is higher than the temperature at the junction X, and if $V_Y > V_Z$, then S_{ab} is positive.

In the case of the Peltier effect, a current I is flowing through the circuit. Heat is then absorbed at one junction, and produced at the other. The Peltier coefficient is defined for the couple a and b:

$$\Pi_{ab} = \frac{Q}{I} \tag{1.4}$$

The sign of Π_{ab} is such as if the current goes from W to X and if the absorption of heat occurs at the junction W, and the production of heat occurs at the junction X, then Π_{ab} is positive.

In the case of the Thomson effect, both an electric current and a temperature gradient are applied. Heat is then generated or absorbed in each part a and b of the thermocouple individually. The thermal flux in each materials is given by the relation:

$$\frac{dQ}{dz} = \tau I \frac{dT}{dz} \tag{1.5}$$

where z is the spatial coordinate and τ is the Thomson coefficient of the material. Those three effects are related, and it was demonstrated by Kelvin that each coefficient characterizing those three effects are also related. The relations are:

$$\Pi_{ab} = S_{ab}T\tag{1.6}$$

$$\tau_a - \tau_b = T \frac{dS_{ab}}{dT} \tag{1.7}$$

In practice, applications for thermoelectric effects require at least two materials linked together to form junctions. The Seebeck coefficient and Peltier coefficients have been defined for the couple of materials a and b. However, the knowledge of the absolute coefficients of each material $(S_a, S_b, \Pi_a \text{ and } \Pi_b)$ is important for their own optimization.

The absolute coefficients are given by:

$$S_{ab} = S_a - S_b \tag{1.8}$$

$$\Pi_{ab} = \Pi_a - \Pi_b \tag{1.9}$$

When one measures the thermopower of a couple of materials, one usually measures the contribution from both part of the thermocouple. But it is possible to measure the absolute Seebeck coefficient of a material by using superconductors. Indeed, in a superconductor, electrons do not carry entropy, and thus superconductors have zero thermopower. The absolute Seebeck, Peltier and Thomson coefficients also obey the relations of Lord Kelvin:

$$\Pi_a = S_a \ T \tag{1.10}$$

$$\tau_a = T \frac{dS_a}{dT} \tag{1.11}$$

1.1.4 Transport equations

Thermoelectric devices consist in two couples which are connected. Each couple is composed of a doped material: one is p-type doped, with S > 0 and the other is ntype doped with S < 0. Those materials are connected by a conductor and one assumes that its thermopower is equal to zero. We also conveniently ignore thermal conduction throught convection and radiation, and we assume that the Seebeck coefficient, as well as the electrical resistivity and thermal conductivity to be temperature independent. All couples in the thermoelectric device are connected in serial for electricity transport and in parallel for heat transport. For the sake of simplicity, one only considers a single couple, with two materials, respectively n-type and p-type doped, with exactly the same section.

Let's consider a thermoelectric cooler (figure 1.4). Such a device consists of a "p" branch with a positive S and an "n" branch with a negative S. These two branches are joined by a metal interconnect. The two legs of each couple and all the other couples in a thermoelectric device are connected thermally in parallel and electrically in series. The objective is to figure out the thermodynamic considerations needed to calculate the efficiency of such a device. There's no loss in generality in analysing a single thermocouple. The applied electric current is such that the charge carriers both



Figure 1.4: A diagram of a single-couple refrigerator. Both holes and electrons goes from the cold source to the hot source.

goes from the cold source to the hot source. In other words, electrons in the n-type doped branch move toward the hot source, and holes in the p-doped branch also move toward the hot source. Thus, both charge carriers carry entropy from the cold source to the hot source, and a thermal flux is induced such as it is opposed to the thermal conduction.

In each branch, the total flux can be written as:

$$Q_p = S_p IT - \kappa_p A_p \frac{dT}{dz} \tag{1.12}$$

$$Q_n = -S_n IT - \kappa_n A_n \frac{dT}{dz} \tag{1.13}$$

 κ_p and κ_n are the thermal conductivities of the p-doped and n-doped materials, A_p and A_n are their sections, S_n and S_p are the absolute Seebeck coefficients, and z is the spatial coordinate.

Heat is transported from the cold source to the hot source with a total flux Q_t :

$$Q_t = (Q_n + Q_p)|_{z=0}$$
(1.14)

At the same time, a Joule effect occurs in the circuit due to the electric current I. The generated heat by this effect is equal to $\frac{I^2\rho}{A}$, where ρ is the resistivity. The energy conservation can be written for both branches of the circuit by considering that the Joule heat supply is balanced by a non constant thermal gradient:

$$\kappa_p A_p \frac{d^2 T}{dz^2} = \frac{I^2 \rho_p}{A_p} \tag{1.15}$$

$$\kappa_n A_n \frac{d^2 T}{dz^2} = \frac{I^2 \rho_n}{A_n} \tag{1.16}$$

Since S is assumed temperature independent, the Thomson coefficient is zero and the thermoelectric current does not supply or extract heat within the branches. We need to consider the following boundary conditions. Let's call L_n and L_p the length of each branch: at the cold source (z = 0), the temperature is equal to the temperature of the cold source. At the hot source $(z = L_p \text{ or } z = L_n)$, the temperature is equal to the temperature of the temperature of the hot source. Then the boundary conditions can be written as:

$$T = T_c \text{ at } z = 0 \tag{1.17}$$

$$T = T_h \text{ at } z = L_n \text{ or } z = L_p \tag{1.18}$$

so that equation (1.15) and (1.16) gives:

$$\kappa_p A_p \frac{dT}{dz} = -\frac{I^2 \rho_p (z - \frac{1}{2}L_p)}{A_p} + \frac{\kappa_p A_p (T_h - T_c)}{L_p}$$
(1.19)

$$\kappa_n A_n \frac{dT}{dz} = -\frac{I^2 \rho_n (z - \frac{1}{2}L_n)}{A_n} + \frac{\kappa_n A_n (T_h - T_c)}{L_n}$$
(1.20)

Substituting these results in eq. (1.12) and (1.13) and using (1.14) the total thermal flux Q_t can be written as:

$$Q_t = (S_p - S_n)IT_f - K\Delta T - \frac{1}{2}I^2R$$
(1.21)

where K is the thermal conductance and R is the electrical resistance of the circuit, both defined as:

$$K = \frac{\kappa_p A_p}{L_p} + \frac{\kappa_n A_n}{L_n} \tag{1.22}$$

$$R = \frac{\mathbf{L}_p \rho_p}{A_p} + \frac{\mathbf{L}_n \rho_n}{A_n} \tag{1.23}$$

Both Joule and Seebeck effects contribute to the dissipated power \mathcal{W} :

$$\mathcal{W} = I.[(S_p - S_n).\Delta T + IR] \tag{1.24}$$

The efficiency ϵ_c of the thermoelectric cooler is the ratio between the extracted heat Q_t and the dissipated electric power W. From equations (1.21) and (1.24), it follows:

$$\epsilon_c = \frac{Q_t}{W} = \frac{(S_p - S_n)IT_f - K\Delta T - \frac{1}{2}I^2R}{I.[(S_p - S_n).\Delta T + IR]}$$
(1.25)

One can directly see that for any fixed temperature difference ΔT , the efficiency depends on the applied current I. From these expressions, it is possible to know which current I can maximize either the efficiency or the extracted heat Q_t .

It is also possible to determine the efficiency of a p-n device designed for generating electricity from a difference of temperature. The efficiency ϵ_e is given by the ratio between the useful electric power delivered to a load resistance r and the thermal flux across the device:

$$\epsilon_e = \frac{\mathcal{W}_{useful}}{Q_t} = \frac{I.[(S_p - S_n).\Delta T + IR]}{(S_p - S_n)IT_f - K\Delta T - \frac{1}{2}I^2(R+r)}$$
(1.26)

Once again, it is possible to use this expression to find the electric current which maximize the efficiency. Both cooling and generating electricity have two particular values of I which maximize either the efficiency of conversion, or the electric power produced or heat extracted. If those two efficiencies are maximized, it can be proved that they only depends on the temperature T_c and T_h , as well as the figure of merit $Z_{pn}T_A$ with $T_A = \frac{T_c + T_h}{2}$ being the average temperature.

The figure of merit $Z_{pn}T_A$ is a dimensionless factor which has been defined for the couple of material. Z_{pn} can be expressed as a function of the intrinsic absolute parameters of the materials from which the couple is made:

$$Z_{pn} = \frac{(S_n - S_p)^2}{(\sqrt{\kappa_p \rho_p} + \sqrt{\kappa_n \rho_n})^2}$$
(1.27)

It is maximal when the efficiency is maximal, which happens when the product RK is minimal, which occurs when:

$$\frac{L_n A_n}{L_p A_p} = \sqrt{\frac{\rho_p \kappa_n}{\rho_n \kappa_p}} \tag{1.28}$$

Within a similar spirit, both the individual p-type and n-type materials have their own intrinsic factor usually called "factor of merit":

$$Z = \frac{S^2}{\rho\kappa} = \frac{S^2\sigma}{\kappa} \tag{1.29}$$

In order to get the highest possible efficiency, one should maximize the factor Z_{pn} by selecting the right components for the device. Looking at expression (1.27), one can claim that optimizing a couple is not just simply optimizing individually the Z factors of both branch for the couple. However, at the temperatures usually used for generating electricity, the thermoelectrics properties of the best p-type and n-type materials are similar and in this case, the factor Z_{np} is not far from the average of the individual factors Z_n and Z_p , and optimizing the materials individually is not unreasonable. This

is why generally, when studying a material, one should look at the transport properties of this material, such as the Seebeck coefficient S, the resistivity ρ or conductivity σ , as well as the thermal conductivity κ , in order to maximize the factor $\frac{S^2}{\sigma\kappa}$.

One can directly see that in order to maximize Z, it is necessary that the considered material has a high Seebeck coefficient as well as a high conductivity: this means that a small temperature difference can induce a high enough voltage, and that there's the lowest dissipation when the current flows across the material. It is also required that the material has a weak thermal conductivity in order to maintain the temperature gradient across the material.

When a thermoelectric device is used for cooling, the efficiency of the device is given by the coefficient of performance COP. It is given by:

$$COP = \frac{\gamma T_c - T_h}{(T_c - T_h)(1 + \gamma)} \tag{1.30}$$

with $\gamma = \sqrt{1 + ZT}$.

In a similar fashion, the maximal yield of conversion for a thermoelectric system generating electricity is given by:

$$\epsilon_{e max} = \frac{(T_h - T_c)(\gamma - 1)}{T_c + \gamma T_h} \tag{1.31}$$

1.1.5 Optimizing the thermoelectric properties of materials

As a consequence of the previous discussion, improving the thermoelectric performance of a material can be achieved by increasing its "factor of merit" (equation (1.27)) or equivalently its dimensionless "figure of merit":

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l} \tag{1.32}$$

The numerator $S^2 \sigma$ is also called power factor that one should maximize. The denominator is the sum of the electronic contribution to thermal conductivity κ_e , and the contribution from the lattice, κ_l , that one should minimize.

Often, both the electrical and thermal conductivities are related. For metals, the ratio between electronic thermal conductivity κ_e and electrical conductivity σ follows the Wiedemann-Franz law:

$$\frac{\kappa_e}{\sigma} = LT \tag{1.33}$$

with L is being a constant and T being the temperature. In other words, at a fixed temperature, the ratio $\frac{\kappa_e}{\sigma}$ stay the same and if one increases σ , so does κ_e . This behavior can be extrapolated to other materials and basically, optimizing these coefficients in opposition ends up being quite tricky.

The recent progress in increasing the figure of merit finds its origin in many concepts and ideas which have been proposed in order to get rid of the interdependence of electrical and thermal conductivities. For example, an interesting and intriguing idea to achieve the highest figure of merit was proposed by Slack [9] and is referred to as

the *phonon-glass electron-crystal* approach (PGEC). Basically, a PGEC material features a very low thermal conductivity normally associated with amorphous materials, but a high electrical conductivity normally associated with good semiconductor single crystals.

Another idea proposed by Hick and Dresselhaus [10] is to confine the electrons in planes forming so-called two-dimensional electron gas (2DEG) in order to yield enhancement of the electrical conductivity. This can typically be realized in nanostructures that further enhance thermal resistivity by increasing phonon scattering at the interfaces between different layers.

In spite of intensive studies, Bi_2Te_3 with a figure of merit as high as 1 still remains among the most powerful thermoelectrics since its discovery six decades ago (with a power factor around $40-50 \ \mu W cm^{-1} K^{-2}$ at room temperature [11]). Nevertheless, the recent concepts and advancements in the field led to the discovery of other materials that go beyond the performance of Bi_2Te_3 compounds, such as Bi_2Te_3/Sb_2Te_3 superlattices which reach ZT = 2.4 [12]. Yet, in order for thermoelectricity to be used in larger scale applications and to become competitive against alternative energy sources, the figure of merit should at least reach a value of 3 and beyond.

For some pratical applications however, research focuses upon improving the power factor only instead of the figure of merit. This is typically the case for recovering wasted heat. A large power factor implies large voltage generation during conversion process. In this case, the power factor is considered as the key quantity to optimize in order to achieve high thermoelectric efficiency. It is in this context that we will work in the present study.

1.2 Oxides as thermoelectric materials: why such an interest ?

Usually, most oxides have their transition metal atoms in their common oxidation degrees that are stable at high temperatures, and they received little attention for thermoelectric applications because of their strong ionic character with narrow conduction band widths arising from weak orbitals overlap, leading to localized electrons with low carrier mobilities and therefore bad transport properties.

However, interest started to gather around oxides as it was discovered that the misfit-layered material Na_xCoO₂ (x = 0.5), consisting of CdI₂-type CoO₂ layers and sodium layers stacked and alternating along the **c**-axis (figure 1.5), had unexpected good thermoelectric properties and attains $S \approx 100 \ \mu \text{VK}^{-1}$ at 300 K and $ZT \approx 0.75$ at 1000 K [13]. Following this discovery, studies started to focus on Co-based layered oxides, such as calcium cobaltite [4, 13] and Bi₂Sr₃Co₂O_y. Research also started to focus around superlattices containing SrTiO₃ and SrRuO₃ layers [14], and they can show good thermoelectric properties if doped with holes. These are p-type compounds. But, as explicited in the previous section, thermoelectric devices use p-type compounds in conjunction with n-type compounds. Amongst the n-type oxides, strontium titanate (SrTiO₃) shows good thermoelectric properties at room temperature if it is heavily doped. In the same fashion, Al-doped ZnO (Al_{0.02}Zn_{0.98}O) displays good thermoelectric performances (ZT = 0.3 at 1000 K) [15].

But let us go back to Na_xCoO_2 . Its peculiar crystallographic structure encouraged scientists to investigate similar materials displaying good thermoelectric properties. This class is the group of layered CoO_2 compounds. The main advantage of these materials is that they present different substructures with different individual transport properties: indeed it is difficult to control an electronic system and a phonon system simultaneously in a simple crystal and those complex crystals are considered ideal in controlling electronic transport and heat transport separately, thus enhancing the total conversion efficiency. For example, in Na_xCoO_2 , the CoO_2 nanosheets serve as electronic transport layers because the electron system in those sheet are strongly correlated, whereas the sodium ion nanoblocks serve as phonon-scattering regions and thus achieve low lattice thermal conductivity.



Figure 1.5: Atomic structure of Na_xCoO_2 .

$1.3 \quad Ca_3Co_4O_9$

Following the discovery of the thermoelectric properties of Na_xCoO_2 , interest extended to $Ca_3Co_4O_9$ as it also displayed interesting thermoelectric properties such as a very high Seebeck coefficient (around 125 $\mu V K^{-1}$ at 300 K). The reason calcium cobaltite is interesting is that the compound happens to be very stable at room temperature and is very resistant against change of temperature, pressure and humidity. Therefore, it could be useful in many applications. The following subsections are a summary of the research performed since its discovery.

1.3.1 Crystallographic structure

The first specimens of $Ca_3Co_4O_9$ were synthetized in 2000. Several groups [4, 7, 16] studied the structure and all converged to the same results. They found out that the compound is a misfit-layer oxide consisting in two monoclinic subsystems direction with identical a, b and β parameters. The first subsystem consist of triple rocksalt-type layers Ca_2CoO_3 and the second consists of CdI_2 -type CoO_2 layers. The two subsystems are stacked along the direction c as shown in figure 1.6. Following the

discovery of Na_xCoO₂'s thermoelectric properties, the CoO₂ planes are expected to be the conducting system whereas the Ca₂CoO₃ subsystem is expected to be the phonon glass. The incommensurate character of the structure is related to the fact that the two subsystems have different b parameters whose ratio is irrational and corresponds to the "golden" ratio¹.

$$\frac{b_1}{b_2} = \frac{1+\sqrt{5}}{2} = 1.61803398...$$

Measurements by X-ray diffraction led by Lambert *et al* [16] showed that the CoO_6 octahedra in the CoO_2 layers were noticeably distorted. This would imply strong interactions between the two subsystems. Two different structural phases were also observed, which would prove the existence of polytypism in the system: orthorhombic and monoclinic lattice symmetries were observed cooexisting in the specimens.



Figure 1.6: Atomic structure of Ca₃Co₄O₉.

Two set of lattice parameters were proposed by Masset *et al* [4] and Miyazaki *et al* [7] from their respective measurements :

$$a^{[4]} = 4.8376(7) \text{ \AA} \quad c^{[4]} = 10.8330(1) \text{ \AA} \quad \beta^{[4]} = 98.06(1)^{\circ} \\ b^{[4]}_1 = 4.5565(6) \text{ \AA} \quad b^{[4]}_2 = 2.8189(4) \text{ \AA}$$

$$a^{[7]} = 4.83 \text{ Å} \quad c^{[7]} = 10.84 \text{ Å} \quad \beta^{[7]} = 98.13^{\circ}$$

 $b_1^{[7]} = 4.56 \text{ Å} \quad b_2^{[7]} = 2.82 \text{ Å}$

Miyazaki *et al* [7] also proposed a structural model for the two subsystems, by setting the individual primitives cells of the two subsystems at the same origin along **b**, then building the structure along this direction by adding successive unit cells for both of these subsystems. The fractional coordinates for each atoms in each subsystems are reported in table 1.1.

¹In the following section, the incommensurate lattice parameters of the rocksalt type and the CoO_2 subsystems are referred respectively as b_1 and b_2

Subsystem	Atom	$\frac{x}{a}exp$	$\frac{z}{c}exp$
CoO_2	Co	0.000	0.000
	01	0.363	0.084
	O2	0.636	0.896
RS	Ca1	0.182	0.281
	Ca2	0.312	0.727
	Co	0.702	0.505
	01	0.718	0.338
	O2	0.183	0.497
	O3	0.837	0.677

Table 1.1: Experimental fractional coordinates from Miyazaki et al's model [7]

Atomic-resolution annular bright-field imaging experiments were also performed by Klie *et al* [17] and they found out that, in contrast to previous reports [7, 16], the oxygen-atomic columns in the CoO_2 subsystem do not exhibit any disorder, while there's a global displacement of the oxygen-atomic columns in the Ca_2CoO_3 subsystem.

Thermal expansion aside, the atomic structure seems stable up to 400 K. Measurement performed by Wu *et al* [2] and Wakisaka *et al* [18] show that the **c** lattice parameter increase monotonically, but the a, b_1 and b_2 lattice parameters for both subsystems have a sudden drop around 400 K before increasing again (figure 1.7), which could be due to a still unresolved structural phase transition.



Figure 1.7: Lattice parameters of $Ca_3Co_4O_9$ between 346 K and 438 K. Sudden anomalies occur in the same temperature range for the a, b_1 and b_2 parameters, around 400 K [2].

1.3.2 Magnetic properties

Even though there is a consensus on the crystallographic structure (at least up to room temperature), the magnetic properties of calcium cobaltite are still under debate.

Masset *et al*'s results [4] showed two different Co-O distances that are resulting in the existence of cobalt with three different oxidation states 2+ in the rocksalt subsystem, and 3+ and 4+ in the CoO₂ subsystem, in agreement with x-ray experiments. The spin state is ambiguous as the splitting of the 3d orbitals of Co into t_{2g} and e_g orbitals is quite weak and two spin state configurations are observed: one of high spin (HS) $t_{2g}^4 e_g^2$ and one of low spin (LS) $t_{2g}^6 e_g^0$. Yang *et al* later proposed their estimation of oxidation degrees from charge transfert measurements: +3 for Co in the rocksalt subsystem and +3.38 for Co in the CoO₂ subsystem [19].

Different magnetic phase transitions are observed and/or proposed are summarized in figure 1.8.

Below 19 K, a ferrimagnetic phase coexisting with a long range incommensurate spin density wave (LR-IC-SDW) is observed. The ferrimagnetic ordering is parallel to the **c**-axis and the IC-SDW existing in the CoO₂ subsystem and propagates in the *ab* plane, with magnetic moments oscillating along the **c**-axis [3, 20, 21]. Above 19 K, the ferrimagnetic order disappears, but the long range IC-SDW persists up to 27 K [3, 20]. At 27 K, a short range incommensurate spin density wave transition appears (SR-IC-SDW) and a gradual evolution of the IC-SDW was observed up to 100 K where it disappears [3, 20, 21]. From 100 K, a paramagnetic phase occurs. The effective magnetic moment is $1.3 \mu_{\rm B}/{\rm Co}$ at 300 K which is explained by a mixture of low-spin and high-spin states [20, 21].

Around 400 K, a spin-state transition is said to occur by some publications [2– 4, 18, 20]. A first argument for this was proposed by by Masset et al [4] who performed measurements of the magnetic susceptibility χ which showed a divergence around 400 K, hence a magnetic transition around this temperature. Below 400 K, the effective magnetic moment measured is 1.3 μ_B/Co , while above this temperature, 2.8 μ_B/Co is found, which could be explained by an intermediate spin state configuration $t_{2q}^5 e_q^0$ for the Co in the CoO₂ subsystem as the splitting between t_{2g} and e_g orbitals is very small, hence a weak energy gain [4]. Sugiyama *et al* argued that the transition is discontinuous and as the temperature decreases, the system goes from a paramagnetic low-spin + intermediate-spin state for the Co atoms (LS+IS) to a paramagnetic highspin + intermediate-spin state (HS+IS). A ferrimagnetic hysteresis loop is observed for an applied magnetic field orthogonal to the *ab* plane which is not the case for an in-plane applied magnetic field, which suggests an anisotropic magnetic behavior, with the ferrimagnetic ordering parallel to \mathbf{c} [20]. We *et al* also doubt the real nature of the phase transition around 400 K as heat capacity measurements show little magnetic field dependence during cooling and warming (figure 1.9). As one can see on 1.9, the relative area of the hysteresis loop of the electrical resistivity decreases as the magnetic field increases. Additionally, the evolution of the specific heat with respect to the temperature is seen independant of the applied magnetic field, further cementing the doubt on the magnetic nature of the phase transition.

Around 500 K, another spin-state transition is observed [2, 5]. Wu *et al* [2] proposed that the transition occurs for the Co^{3+} ions which go from a low-spin state to high-spin

state



Figure 1.8: Magnetic phases observed for low and high temperature. The transition around 400 K is still up to debate and we do not know its exact nature.



Figure 1.9: Resistivity and specific heat measurements (during cooling and warming) by Wu *et al* [2].

1.3.3 Thermoelectric properties

The Seebeck coefficient has been measured by many groups [2–4] and all of them found values between 125 and 133 μ VK⁻¹. The positive value of the Seebeck coefficient

implies that holes are the charge carriers. From 100 K to 300 K, the Seebeck coefficient does not change much as one can see in figure 1.10, and this is quite interesting for optimizing other properties in this temperature range.



Figure 1.10: Seebeck coefficient as measured by Miyazaki [3].

The temperature dependence of the resistivity was also measured. A first measurement by Masset et al on a bar of $Ca_3Co_4O_9$ ceramic showed an anomaly at 400-420 K, which should be related to the structural and/or magnetic phase transitions described in the previous subsections [4]. They also measured the resistivity ρ_{ab} along the CoO_2 layers (in-plane) from 0 K to 300 K, as well as the out-of-plane resistivity ρ_c . The resistivity also exhibits a strong anisotropic behavior as ρ_c is at least one order of magnitude higher than ρ_{ab} (figure 1.11). Such a strong anisotropic behavior is indeed intended and a reason why such a misfit-layered compound gathers so much interest. The electronic transport along the \mathbf{c} direction is not as good as the one along ab which is why only in-plane properties are investigated. Such behavior is typical to $-CoO_2$ layered compounds. Limelette *et al* [5] further analyzed the temperature dependence of the in-plane resistivity from 0 to 600 K (figure 1.12). The three temperatures T_{min} , T^* , and T^{**} separate respectively an insulating behavior, a strongly correlated Fermi liquid, an incoherent metal and a high-temperature insulator. Comparing Masset et al and Limelette et al's respective in-plane resistivity measurements (figures 1.11 and 1.12), one can notice that they are quite different : around room temperature, the in-plane resistivity measured by Masset is three times superior to the one measured by Limelette.

Miyazaki et al performed measurements on polycrystalline samples [3] and got the following results at room temperature:

$$ZT_{300K} = 3.5E - 2$$

This figure of merit is quite low in comparison to what one should expect of a good thermoelectric, but the composition of the sample used is quite different from the usual monocrystals used in other experiments. Unfortunately, no other figure of merit at room temperature was reported to our knowledge.



Figure 1.11: In-plane (ρ_{ab}) and out-of-plane (ρ_c) resistivities as measured by Masset [4].



Figure 1.12: In plane resistivity as measured by Limelette [5].

Finally, recently, Klie *et al* [17] performed experiments on thin films of $Ca_3Co_4O_9$ and reported the achievement of a 27 % increase in the room temperature in-plane Seebeck coefficient.

1.3.4 Electronic properties

High-resolution photoemission spectroscopy experiments on many cobalt oxides, including $Ca_3Co_4O_9$, were performed by Takeuchi [22], who observed that the electronic population near the Fermi level comes from the *d* orbitals of the cobalt atoms in the CoO_2 layers, yields an intense peak in the density of states just below the Fermi level, which means that the transport properties actually comes from the CoO_2 layers, like the usual $-CoO_2$ thermoelectric oxides and that the charge carriers are holes. This was confirmed by other research groups [3, 19]. They also suggested that a gap open across the Fermi level below 50 K, and indeed, their ultraviolet photoemission spectra showed an empty density of state around E_F below 10 K. The gap measured was estimated to be around 20 meV at 10 K. This is coherent with the observed insulating behavior of the electrical resistivity observed below 50 K. Klie *et al* performed bright-field imaging and electron energy-loss spectroscopy and found out

- 1. that the oxygen atoms in the CoO₂ subsystem are highly ordered, whereas the oxygen-atomic columns in the Ca₂CoO₃ subsystem are globally displaced;
- 2. that holes in the CoO_2 layers are very delocalized, further proving that this subsystem is the one exhibiting the p-type electrical conductivity.

These properties have been investigated from a theoretical point of view using the DFT formalism as well as chemical quantum calculations. The first DFT calculations were performed by Asahi *et al* [23] within the local density approximation. Their calculations yielded an electronic structure showing a high contribution of the 3d orbitals of Co in the rocksalt subsystem around the Fermi level, without any contribution from the 3d orbitals of Co in the CoO₂ subsystem around, which means that the transport properties actually comes from the Ca_2CoO_3 subsystem, and not the CoO_2 subsystem, unlike what was observed in $Na_x CoO_2$, and thus failed to reproduce Takeushi's results. Rébola et al [6] performed DFT+U calculations to take better treat strong electronic correlations. They performed different calculations on supercells of different size in order to model the incommensurability along **b** Their LDA results showed that the states around the Fermi level come from a strong hybridation of the O 2p and Co 3dorbitals, and that the rocksalt type subsystem mainly contribute to the population at the Fermi level. Not much difference with Asahi's results were noticed except a small contribution of the d orbitals of Co in the CoO_2 . However, the DFT+U calculations managed to contradict Asahi et al's results: when strong electronic correlations are taken into account, which was not the case in Asahi's calculations, they found that the electronic population near the Fermi level comes from the t_{2q} orbitals of Co in the CoO_2 subsystem, with almost no contribution from the rocksalt type subsystem (figure 1.13). The e_q orbitals of Co in the CoO₂ subsystem are located around 2.3 eV from the Fermi level and are not occupied whereas the t_{2g} ones are mainly occupied. The electronic structure showed little dependence upon the supercell used: the contribution of the 3d orbitals of Co in the rocksalt subsystem increases weakly with the volume of the unit cell, but this increment is negligible compared to the contribution of the CoO_2 subsystem. Thus, they concluded that the electronic properties should be weakly dependant of the incommensurability.

The electronic structure computed with chemical quantum calculations performed on clusters by Soret and Lepetit [24] displayed interesting properties. As the Co and the O form octahedra in both the CoO₂ and rocksalt type subsystem (figure 1.14), the 3d orbitals of the cobalts are bound to split according to the crystal field theory. The crystal field theory predicts that such a configuration, which is called octahedral crystal field, induce a splitting between the 3d orbitals of the transition metal, which is purely due to electrostatic interactions. The six O ions generate an electrostatic field and their influence depends on the orientation of those oxygens. In a case of a perfect



Figure 1.13: Spin-up and spin-down partial density of states, computed within LDA+U by Rébola [6], projected into d orbitals of Co atoms in the CoO₂ subsystem (top) and in the rocksalt type subsystem (bottom). The Fermi level is shown with the red dashed lines.



Figure 1.14: CoO_6 octahedron as it appears in the CoO_2 subsystem.

octahedron, the d orbitals are not equivalents anymore with respect to the oxygens, hence a splitting:

- The orbitals d_{xy} , d_{yz} , d_{xz} are stabilized as they point between the oxygen p orbitals. Therefore, an electron occupying one of those orbitals will interact less with the oxygens and their energy is lowered. Those orbitals are called t_{2g} .
- The orbitals $d_{x^2-y^2}$ and d_{z^2} are destabilized as they point toward the oxygen p orbitals. Thus, an electron occupying one of those orbitals will interact more with the oxygens and their energy is raised. Those orbitals are called e_q .

Such a splitting is important, as the occupation of the orbitals are influenced by the relative height of their energy levels. However, because the CoO₆ octahedra in the CoO₂ layers are deformed, there is an additional splitting of t_{2g} orbitals into one a_{1g} and two e'_g orbitals. Up until then, such a splitting was observed in DFT calculations but the relative order of the orbitals was unclear. Soret and Lepetit managed to prove that the a_{1g} orbital is always higher than the e'_g orbitals of about 240 meV, which results in Co atoms always in the low-spin state whatever its oxidation degree is (Co³⁺ or Co⁴⁺. For instance, the energy of the low-spin state for Co⁴⁺ is about 700 meV lower than the energy in the high-spin state. This has an important consequence : the a_{1g} orbital is the one always carrying the hole involved in electrical conductivity (figure 1.15), and the DFT+U calculations of Rébola failed to reproduce the splitting of the t_{2g} orbitals. Their results also showed that the electronic properties are strongly



Figure 1.15: Schematic positions of the e_g , e'_g and a_{1g} orbitals of Co in the CoO₂ subsystem. The green arrows represent the electronic population for Co⁴⁺.

modulated by the incommensurate nature of the crystal, in contradiction with Rébola $et \ al$'s own results.

1.4 Motivations

As one can see, $Ca_3Co_4O_9$ is an interesting compound that has attracted significant experimental interest. Yet, there are still many things to clarify about its behavior, especially above room temperature.

There is also a relative lack of theoretical studies of this compound, which can be attributed to its incommensurate nature and the impossibility to treat its exact structure. Few research groups nevertheless managed to bypass this problem and investigated the properties of $Ca_3Co_4O_9$ from a theoretical point of view, with more or less success [6, 23, 24]. Seminal investigations within density functional theory and the LDA [23] did not manage to reproduce an electronic structure in agreement with the experimental studies by Takeuchi *et al* [22]. More recent DFT+U calculations [6] managed to yield an electronic density of states around the Fermi level in better agreement with experiments, but failed to properly explain the magnetic structure and the thermoelectric properties. DFT+U includes also an empirical Hubbard correction term, associated to a lack of predicting power: several calculations with different Hubbard corrections were performed by Rébola *et al*, and they published the results of those agreeing the most with experimental observations.

Here, we decided to study $Ca_3Co_4O_9$ and its structural and electronic properties within the density functional theory, but going beyond the usual LDA(+U) and GGA(+U) formalism and using instead an original hybrid functional approach. Going further we plan to use the electronic structure so obtained at the first-principles level to access for the first time the thermoelectric properties of $Ca_3Co_4O_9$ within the Boltzmann theory formalism.

Our purpose is to validate the hybrid approach for the study of $Ca_3Co_4O_9$ and then use it to clarify its properties. The main questions we want to answer are:

- 1. Can we reproduce the expected electronic structure near the Fermi level and specially the splitting of the *d*-levels with our hybrid functional approach ? Is this compound intrinsically a metal or a semiconductor ?
- 2. Can we get, at our level of approximation, a magnetic ground state structure in qualitative agreement with experimental findings ?
- 3. Does the incommensurate nature of $Ca_3Co_4O_9$ strongly influence its properties ?
- 4. Can we access the transport coefficients within Boltzmann transport theory ? Are their temperature dependence strongly influenced by spin and electronic transitions ?

Chapter 2

Theoretical framework

The aim of the present work is to study theoretically the electronic and thermoelectric properties of calcium cobaltite $Ca_3Co_4O_9$. In order to perform such a study, we will use density functional theory, which allows to model the electronic structure in periodic systems and will give us insight on the bulk electronic properties of the material of interest. Then, from the obtained electronic structure, we will compute the transport properties of $Ca_3Co_4O_9$ using the Boltzmann transport equation, which will gives us some insight on its transport properties (electrical and thermal conductivities, Seebeck coefficient) and thermoelectric performances (power factor $S^2\sigma$ and figure of merit ZT). This chapter is devoted to a basic description of density functional theory providing access to ground state properties, of Boltzmann transport theory providing access to thermoelectric properties, and of the computational tools implementing those theories we used: Crystal09 [25] and BoltzTraP [26].

2.1 Ground state properties

2.1.1 The many-body problem

A crystal consists in a primitive unit cell containing atoms and repeated periodically all over the space. The following theory is general and apply to any kind of solid. Let us consider a quantum system which contains N^0 nuclei, and N electrons in interactions. Such a system can be characterized by a wave function which can be obtained by solving the Schrödinger equation:

$$H(\mathbf{r},\mathbf{R})|\Psi(\mathbf{r},\mathbf{R})\rangle = E|\Psi(\mathbf{r},\mathbf{R})\rangle$$

Where $|\Psi(\mathbf{r}, R)\rangle$ is the eigenfunction and H is the hamiltonian operator, which is the sum of distinct operators related to the kinetic and interaction energies between electrons and nuclei:

$$H(\mathbf{r}, \mathbf{R}) = T_{core}(\mathbf{R}) + U_{core-core}(\mathbf{R}) + T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{core-e}(\mathbf{r}, \mathbf{R})$$

The mathematical expressions in this chapter will make use of the following notations:

- N^0 is the total number of nuclei in the system,
- N is the total number of electrons in the system,
- the indexes κ and κ' refer to the nuclei,
- the indexes i and j refer to the electrons,
- \mathbf{r}_i is the position of the electron i,
- \mathbf{R}_{κ} is the position of the nucleus κ ,
- Z_{κ} is the charge of the nucleus κ .

If we work in atomic units¹, we have:

$$\frac{1}{4\pi\epsilon_0} = 1 \quad \hbar = 1 \quad e = 1$$
$$m_{e^-} = 1 \qquad c = 137.036$$

and the different terms can be written as:

$$T_{core}(\mathbf{R}) = -\sum_{\kappa=1}^{N^0} \frac{1}{2M_{\kappa}} \Delta_{\mathbf{R}_{\kappa}}$$
(2.1)

$$U_{core-core}(\mathbf{R}) = + \sum_{\kappa < \kappa'} \frac{Z_{\kappa} Z_{\kappa'}}{|\mathbf{R}_{\kappa} - \mathbf{R}_{\kappa}'|}$$
(2.2)

$$T_e(\mathbf{r}) = -\sum_{i=1}^N \frac{1}{2} \Delta_{\mathbf{r}_i}$$
(2.3)

$$U_{ee}(\mathbf{r}) = +\sum_{i < j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|}$$
(2.4)

$$U_{core-e}(\mathbf{r}, \mathbf{R}) = -\sum_{\kappa, i} \frac{Z_{\kappa}}{|\mathbf{r}_i - \mathbf{R}_{\kappa}|}$$
(2.5)

- Eq. (2.1) is the operator related to the kinetic energy of the nuclei,
- Eq. (2.2) is the operator related to the interaction energy between the nuclei,
- Eq. (2.3) is the operator related to the kinetic energy of the electrons,
- Eq. (2.4) is the operator related to the interaction energy between electrons,
- Eq. (2.5) is the operator related to the interaction energy between the nuclei and the electrons.

¹From this point and onward, we will make use of atomic units, unless if specified.

In practice, the previous equation is impossible to solve analytically. It is therefore necessary to make use of a few approximations in order to simplify the problem.

We notice that the nuclei have masses that are way more important than the mass of the electrons $(M_{\kappa} \approx 1000 \ m_e)$. In that case, the term $T_i(\mathbf{R})$ becomes very small compared to T_e , and we can consider it as a perturbation. This hypothesis is the Born-Oppenheimer approximation, which was published in 1927 [27]. It means that the electrons are more mobile than the cores and follow adiabatically ionic motions. In other words, the inertia of the electrons dragged by the ions they are bound to is considered negligible.

The unperturbed hamiltonian is the Born-Oppenheimer hamiltonian:

$$H_{BO}(\mathbf{r}, \mathbf{R}) = U_{core-core}(\mathbf{R}) + T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{core-e}(\mathbf{r}, \mathbf{R})$$
(2.6)

and the Born-Oppenheimer energy can be obtained by solving the Born-Oppenheimer Schrödinger equation:

$$H_{BO}(\mathbf{r}, \mathbf{R}) |\psi(\mathbf{r}, \mathbf{R})\rangle = E_{BO}(\mathbf{R}) |\psi(\mathbf{r}, \mathbf{R})\rangle$$
(2.7)

Since the Born-Oppenheimer hamiltonian does not have any differential operator on \mathbf{R} , \mathbf{R} just becomes a simple parameter of the hamiltonian. By fixing \mathbf{R} , $U_{core-core}(\mathbf{R})$ becomes a global shift of the electronic energy so that we can further write:

$$H_{BO}(\mathbf{r}, \mathbf{R}) = H_{el}(\mathbf{r}, \mathbf{R}) + U_{core-core}(\mathbf{R})$$
(2.8)

with

$$H_{el}(\mathbf{r}, \mathbf{R}) = T_e(\mathbf{r}) + U_{ee}(\mathbf{r}) + U_{core-e}(\mathbf{r}, \mathbf{R})$$

In practice, the Born-Oppenheimer approximation allows us to treat separately the electrons and the nuclei:

1. the electronic ground state can be found for any given configuration of the nuclei by solving

$$H_{el}(\mathbf{r}, \mathbf{R}) |\Psi(\mathbf{r}, \mathbf{R})\rangle = E_{el}(\mathbf{R}) |\Psi(\mathbf{r}, \mathbf{R})\rangle$$
(2.9)

or by using the variational principle:

$$E_{el}(\mathbf{R}) = \min_{\Psi} \langle \Psi | H_{el} | \Psi \rangle \tag{2.10}$$

2. then the ground state configuration of the nuclei \mathbf{R}^0 and the related energy are found as the minimum of the Born-Oppenheimer energy

$$E_{BO}(\mathbf{R}) = E_{el}(\mathbf{R}) + E_{core-core}(\mathbf{R})$$
(2.11)

$$\rightarrow E_{BO}(\mathbf{R}^0) = \min_{\mathbf{R}} (E_{el}(\mathbf{R}) + E_{core-core}(\mathbf{R}))$$
(2.12)

At this stage the central problem is to solve equation (2.9). There are many methods to solve such a problem. Density functional theory is one of them and is the topic of the following section.

2.1.2 Density Functional Theory

Up until now, we considered the many-body wave function Ψ as the "variable" of our problem. Within the density functional theory (DFT), the approach is different: the fundamental variable is no more the wave function, but the electronic density. If the wave function associated to the ground state of the N-electron system depends on the spatial coordinates \mathbf{r}_1 , \mathbf{r}_2 , \mathbf{r}_3 , ..., \mathbf{r}_N , the electronic density is defined as:

$$d(\mathbf{r}) = \sum_{i}^{N} \delta(\mathbf{r} - \mathbf{r}_{i})$$
(2.13)

$$n(\mathbf{r}) = \langle \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) | d(\mathbf{r}) | \Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N) \rangle$$
(2.14)

$$n(\mathbf{r}_1) = N(\int \int |\Psi(\mathbf{r}_1, \mathbf{r}_2, ..., \mathbf{r}_N)|^2 dr_2 ... dr_N)$$
(2.15)

As the density is space-dependent, from a problem with $3 \ge N$ variables, we get to a problem with only 3 spatial variables. In other words, it is much easier to solve and less demanding in terms of computational resources.

The reformulation of the many-body problem in terms of the density relies on the two Honenberg-Kohn theorems and the Kohn-Sham ansatz that are now described.

2.1.2.1 The first Hohenberg-Kohn theorem

We will now see how the many-body problem can be recast into a problem which only make use of the electronic density [28, 29].

The first Hohenberg-Kohn theorem stipulates:

"the density of the ground state $n_0(\mathbf{r})$ of the many-body electronic system is entirely and uniquely determined by the external potential $U_{ext}(\mathbf{r})$ modulo a constant" Let us consider a family of hamiltonian H_{el} which all have identical T_e and U_{ee} oper-

Let us consider a family of framitoman T_{el} which an nave identical T_e and U_{ee} operators, but which actually differ in their external potential U_{ext} .

Proof² : Ad absurdum. Let us consider two external potentials $U_{ext}^{(1)}(\mathbf{r})$ and $U_{ext}^{(2)}(\mathbf{r})$ which are different (in more ways than just an additive constant), associated to the same ground state electronic density $n_0(\mathbf{r})$. These two potentials leads to two different hamiltonians, $H^{(1)}$ and $H^{(2)}$, with two different ground state wave functions $|\Psi^{(1)}\rangle$ and $|\Psi^{(2)}\rangle$. As $|\Psi^{(2)}\rangle$ is not the ground state of the system with the hamiltonian $H^{(1)}$, we have

$$\begin{split} E^{(1)} &= \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle \\ &< \langle \Psi^{(2)} | H^{(1)} | \Psi^{(2)} \rangle \\ &< \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle + \langle \Psi^{(2)} | H^{(1)} - H^{(2)} | \Psi^{(2)} \rangle \\ &< E^{(2)} + \int d\mathbf{r} [U_{ext}^{(1)} - U_{ext}^{(2)}] n_0(\mathbf{r}) \\ &\Rightarrow E^{(1)} < E^{(2)} + \int d\mathbf{r} [U_{ext}^{(1)} - U_{ext}^{(2)}] n_0(\mathbf{r}) \end{split}$$

 $^{^{2}}$ For the sake of simplicity, this proof is only for the non-degenerated case. The proof can be extended to degenerates cases.

Similarly, as $|\Psi^{(1)}\rangle$ is not the ground state of the system with the hamiltonian $H^{(2)}$,

$$\begin{split} E^{(2)} &= \langle \Psi^{(2)} | H^{(2)} | \Psi^{(2)} \rangle \\ &< \langle \Psi^{(1)} | H^{(2)} | \Psi^{(1)} \rangle \\ &< \langle \Psi^{(1)} | H^{(1)} | \Psi^{(1)} \rangle + \langle \Psi^{(1)} | H^{(2)} - H^{(1)} | \Psi^{(2)} \rangle \\ &< E^{(1)} + \int d\mathbf{r} [U_{ext}^{(2)} - U_{ext}^{(1)}] n_0(\mathbf{r}) \\ &\Rightarrow E^{(2)} < E^{(1)} + \int d\mathbf{r}^3 [U_{ext}^{(2)} - U_{ext}^{(1)}] n_0(\mathbf{r}) \end{split}$$

Summing these two inequalities yields $E^{(1)} + E^{(2)} < E^{(2)} + E^{(1)}$, which is not possible. The assumption that the same density is associated with the two different external potentials is wrong. In other words only the external potential modulo a constant determines the electronic density.

2.1.2.2 The second Hohenberg-Kohn theorem

The second theorem can be summarized as [28, 29]:

"A universal functional E[n], which gives the energy in regards to the electronic density $n(\mathbf{r})$, exists for any external potential $U_{ext}(\mathbf{r})$. For each $U_{ext}(\mathbf{r})$, the ground state energy is the energy which minimizes this functional, and the associated density $n(\mathbf{r})$ is the exact ground state density $n_0(\mathbf{r})$ "

Proof: As any properties are defined by the knowledge of the electronic density $n(\mathbf{r})$, they can be written as density functionals. The total energy can be written:

$$E[n] = T[n] + U[n] + \int U_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$
(2.16)

$$= F[n] + \int U_{ext}(\mathbf{r})n(\mathbf{r})d\mathbf{r}$$
(2.17)

F[n] is a partial contribution of the electronic system (kinetic and electrons-electrons energies) to the total energy. As this functional is the same for any electronic system and for any external potential, F is a "universal functional" of the density.

Let us now consider a system which has a ground state density $n^{(1)}$ which is given by an external potential $U_{ext}^{(1)}(\mathbf{r})$. In this case, the Hohenberg-Kohn functional is equal to the expected value of the hamiltonian of the ground state $|\Psi^{(1)}\rangle$:

$$E^{(1)} = \left\langle \psi^{(1)} \left| H^{(1)} \right| \psi^{(1)} \right\rangle$$
(2.18)

If we consider a second density $n^{(2)}$ associated to another wave function $|\Psi^{(2)}\rangle$, which is different than $|\Psi^{(1)}\rangle$ and therefore is not associated to the ground state, we can see that the energy $E^{(2)}$ of this other state is higher than the ground state energy $E^{(1)}$:

$$E^{(1)} = \left\langle \psi^{(1)} \left| H^{(1)} \right| \psi^{(1)} \right\rangle < \left\langle \psi^{(2)} \left| H^{(1)} \right| \psi^{(2)} \right\rangle < E^{(2)}$$
(2.19)

Therefore, the value of the energy functional evaluated for the ground state density $n_0(\mathbf{r})$ must be inferior to the value obtained for any other density n. If the universal functional F[n] is known, minimizing the total energy by changing the electronic density function $n(\mathbf{r})$ while conserving all the particles in the system leads to the energy and the density of the ground state.

2.1.2.3 The Kohn-Sham ansatz

While DFT is a beautiful theory, there is no pratical way to implement it in order to find a solution to the many-body problem because the analytic form of F[n] is not known. This would have made the theory useless in practice, but Kohn and Sham had a brilliant idea in changing the unsolvable problem to a simpler and solvable problem leading to the same solution.

This approach is the Kohn-Sham ansatz. Let us consider a system of non-interacting particles, which are moving in an external potential v_s and produce the same ground state density as the many-body system. The key point of the Kohn-Sham ansatz is that the whole electronic system can be expressed by a single product of each individual wave function as the particles are considered independents from each other:

$$|\Psi_{KS}\rangle = \left|\prod_{i=1}^{N} \Psi_i(\mathbf{r}_i)\right\rangle \tag{2.20}$$

The many-body wave function which characterize this system is a Slater determinant of monoelectronic orbitals $|\Psi_i(\mathbf{r}_i)\rangle$, which are solutions of the Schrödinger equation:

$$\left[-\frac{1}{2}\Delta_{\mathbf{r}_{i}}+v_{s}(\mathbf{r})\right]|\Psi_{i}(\mathbf{r}_{i})\rangle = \epsilon_{i}|\Psi_{i}(\mathbf{r}_{i})\rangle \qquad (2.21)$$

$$n(\mathbf{r}) = \sum_{i}^{N} |\Psi_i(\mathbf{r}_i)|^2 \qquad (2.22)$$

The universal functional F[n] can be expressed as the sums of three terms. One represents the kinetic energy of the non-interacting particle, one the interaction of the density with itself, and one represents the energy of exchange and correlation in the system:

$$F[n] = T_{KS}[n] + E_H[n] + E_{xc}[n]$$
(2.23)

 T_{KS} is the kinetic energy of the non-interacting particles, which can be expressed as a kinetic energy of the associated Slater determinant:

$$T_{KS} = -\frac{1}{2} \sum_{i=1}^{N} \langle \Psi_i | \nabla_{\mathbf{r}_i}^2 | \Psi_i \rangle$$
(2.24)

 $E_H[\mathbf{n}]$ is called Hartree energy. It is the classical coulombian interaction energy of the electronic density interacting with itself. Its expression is:

$$E_H[n] = \frac{1}{2} \int \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}'$$
(2.25)
Finally, the term E_{xc} corresponds to the exchange-correlation energy, which contains the indiscernability of the electrons (Pauli's principle) and the spatial correlations between electrons (quantum fluctuations). It also contains the difference of kinetic energy between the real system (interacting particles) and the Kohn-Sham system (non-interacting particles): even if the electronic density of their ground state may be the same, there is no reason that the density operator for both systems is the same, and thus, there is no reason that both system must have the same kinetic energy. E_{xc} can be considered as a "melting pot" which contains all effects that we cannot treat correctly.

We must now replace the Schrödinger equation of the many-body system by the Schrödinger equation associated with the non-interacting particles system. We can write the hamiltonian as:

$$H = -\frac{1}{2} \sum_{i=1}^{N} \Delta_{\mathbf{r}_{i}} + \sum_{i=1}^{N} v_{s}(\mathbf{r}_{i})$$
(2.26)

$$= -\frac{1}{2}\sum_{i=1}^{N} \Delta_{\mathbf{r}_{i}} + \sum_{i=1}^{N} u_{ext}(\mathbf{r}_{i}) + \sum_{i=1}^{N} u_{H}(\mathbf{r}_{i}) + \sum_{i=1}^{N} u_{xc}(\mathbf{r}_{i})$$
(2.27)

with $U_H(\mathbf{r})$ being the Hartree potential

$$u_H(\mathbf{r}) = \frac{\delta E_H[n]}{\delta n(\mathbf{r})} = \int \frac{n(\mathbf{r}')}{\mathbf{r} - \mathbf{r}'} d\mathbf{r}'$$
(2.28)

and $U_{xc}(\mathbf{r})$ being the exchange-correlation potential

$$u_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n]}{\delta n(\mathbf{r})} = \epsilon_{xc}[n] + \frac{d\epsilon_{xc}[n]}{dn}$$
(2.29)

If one expresses E_{xc} as:

$$E_{xc}[n] = \int \epsilon_{xc}[n]n(\mathbf{r})d\mathbf{r}$$
(2.30)

The energy functional $E[n] = \sum_{i=1}^{N} \langle \Psi_i | H | \Psi_i \rangle$ can be written as:

$$E[n] = -\frac{1}{2} \sum_{i=1}^{N} \langle \Psi_i | \Delta_{\mathbf{r}_i} | \Psi_i \rangle + \int n(\mathbf{r}) u_{ext} d\mathbf{r} + E_H[n] + E_{xc}[n]$$

$$= -\frac{1}{2} \sum_{i=1}^{N} \int \Psi_i^{\dagger}(\mathbf{r}) [\Delta_{\mathbf{r}} \Psi_i(\mathbf{r})] d\mathbf{r} + \sum_{i=1}^{N} \int u_{ext} |\Psi_i(\mathbf{r})|^2 d\mathbf{r}$$

$$+ \frac{1}{2} \sum_{i=1}^{N} \int u_H |\Psi_i(\mathbf{r})|^2 d\mathbf{r} + \sum_{i=1}^{N} \int \epsilon_{xc}[n(\mathbf{r})] |\Psi_i(\mathbf{r})|^2 d\mathbf{r} \qquad (2.31)$$

One can see that the energy functional only contains monoelectronic operators. This means that solving the Schrödinger equation for the Kohn-Sham system can be done for each electrons individually. Thus, one can find each individual wave functions by solving the eigenvalue problem:

$$\left(-\frac{1}{2}\Delta_{\mathbf{r}} + u_{ext}(\mathbf{r}) + u_{H}(\mathbf{r}) + u_{xc}(\mathbf{r})\right)|\Psi_{i}(\mathbf{r})\rangle = \epsilon_{i}|\Psi_{i}(\mathbf{r})\rangle$$
(2.32)

with ϵ_i being the energy of the electron in the state $|\Psi_i(\mathbf{r})\rangle$.

The Kohn-Sham ansatz allows us to find the electronic density associated with the ground state of the interacting electron system. However, even though the equation are seemingly simpler to solve, there is still a major problem: there is no exact analytic expression for the exchange-correlation energy functional $E_{xc}[n]$. If it was known, than it would be possible to find the exact ground state energy. Unfortunately, this is not the case, so it will be necessary to approximate $E_{xc}[n]$. Fortunately, many options are avalable to us, and those shall be presented in subsection 2.1.4.

2.1.3 Solving the Kohn-Sham equations

The Kohn-Sham equations prove themselves to be extremelly useful. From these equations, we are able to find the *exact* density and energy of the ground state of a manybody electron problem just using an independent-particles approach. The only remaining issue is the form of the exchange-correlation energy E_{xc} , which is unknown and need to be approximated as it will be further discussed in the next section. Assuming that issue solved, we now have all the necessary ingredients in order to find the ground state.

How can the Kohn-Sham equations be solved in practice? As we've seen, the external Kohn-Sham potential $v_s(\mathbf{r})$ is implicitely dependent on the electronic density $n(\mathbf{r})$. They must be consistent. The actual procedure in a numerical calculation successively changes v_s and n to approach the self-consistent solution as illustrated in figure 2.1.

What is done is that we use an initial guess for the electronic density n_i , which generates the effective KS potential v_s . The Kohn-Sham equations are then solved, which generates a new electronic density. If the self-consistency is reached, the calculation is over. If not, the new electronic density is used to generate a new effective potential, which is used to solve the Kohn-Sham equations, and so on... [28]

The iterative progression converges with a judicious choice of the new potential in terms of the potential or density found at the previous step(s).

Sometime, achieving self-consistency can be a true challenge because it is necessary to make a good choice for updating the potential v_s or the density n in each iterations of the previous progression. It is simpler to describe in term of the electronic density, which is unique, whereas the external potential is unique modulo a constant.

The simplest approach is the *linear mixing*, which we are about to describe and which has been used for our own calculations [28]. This approach is simple: the electronic density input at step i + 1 is estimated as a fixed linear combination of n_i^{input} and n_i^{output} at step i:

$$n_{i+1}^{input} = \alpha n_i^{output} + (1-\alpha)n_i^{input} = n_i^{input} + \alpha (n_i^{output} - n_i^{input})$$
(2.33)



Figure 2.1: Schematic representation of the self-consistent loop for solution of Kohn-Sham equations.

As any other information is missing during a calculation, this is indeed the best choice to make and is essentially moving in an approximate *steepest descent* direction for minimizing the energy. One cannot take the output density at one step as the input of the next step. The main issue here is that doing so would make the consecutive solutions jump around the bottom of the energy well, without ever reaching it.

2.1.4 Approximate exchange-correlation energy functional

In theory, $E_{xc}[n]$ is an universal density functional, which would have the same analytical form for any kind of material. However, as said previously, its analytical form is not known. Also, the kinetic energy of the real system is not guaranteed to be equal to the kinetic energy of the fictional Kohn-Sham system, and $E_{xc}[n]$ must contain the difference between these two energies. It is necessary to approximate it, and there are many different options available to us. We shall review the most common approximations.

2.1.4.1 LDA - Local Density Approximation

The result of this approximation is a functional which happens to be the most widely used in applied density functional theory. It is based on the homogeneous electron gas model, which is a simple model which allows to treat the exchange part analytically: in such a gas, all the physical properties depends on a single parameter, the density $n(\mathbf{r})$, which is identical for any \mathbf{r} : $n(\mathbf{r}) = n_0$. Therefore, the exchange-correlation energy also depends on the density: $E_{xc} = E_{xc}[n(\mathbf{r})] = E_{xc}[n_0]$. The knowledge of the energy of such a gas leads to the knowledge of the exchange-correlation part. If we make the approximation that the exchange-correlation energy density at a point \mathbf{r} , $\epsilon_{xc}(\mathbf{r})$, only depends on the density at this point and that it is equal to the exchange-correlation energy per particle of a homogeneous gas of density n_0 , we can use ϵ_{xc} locally for any system where $n(\mathbf{r})$ is not uniform, which is usually the case in many systems, we can express the exchange-correlation energy as a local functional of the density:

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r}) \epsilon_{xc}^{hom}(n(\mathbf{r})) d\mathbf{r}$$
(2.34)

(2.35)

The exchange-correlation energy can be written as the sum of two contributions, the exchange part E_x^{hom} and the correlation part E_c^{hom} :

$$E_{xc}^{hom}[n] = E_x^{hom}[n] + E_c^{hom}[n]$$
(2.36)

The exchange part can be calculated analytically Hartree-Fock methods, which yields [28]:

$$E_x^{hom}[n] = -\frac{3}{4} \left(\frac{3}{\pi}\right)^{\frac{3}{3}} \int n^{4/3}(\mathbf{r}) d\mathbf{r}$$
 (2.37)

The correlation energy part $E_c[n]$ is approximated by fitting an analytical function on curves obtained using Quantum Monte-Carlo simulations of an homogeneous electron gas, by subtracting the known exchange and kinetic parts of the total energy.

The most used formulations are those of Vosko, Wilkes and Nussair [30] (called VWN) and Perdew and Zunger [31] (called PZ).

While LDA has proved to be very efficient, the approximation does have its weaknesses: it tends to underestimate lattice parameters and cannot treat strong electronic correlations. However, many calculations has shown great accuracy in comparison to experimental results, which is the reason why the local density approximation is so popular among physicists.

The local density approximation can be generalized to magnetic systems by taking the spin of each electron into account. If we consider that the magnetic properties originates solely from the intrinsic magnetic moment of the electrons, this means that we can treat two different electron densities: the spin-up electronic density $n^{\uparrow}(\mathbf{r})$ and the spin-down electronic density $n^{\downarrow}(\mathbf{r})$. Basically, we have two times more equations to solve in this case.

It is also necessary to define a spin-dependent exchange-correlation energy $E_{xc}[n] = E_{xc}[n^{\uparrow}, n^{\downarrow}]$. In the case of collinear magnetism, this means that we must use two exchange-correlation potentials:

$$U_{xc}^{\uparrow} = \frac{\delta E_{xc}[n^{\uparrow}, n^{\downarrow}]}{\delta n^{\uparrow}} \text{ and } U_{xc}^{\downarrow} = \frac{\delta E_{xc}[n^{\uparrow}, n^{\downarrow}]}{\delta n^{\downarrow}}$$

The generalized approximation is the *local spin density approximation* (LSDA) and the exchange functional is expressed as:

$$E_x^{LSDA}[n^{\uparrow}, n^{\downarrow}] = -2^{\frac{2}{3}} \frac{3}{4} \left(\frac{3}{\pi}\right)^{1/3} \int \left(n^{\uparrow \frac{4}{3}} + n^{\downarrow \frac{4}{3}}\right) d\mathbf{r}$$
(2.38)

2.1.4.2 GGA - Generalized Gradient Approximation

The local density approximation may be popular and yields results quite coherent with experimental measurements, yet there is no reason for the electronic density $n(\mathbf{r})$ at a given \mathbf{r} does not depend on the electronic density around it. It is more than reasonable to consider that the electronic density is not spatially uniform and that the density at a given position \mathbf{r} depends on the density around that position. The GGA methods are semi-local approximations which are similar to the local density approximation, but take into account the variations of the electronic density by expressing the exchange-correlation energy as a functional of the density, but also as a functional of its gradient and higher order derivatives:

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r})\epsilon_{xc}[n, \nabla n, \nabla^2 n, ...]d\mathbf{r}$$
(2.39)

The most popular functionals of this type are those of Perdew, Burke and Ernzerhof (PBE) [32] and Perdew and Wang (PW91) [33].

2.1.4.3 Hybrid functionals

As local and semi-local approaches, the LDA and GGA are known to illy treat strong correlation effects. One solution to go beyond is the DFT+U formalism, which consists in adding a Hubbard correction U to increase repulsions in d and f orbitals (which are very localized), therefore better treating electronic correlations. Another solution is to better treat the exchange part, which is the topic of the following subsection.

Hybrid functionals has been introduced since the beginning of the nineties and are mainly used in quantum chemistry calculations. These functionals try to solve problems arising from the local density approximation and generalized gradient approximation. By adding explicitly a fraction of the real exchange energy which can be obtained by Hartree-Fock methods. They are used to take into account many non-local effects of the exchange energy [28]. Hybrid functionals are expressed as a combination of various LDA and GGA functionals with exact exchange:

$$E_{xc}^{hyb}[n] = E_{xc}^{LDA} + a_0(E_x^0 - E_x^{LDA}) + a_x(E_x^{GGA} - E_x^{LDA}) + a_c(E_c^{GGA} - E_c^{LDA})$$

The different terms are:

- E_{xc}^{LDA} : exchange-correlation functional as defined in the local density approximation.
- E_x^0 : exact exchange obtained for the non-interacting particles system.
- E_x^{LDA} : LDA exchange functional.
- E_x^{GGA} : GGA exchange functional.
- E_c^{LDA} : LDA correlation functional.
- E_c^{GGA} : GGA correlation functional.

The coefficient a_0 , a_x and a_c are optimized with different LDA and GGA exchangecorrelation functionals.

The nomenclature of hybrid functionals is such as the first letter correspond to the GGA functional used for the exchange energy, followed by the number of coefficients a_0 , a_x and a_c to be optimized, followed by the letters corresponding to the GGA functional used for the energy.

The B3LYP functional is the most used one and uses the *Becke* GGA functional for the exchange energy, and the *Lee-Yang-Parr* [34] GGA functional for the correlation energy. The three coefficients are :

$$a_0 = 0.20$$

 $a_x = 0.72$
 $a_c = 0.81$

The B1WC functional has been optimized by D.I. Bilc *et al* [35] at the "Université de Liège" and uses the *Becke* GGA functional for the exchange energy, and the *Wu-Cohen* [34] GGA functional for the correlation energy. Only a_0 is optimized. A value of $a_0 = 0.16$ has been obtained. The other coefficients are fixed at: $a_x = 1 - a_0$ and $a_c = 1$. This functional has proved itself to be very useful to treat ferroelectric and magnetic oxide materials. For the following calculations, we will make use of the B1WC functional. As it contains a fraction of the exact exchange energy, it is expected to give better results for magnetic materials. By using it, we aim at proving that it is a conveniant alternative to DFT+U that can indeed be used to model the ground state properties of calcium cobaltite, correcting the usual errors associated to the local density approximation.

2.1.5 Crystal09, software and technical details

The present section is devoted to the software used to perform our calculation within the DFT formalism, as well as the technical details relative to the computation of the ground state properties.

2.1.5.1 General features

Crystal09 has been used in order to calculate the electronic properties of $Ca_3Co_4O_9$ within the DFT framework.

The Crystal09 [25, 36] package allows to perform *ab initio* calculations of the ground state energy, energy gradients, electronic wave function, density and various properties of periodic systems. The fundamental aspect of Crystal09, which differentiates it from other *ab initio* calculation packages, is that the single particle wave functions $\psi_i(\mathbf{r}; \mathbf{k})$ are expanded as a linear combination of atomic orbitals defined in terms of local functions. This method is usually known as the LCAO method (Linear Combination of Atomic Orbitals). The local functions consist of linear combinations of Gaussian type functions, whose exponents and coefficients are defined by input. Different functions of symmetry *s*, *p*, *d*, *f* and even *sp* can be used. LCAO methods are usually utilized in calculations for finite system. Many other codes actually work with plane waves [28, 29]. Local Gaussian orbitals nevertheless present some advantages:

- the exchange energies are easier to calculate, however this is not the case for kinetic energies;
- the interactions between electrons localized in 3d orbitals around the Fermi level are better reproduced with local orbitals than plane waves because these orbitals are very localized.

Each atomic orbital is a combination of gaussian functions:

$$\chi(r,\theta,\phi) = \left(\sum_{j} C_{j} e^{-\alpha_{j} r^{2}}\right) \left[r^{l} Y_{lm}(\theta,\phi)\right]$$
(2.40)

with α_j being the exponents and C_j the coefficients of the radial parts of the atomic orbitals.

The choice of the basis set is a fundamental and crucial step in defining the level of calculation and its accuracy, especially when dealing with periodic systems where many chemical bonding can be found.

With Crystal09, we've been able to compute the following properties:

- the electronic structure: wave functions, eigenenergies and related band structure and density of states;
- forces and stresses to relax the atomic structure and find the configuration of minimal energy;
- magnetic properties within the collinear-spin approximation.

2.1.6 Technical details

The first calculations has been performed within the local density approximation with the VWN [30] correlation functional. We also used the B1WC hybrid functional to better treat correlations between electrons.

The same basis sets are used for all calculations. For the neutral atoms, we have each orbitals populated as:

$$\begin{array}{rcl} Co &:& 1s^22s^22p^63s^23p^64s^23d^7\\ Ca &:& \left[1s^22s^22p^6\right]3s^23p^64s^2\\ O &:& 1s^22s^22p^4 \end{array}$$

A pseudopotential is used to treat the core electrons of the calcium atoms (between the square brackets). The details of our basis sets are reported in tables 2.1, 2.2, 2.3 and in [37, 38].

Spin-polarized calculations were performed for different magnetic structure : seven different magnetic structures were set as a starting point and are labeled:

• FM1: the total magnetic spin is set at $2 \mu_B$ for all cobalt atoms in the primitive cell;

ATOM	TYPE	EXP	S COEF	P COEF	D/F/G COEF
Oxygen	\mathbf{S}	7.817E + 03	1.176E-03	0.000E + 00	0.000E + 00
		1.176E + 03	8.968E-03	0.000E + 00	0.000E + 00
		2.732E + 02	4.287 E-02	0.000E + 00	0.000E + 00
		8.117E + 01	1.439E-01	0.000E + 00	0.000E + 00
		$2.718E{+}01$	3.556E-01	0.000E + 00	0.000E + 00
		9.532E + 00	4.612E-01	0.000E + 00	0.000E + 00
		3.414E + 00	1.402E-01	0.000E + 00	0.000E + 00
	\mathbf{S}	9.532E + 00	-1.542E-01	0.000E + 00	0.000E + 00
		9.398E-01	1.057E + 00	0.000E + 00	0.000E + 00
	\mathbf{S}	2.846E-01	1.000E + 00	0.000E + 00	0.000E + 00
	Р	$3.518E{+}01$	0.000E + 00	1.958E-02	0.000E + 00
		7.904E + 00	0.000E + 00	1.242E-01	0.000E + 00
		2.305E + 00	0.000E + 00	3.947E-01	0.000E + 00
		7.171E-01	0.000E + 00	6.274 E-01	$0.000 \text{E}{+}00$
	Р	2.137E-01	0.000E + 00	1.000E + 00	$0.000 \text{E}{+}00$

Table 2.1: Basis set for the oxygen atoms

ATOM	TYPE	EXP	S COEF	P COEF	D/F/G COEF
Calcium	\mathbf{S}	$1.231E{+}01$	5.874E-02	0.000E + 00	0.000E + 00
		4.393E + 00	-4.013E-01	0.000E + 00	0.000E + 00
		9.380E-01	5.929E-01	0.000E + 00	0.000E + 00
	\mathbf{S}	4.217E-01	1.000E + 00	0.000E + 00	0.000E + 00
	\mathbf{S}	2.000E-01	1.000E + 00	0.000E + 00	0.000E + 00
	Р	5.974E + 00	0.000E + 00	-8.230E-02	0.000E + 00
		1.567E + 00	0.000E + 00	3.465 E-01	0.000E + 00
		6.562 E-01	0.000E + 00	5.601E-01	0.000E + 00
	Р	2.585 E-01	0.000E + 00	1.000E + 00	0.000E+00

Table 2.2: Basis set for the calciums atoms

ATOM	TYPE	EXP	S COEF	P COEF	D/F/G COEF
Cobalt	\mathbf{S}	3.417E + 05	2.270E-04	0.000E + 00	0.000E + 00
		4.885E + 04	1.929E-03	0.000E + 00	0.000E + 00
		1.040E + 04	1.110E-02	0.000E + 00	0.000E + 00
		2.719E + 03	5.010E-02	0.000E + 00	0.000E + 00
		8.197E + 02	1.705E-01	0.000E + 00	0.000E + 00
		2.839E + 02	3.692 E-01	0.000E + 00	0.000E + 00
		1.110E + 02	4.033E-01	0.000E + 00	0.000E + 00
		4.648E + 01	1.433E-01	0.000E + 00	0.000E + 00
	\mathbf{SP}	8.556E + 02	-5.400E-03	8.800E-03	0.000E + 00
		2.065E + 02	-6.840E-02	6.200 E-02	0.000E + 00
		$6.905E{+}01$	-1.316E-01	2.165 E-01	0.000E + 00
		2.727E + 01	2.616E-01	4.095E-01	0.000E + 00
		1.154E + 01	6.287 E-01	3.932E-01	0.000E + 00
		4.202E + 00	2.706E-01	2.250E-01	0.000E + 00
	\mathbf{SP}	5.151E + 01	1.820E-02	-2.870E-02	0.000E + 00
		1.889E + 01	-2.432E-01	-9.370E-02	0.000E + 00
		7.719E + 00	-8.490E-01	2.036E-01	0.000E + 00
		3.540E + 00	8.264 E-01	$1.419E{+}00$	0.000E + 00
	\mathbf{SP}	1.495E + 00	1.000E + 00	1.000E + 00	0.000E + 00
	\mathbf{SP}	5.985E-01	1.000E + 00	1.000E + 00	0.000E + 00
	D	3.061E + 01	0.000E + 00	0.000E + 00	6.170 E-02
		8.309E + 00	0.000E + 00	0.000E + 00	2.835E-01
		2.706E + 00	0.000E + 00	0.000E + 00	5.290 E-01
		9.080E-01	0.000E + 00	0.000E + 00	4.976E-01
	D	2.824E-01	0.000E + 00	0.000E + 00	1.000E + 00

Table 2.3: Basis set for the cobalt atoms

- FM2: the total magnetic spin is set at $2 \mu_B$ for all cobalt atoms in the rocksalt type subsystem, and set to 0 for the cobalt atoms in the CoO_2 subsystem;
- FM3: the total magnetic spin is set at $2 \mu_B$ for all cobalt atoms in the CoO_2 subsystem, and set to 0 for the cobalt atoms in the rocksalt type subsystem;
- NM: a spin polarization is not allowed in the calculation.
- AFM1: an antiferromagnetic order is set for the cobalt atoms in the rocksalt type subsystem and set to 0 for the cobalt atoms in the *CoO*₂ subsystem;
- AFM2: an antiferromagnetic order is set for the cobalt atoms in the CoO_2 subsystem and set to 0 for the cobalt atoms in the rocksalt type subsystem;
- AFM3: an antiferromagnetic order is set for the cobalt atoms between the two subsystems;

The linear mixing has been set at $\alpha = 0.01$. We used a 6x3x3 k-point grid for summation over the Brillouin zone. The energy convergence criterium was set at 10^{-7} Hartree.

2.2 Thermoelectric properties

The present section is devoted to the theoretical formalism providing access to the thermoelectric properties of $Ca_3Co_4O_9$. We will present a brief description of the theory, followed by the description of the software implementing it.

2.2.1 Boltzmann transport theory

As seen previously in the phenomenological description of thermoelectrics, those materials can be characterized by a dimensionless factor estimating their efficiency to convert an applied voltage to heat and *vice-versa*, while having a very high eletrical conductivity and a very low thermal conductivity. This factor can be seen as the figure of merit ZT, and a crucial part in engineering functional thermoelectric materials is to optimize this factor [8, 26].

$$ZT = \frac{S^2 \sigma T}{\kappa_e + \kappa_l} \tag{2.41}$$

Modelizing such materials requires the ability to evaluate the different transport coefficients which are involved. Those are:

- the Seebeck coefficient S;
- the electrical conductivity σ ;
- the electronic thermal conductivity κ_e .
- the lattice contribution to thermal conductivity, κ_l

It is possible to calculate these properties (except κ_l) from the Boltzmann transport equation. This equation (eq.(2.42)) describes the statistical behaviour of a fluid not being in the thermodynamic equilibrium. In the present case, we consider a fluid of electrons. This time, for clarity, these equations will be written in SI units.

$$\frac{df(\mathbf{r},\mathbf{k},t)}{dt} = \nabla_{\mathbf{r}} f(\mathbf{r},\mathbf{k},t) \cdot \mathbf{v}_{\mathbf{k}} + \nabla_{\mathbf{k}} f(\mathbf{r},\mathbf{k},t) \cdot \frac{\mathbf{F}}{\hbar} + \frac{\partial f(\mathbf{r},\mathbf{k},t)}{\partial t} = \left. \frac{\partial f(\mathbf{r},\mathbf{k},t)}{\partial t} \right|_{scatt}$$
(2.42)

with

- $f(\mathbf{r}, \mathbf{k}, t)$ being the distribution of the electrons and can be both space and time dependent (the **r** and **k** values are altered by external fields and collisions);
- $\epsilon_{\mathbf{k}}$ is the energy of the electrons with a momentum \mathbf{k} ;
- **F** is the force giving birth to their group motion and originates from the applied fields;
- $\frac{\partial f(\mathbf{r},\mathbf{k},t)}{\partial t}|_{scatt}$ is the variation in distribution due to scattering;
- $v_{\mathbf{k}}$ is the group velocity of electrons with a momentum \mathbf{k} .

$$\mathbf{v}_{\mathbf{k}} = \frac{1}{\hbar} \nabla_{\mathbf{k}} \epsilon_{\mathbf{k}} \tag{2.43}$$

The electrons are submitted to a temperature gradient and an electric field. Under such constraints, the electron distribution change and reach a steady state. For the steady state case with small temperature and/or concentration gradient and electric field, the time variation of the distribution function is much smaller than the space variation distribution, so the term $\frac{\partial f}{\partial t}$ is negligible. The Boltzmann equation can be written as:

$$\mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_{\mathbf{k}}}{\partial T} \nabla T + \mathbf{v}_{\mathbf{k}} \cdot (-e) \frac{\partial f_{\mathbf{k}}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E} = \left. \frac{\partial f_{\mathbf{k}}}{\partial t} \right|_{scatt}$$
(2.44)

where (-e) is the charge of electron, T is the temperature and \mathbf{E} is the electric field. Under the relaxation-time approximation, which considers a linear evolution from equilibrium to the steady state under a temperature gradient and an applied electric field, it follows:

$$\mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_{\mathbf{k}}}{\partial T} \nabla T + \mathbf{v}_{\mathbf{k}} \cdot (-e) \frac{\partial f_{\mathbf{k}}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E} = \frac{f_{\mathbf{k}}^0 - f_{\mathbf{k}}}{\tau_{\mathbf{k}}}$$
(2.45)

$$f_{\mathbf{k}}^{0} = \frac{1}{e^{(\epsilon_{\mathbf{k}}-\mu)/k_{B}T} + 1}$$
(2.46)

where $f_{\mathbf{k}}^{0}$ is the electronic distribution at the equilibrium, μ is the chemical potential and $\tau_{\mathbf{k}}$ is the relaxation time.

Now let us take a look to the transported quantities, *i.e.* the electric current and

thermal current. Those currents are both due to the thermal gradient and the applied electric field. We have the following expressions, associating the sources of motion and their respective coefficients:

$$\mathbf{J} = L_{EE}\mathbf{E} + L_{ET}\nabla T \tag{2.47}$$

$$\mathbf{Q} = L_{TE}\mathbf{E} + L_{TT}\nabla T \tag{2.48}$$

The electrical conductivity is defined under an electric field only $(\nabla T = 0)$:

$$\mathbf{J} = \sigma \mathbf{E} \Longrightarrow \sigma = L_{EE} \tag{2.49}$$

The thermal conductivity is defined when there is no current $(\mathbf{J} = 0)$:

$$Q = -\kappa \nabla T \Longrightarrow \kappa = -\left(L_{TT} - \frac{L_{TE} \cdot L_{ET}}{L_{EE}}\right)$$
(2.50)

The Seebeck coefficient is also defined when there is no current, and using equation (2.47) and (2.48) it follows that:

$$\mathbf{E} = S\nabla T \Longrightarrow S = -\frac{L_{ET}}{L_{EE}} \tag{2.51}$$

Let us go back to Boltzmann's equation (2.45). We have:

$$f_{\mathbf{k}} = f_{\mathbf{k}}^{0} - \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. \frac{\partial f_{\mathbf{k}}}{\partial T} \nabla T - \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. (-e) \frac{f_{\mathbf{k}}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E}$$
(2.52)

If we consider that the steady state is a small deviation from the local equilibrium distribution function, we have $f_{\mathbf{k}} \approx f_{\mathbf{k}}^0$ and we can express the derivatives

$$\mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_{\mathbf{k}}}{\partial T} \nabla T \approx \mathbf{v}_{\mathbf{k}} \cdot \frac{\partial f_{\mathbf{k}}^{0}}{\partial T} \nabla T = \mathbf{v}_{\mathbf{k}} \cdot \left(-\frac{\epsilon_{\mathbf{k}} - \mu}{T}\right) \frac{\partial f_{\mathbf{k}}^{0}}{\partial \epsilon_{k}} \nabla T$$
(2.53)

$$\mathbf{v}_{\mathbf{k}}.(-e)\frac{f_{\mathbf{k}}}{\partial\epsilon_{\mathbf{k}}}\mathbf{E}\approx\mathbf{v}_{\mathbf{k}}.(-e)\frac{f_{\mathbf{k}}^{0}}{\partial\epsilon_{\mathbf{k}}}\mathbf{E}$$
(2.54)

We now have a linearized Boltzmann equation:

$$f_{\mathbf{k}} = f_{\mathbf{k}}^{0} - \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. \frac{\partial f_{\mathbf{k}}^{0}}{\partial T} \nabla T - \tau_{\mathbf{k}} \mathbf{v}_{\mathbf{k}}. (-e) \frac{f_{\mathbf{k}}^{0}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E}$$
(2.55)

Now, if we express the thermal current \mathbf{Q} and the electric current \mathbf{J} in term of the steady state electronic distribution $f_{\mathbf{k}}$, only considering electronic transport, we have:

$$\mathbf{J} = \frac{1}{\Omega}(-e)\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} = \frac{1}{\Omega}(-e)\sum_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \tau_{\mathbf{k}} \left[e \frac{\partial f_{\mathbf{k}}^{0}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E} - \frac{\partial f_{\mathbf{k}}^{0}}{\partial T} \nabla T \right]$$
(2.56)

$$\mathbf{Q} = \frac{1}{\Omega} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} f_{\mathbf{k}} = \frac{1}{\Omega} \sum_{\mathbf{k}} \epsilon_{\mathbf{k}} \mathbf{v}_{\mathbf{k}} \tau_{\mathbf{k}} \left[\frac{\partial f_{\mathbf{k}}^{0}}{\partial T} \nabla T - e \frac{\partial f_{\mathbf{k}}^{0}}{\partial \epsilon_{\mathbf{k}}} \mathbf{E} \right]$$
(2.57)

where Ω is the unit cell volume of the crystal. Expressions (2.56) and (2.57) show that the coefficients L_{EE} , L_{ET} , L_{TE} and L_{TT} in equations (2.47) and (2.48) can be

calculated from the derivatives of the energies and the derivative of the equilibirum distribution. As $\frac{\partial f_{\mathbf{k}}^{0}}{\partial \epsilon_{\mathbf{k}}}$ takes significative values around the Fermi level, the electrons who contributes to the conductivity are those with energies around the Fermi level.

As the different transport properties can be anisotropic, they need to be expressed as tensors. Similarly to the density of states, the conductivity distribution tensor is a distribution over the energies, is defined in equation (2.58) and is the contribution to the conduction of electrons with an energy ϵ :

$$\sigma_{\alpha\beta}(\epsilon) = e^2 \sum_{\mathbf{k}} \tau_{\mathbf{k}} v_{\alpha}(\mathbf{k}) v_{\beta}(\mathbf{k}) \delta(\epsilon - \epsilon_{\mathbf{k}})$$
(2.58)

Now, if we make the approximation that, for any quantum state \mathbf{k} , the relaxation time is constant, the conductivity distribution becomes

$$\sigma_{\alpha\beta}(\epsilon) = e^2 \tau \sum_{\mathbf{k}} v_{\alpha}(\mathbf{k}) v_{\beta}(\mathbf{k}) \delta(\epsilon - \epsilon_{\mathbf{k}})$$
(2.59)

From the conductivity distribution, the total transports properties can be calculated by integrating all over the energies [26]:

$$\sigma_{\alpha\beta} = \frac{1}{\Omega} \int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon) (-\frac{\partial f}{\partial \epsilon}) d\epsilon$$
(2.60)

$$\kappa^{e}_{\alpha\beta} = \frac{1}{e^2 T \Omega} \int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon) (\epsilon - \mu)^2 (-\frac{\partial f}{\partial \epsilon}) d\epsilon$$
(2.61)

$$S_{\alpha\beta} = \frac{1}{eT} \frac{\int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon)(\epsilon - \mu)(-\frac{\partial f}{\partial \epsilon})d\epsilon}{\int_{-\infty}^{+\infty} \sigma_{\alpha\beta}(\epsilon)(-\frac{\partial f}{\partial \epsilon})d\epsilon}$$
(2.62)

2.2.2 BoltzTraP software and technical details

2.2.2.1 General features

BoltzTraP is a computational tool which makes use of this theory. It is based on smooth Fourier interpolations of the band energies. The group velocities are calculated as derivatives of the energies; therefore, the band energies must be well resolved. The information about the energies are preliminary computed with Crystal09 and is taken as input of BoltzTraP. The code uses the interpolated band structure to calculate the derivatives necessary to evaluate the transport properties.

2.2.2.2 Technical details

Following the results of our various DFT calculations, the thermoelectric properties of $Ca_3Co_4O_9$ have been computed

- from an electronic band structure resolved on a 36x18x18 k-point grid;
- for chemical potentials ranging from $-2 \ eV$ to $2 \ eV$ (the Fermi level being set at $0 \ eV$),

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• for temperatures from 5 K to 600 K.

Additionnal details about the electronic band structure used as input of BoltzTraP will be explicited in Chapter 3.

Chapter 3

Results and discussion

In the present chapter we present the results we have obtained on $Ca_3Co_4O_9$. We will first describe the approximation we used to model the incommensurate crystallographic structure of the misfit compound. Then, we will present and discuss the ground state crystallographic, magnetic and electronic properties we obtained from DFT calculations, comparing what we get within different approximations. Finally, we shall presents the thermoelectric properties calculated within Boltzmann transport theory.

As explained in Chapter 1, $Ca_3Co_4O_9$ is an incommensurate crystal, while DFT codes like Crystal09 make use of periodic boundary conditions to model it in practice. Hence, it is necessary to use an approximate unit cell of the real structure. Rébola *et al* [6] performed DFT and DFT+U calculations and obtained the electronic structure of calcium cobaltite using successive rational approximants to model the incommensurate nature of the crystal. As the ratio between the two lattice parameters b_1 and b_2 is rather close to the golden ratio $1.618...^1$, they performed calculations on many approximed structure of $Ca_3Co_4O_9$ whose ratio b_1/b_2 is the ratio between two consecutive Fibonnaci numbers (*i.e.* $b_1/b_2 = F(n+1)/F(n) = 3/2, 5/3, 8/5, ...$) which resulted in an approximated unit cell of composition (Ca_2CoO_3)_{2F(n)}(CoO_2)_{2F(n+1})... As *n* increases, the ratio gets closer to its experimental value.

Similarly to Rébola *et al* [6], we computed the electronic structure of Ca₃Co₄O₉ using two approximated commensurate structures with $b_1/b_2 = 3/2$ and $b_1/b_2 = 5/3$, resulting respectively to primitive cells of composition (Ca₂CoO₃)₄(CoO₂)₆ (a unit cell containing 42 atoms) and (Ca₂CoO₃)₆(CoO₂)₁₀ (a unit cell containing 66 atoms) as shown in figure 3.1. The space group used for these two unit cells is Pm. These approximated structures will be referred to by their rational approximant and respectively labeled RA = 3/2 and RA = 5/3. Results will be presented for two functionals (LDA and B1WC), as well as the rational approximant used to model the structure as a periodic crystal. We will discuss the atomic structure, the magnetic properties, the electronic structure, and finally, the transport properties and the thermoelectric performances.

¹We remind the reader that $b_1 = b_{RS}$ and $b_2 = b_{CoO_2}$



Figure 3.1: Supercells $(Ca_2CoO_3)_4(CoO_2)_6$ (left) and $(Ca_2CoO_3)_6(CoO_2)_{10}$ (right).

3.1 Ground state properties

In this section, we discuss the ground state properties obtained from our DFT calculations. Three different sets of calculations were performed : the first within the LDA, with RA = 3/2, the second using the B1WC hybrid functional, with RA = 3/2. The good results from these calculations encouraged us to perform a third set of calcultions, still using the B1WC functional, but with RA = 5/3 this time. We will successively present the results for each set and then compare them in order to study the influence of the functional used for the exchange-correlation energy and the rational approximant used to approximate the crystallographic structure.

3.1.1 LDA calculations with RA = 3/2

Preliminary calculations were performed within the local density approximation in order to see if we can reproduce Asahi's results [23]. These calculations have only been performed with the $\frac{3}{2}$ rational approximant. Several magnetic ordering were tested as discussed in Chapter 2.

3.1.1.1 Crystallographic properties

We performed the full relaxation of the lattice parameters and the atomic positions of RA = 3/2 for different magnetic orderings (FM1, FM2, AFM1, AFM2, AFM3). The optimized lattice parameters are given in the following table 3.1. Within LDA, the results are relatively insensitive to the magnetic order. For the AFM1 calculation, relative errors on the *a* and *c* lattice parameters are respectively about -1.5% and -0.5%. These lattice parameters are underestimated, which is consistent with the usual trend of the local density approximation. The relative error on b_1 is by far the largest, being of about -5% for each calculation. The relative error on b_2 is around +2%. The biggest errors are so on the *b* parameters of the two subsystems. They come from the 3/2 approximant which is far from the value of the golden ratio, obliging the

	$\mathbf{a}(\mathrm{\AA})$	$\mathbf{b}_2(\mathrm{\AA})$	$\mathbf{b}_1(\mathrm{\AA})$	$\mathbf{c}(\mathrm{\AA})$	$\beta(^{\circ})$
Exp (300 K) [7]	4.830	2.820	4.560	10.840	98.130
$\mathrm{FM1}$	4.747	2.877	4.315	10.793	97.784
FM2	4.746	2.876	4.314	10.795	97.777
AFM1	4.762	2.876	4.314	10.789	97.837
AFM2	4.763	2.875	4.313	10.789	97.842
AFM3	4.747	2.876	4.314	10.794	97.784

Table 3.1: Experimental and optimized lattice parameters for each magnetic ordering within the local density approximation for RA = 3/2.

two layers to fit within the same unit cell, putting the rocksalt layer in compression and the CoO_2 planes in tension. The other calculations (FM1, FM2, AFM2 and AFM3) provide similar results and errors.

The structural optimization of atomic coordinates gives results listed in table 3.2 in comparison with the experimental results of Miyazaki *et al* [7]. Our results are generally in good agreement with the experimental fractional coordinates. However, the fractional coordinates of O_2 in the rocksalt-type subsystem along the **a**-axis and O_1 in the CoO₂ subsystem along the **c**-axis are rather off compared to experimental data. These errors may originate from the fact that we use an approximated unit cell, and the "experimental" atomic positions only represent a structural model.

One can see in table 3.2 that the fractional coordinates are very similar between all the magnetic phases we computed so that we can be confident in the fact that the crystallographic structure does not depend on the magnetic ordering.

3.1.1.2 Magnetic properties

We next compared the energies of the different relaxed structures for different magnetic orders of Co atoms for each subsystems. The results are summarized in table 3.3.

Despite some discrepancies, AFM1 and AFM2 actually converge toward the same solution, as FM1, FM2 and AFM3 do. As one can see in table 3.3, AFM1 is the calculation yielding the lowest total energy, and thus is assumed to be the ground state at our level of approximation. This is why in what follows, we will focus upon the ground state electronic structure yielding the antiferromagnetic order AFM1.

The magnetic moments for each cobalt atom in both subsystems are given in table 3.4. One can see that, in our calculations, the magnetic properties are mainly localized in the rocksalt type subsystem². If we perform the average over the *modulus* of the individual magnetic moments of Co atoms for the whole system, we get $\mu_{tot.}^{ave.} = 0.750 \ \mu_{\rm B}/{\rm Co}$, which is relatively far from the value measured by Masset *et al* (1.3 $\mu_{\rm B}/{\rm Co}$) [4]. It can be argued that as the rocksalt subsystem hold a non-zero effective magnetic moment (-0.048 $\mu_{\rm B}$), our AFM1 calculation tend to reproduce the ferrimagnetic state proposed for calcium cobaltite below 19 K [3, 20]. However, as explained in Chapter 2, we performed our spin-polarized calculations within the collinear

 $^{^{2}}$ The magnetic order obtained with all of our calculation is either ferromagnetic (FM1, FM2 and AFM3 yield such an order) or antiferromagnetic (AFM1 and AFM2)

System	n		FM1	FM2	AFM1	AFM2	AFM3	Exp
	Co	x/a	-0.008	-0.008	-0.009	-0.009	-0.008	0.000
		z/c	0.000	0.000	0.000	0.000	0.000	0.000
$C_{2}O_{2}$	O_1	x/a	0.357	0.358	0.356	0.356	0.357	0.363
$C00_2$		z/c	0.090	0.090	0.090	0.090	0.090	0.008
	O_2	x/a	-0.373	-0.373	-0.374	-0.374	-0.373	-0.364
		z/c	-0.091	-0.091	-0.091	-0.091	-0.091	-0.104
	Ca_1	x/a	0.172	0.172	0.173	0.173	0.173	0.182
		z/c	0.271	0.271	0.270	0.271	0.271	0.281
	Ca_2	x/a	0.311	0.311	0.312	0.312	0.311	0.312
		z/c	-0.272	-0.272	-0.272	-0.272	-0.272	-0.273
	Co	x/a	-0.302	-0.302	-0.306	-0.306	-0.302	-0.298
BS		z/c	-0.500	-0.500	-0.500	-0.500	-0.500	-0.495
105	O_1	x/a	-0.305	-0.306	-0.304	-0.304	-0.305	-0.282
		z/c	0.336	0.336	0.336	0.336	0.336	0.338
	O_2	x/a	0.295	0.294	0.299	0.300	0.295	0.183
		z/c	0.500	0.500	0.500	0.500	0.500	0.497
	O_3	x/a	-0.203	-0.203	-0.202	-0.202	-0.203	-0.163
		z/c	-0.337	-0.337	-0.337	-0.337	-0.337	-0.323

Table 3.2: Optimized fractional coordinates within LDA (RA = 3/2) and experimental data [7].

	ΔE per unit cell (meV)
$E_{FM1} - E_{AFM1}$	74.30
$E_{FM2} - E_{AFM1}$	67.49
$E_{AFM2} - E_{AFM1}$	1.7
$E_{AFM3} - E_{AFM1}$	67.06

Table 3.3: Energy differences from the spin-polarized AFM1 calculation. AFM1 yields the lowest total energy.

approximation, it is therefore impossible to obtain the incommensurate spin density wave in the CoO_2 subsystem as observed in experiments [3, 20]. The latter is nevertheless expected to have no significant effect on the properties of interest in this work.

3.1.1.3 Electronic properties

We then investigated the electronic properties of $Ca_3Co_4O_9$ by plotting the band structure (figure 3.2) and the density of states around the Fermi level (figure 3.3, the positive values are for the majority spin channel, the negative values are for the minority spin channel), for the magnetic phase AFM1. In the band structure, the full black bands are fully populated, the full red bands are partly occupied, and the black dashed bands are unoccupied. As one can see in both figures, there is no band gap across the Fermi

AFM1							
CoO_2	$\mu_s(\mu_B)$	RS	$\mu_s(\mu_B)$				
Co1-1	-0.035	Co1-1	1.892				
Co1-2	-0.023	Co1-2	1.733				
Co2-1	-0.023	Co2-1	-1.836				
Co2-2	-0.044	Co2-2	-1.836				
Co3-1	-0.044						
Co3-2	-0.030						
Average	-0.033		-0.012				

Table 3.4: Individual magnetic moments for Co atoms belonging to the CoO₂ and rocksalt-type subsystem computed within the local density approximation, with RA = 3/2, for the AFM1 magnetic structure.

level and therefore, our LDA calculation suggests that calcium cobaltite is a metal.

To further study the electronic structure, and in regards to Takeuchi *et al*'s results about the role of the *d* orbitals of Co atoms in the conduction properties [22], we plotted the partial density of states projected into *d* orbitals of Co for both CoO₂ and rocksalt subsystems (figure 3.4 and 3.5), resolved in local axis oriented along the octahedra in the two different subsystems³. The Fermi level E_F is shown with the vertical dashed lines.

One can see that the contribution around the Fermi level comes from those d orbitals from both subsystems. However, the contribution at E_F mainly comes from the rocksalt subsystem, which is coherent with Asahi *et al* and Rébola *et al*'s LDA calculations [6, 23], but ultimately fails to reproduce the experimental results of Takeuchi *et al* [22] who found very little, if any, contribution from the rocksalt at the Fermi level: they reported that, like Na_xCoO₂, the main contribution around the Fermi level comes from the *d* orbitals of Co atoms in the CoO₂ subsystem.

However, the splitting [24] between of the 3d orbitals of Co in the CoO₂ as t_{2g} (blue plots in figure 3.4) and e_g orbitals is well obtained (around 1.2 eV): the d_{xy} and d_{xz} orbitals are mainly occupied, the d_{yz} is not fully occupied, and the d_{z^2} and $d_{x^2-y^2}$ are not occupied. The d_{yz} is the one holding the hole involved in the electrical conduction, in agreement with Klie *et al*'s experiments [17] and with Soret and Lepetit's quantum chemistry calculations [24].

With these results, we confirm the failure of the local density approximation to yield the correct electronic structure so we did not compute the thermoelectric properties within this approximation.

 $^{^{3}}$ Co atoms are at the center of oxygen octahedra in both layers. In order to resolve the individual d contributions, we used a set of local cartesian coordinates, aligned along the O-Co-O diagonals. In practice, after structural relaxation the octahedra are deformed and the diagonals not exactly orthogonal anymore. Thus, we consider a set of local cartesian coordinates that display good average alignment with the diagonals.



Figure 3.2: Electronic band structure of $Ca_3Co_4O_9$ (AFM1) obtained within the local density approximation with RA = 3/2, for each spin channel.



Figure 3.3: Total density of states of $Ca_3Co_4O_9$ (AFM1) obtained within the local density approximation with RA = 3/2, for each spin channel.



Figure 3.4: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the CoO₂ subsystem for the LDA calculation AFM1 with RA = 3/2. The states of the t_{2g} bands are the blue curves.



Figure 3.5: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the rocksalt subsystem for the LDA calculation AFM1 with RA = 3/2.

3.1.2 B1WC calculations with RA = 3/2

Then, we decided to use the B1WC hybrid functional to treat the electronic structure of $Ca_3Co_4O_9$. Our choice is motivated by the success [39] of B1WC to treat materials containing manganese which is a transition metal such as Co. The main problem is that cobalt presents 3d orbitals which are spatially localized: within the hybrid functional formalism, we ought to better treat exchange effects on these orbitals. Using exactly the same input parameters we used for the LDA calculations and still using the rational approximant 3/2, we let the lattice, the atomic positions and the electronic structure relax from different starting points as described by the previous chapter. Only FM2 and AFM1 managed to converge.

3.1.2.1 Crystallographic properties

The optimized and experimental lattice parameters are given table 3.5. The AFM1

	$\mathbf{a}(\mathrm{\AA})$	$\mathbf{b}_2(\mathrm{\AA})$	$\mathbf{b}_1(\mathrm{\AA})$	c(Å)	$\beta(^{\circ})$
Exp (300 K) [7]	4.830	2.820	4.560	10.840	98.130
FM2	4.822	2.861	4.292	10.924	97.924
AFM1	4.827	2.863	4.295	10.919	97.933

Table 3.5: Experimental and optimized lattice parameters for each calculations using the B1WC functional for the exchange-correlation energy, with RA = 3/2.

results are globally closer to the experimental values compared to the FM2 ones. The AFM1 calculation yields for the β parameter a result very close to the experimental value, underestimated by 0.2%. The *a* parameter is underestimated by 0.1% while the *c* parameter is overestimated of 0.7%. On the other hand, the relaxed b_2 and b_1 parameters show larger deviations from the experimental values, respectfully overestimated by 1.5% and underestimated by 6%. The similarity with LDA results confirm that the bad estimation of b_1 and b_2 is not a problem of functional but rather inherent to the 3/2 approximant that is relatively far from the value of the golden ratio.

The structural optimization AFM1 and FM2 yield results listed in table 3.6 and are compared to the experimental values of Miyazaki [7]. The agreement of our results with the experimental fractional coordinates is reasonable within a few percents. Once again, the fractional coordinates of O_2 in the rocksalt-type subsystem along the **a**-axis and O_1 in the CoO₂ subsystem along the **c**-axis are rather off compared to experimental data, which can be explained by our structural approximation. One can also observe that the optimized crystallographic structure is totally independent of the magnetic order.

Finally, the use of the hybrid functional B1WC allowed us to obtain more accurate lattice parameters of $Ca_3Co_4O_9$ in comparison to the experiment, but unfortunately we were not able to correct the errors we already had with the LDA calculations and that are related to the rational approximant. Overall, the choice of the exchange-correlation functional does not seem to affect the agreement of the computed structures with the experimental ones.

Subsystem			FM2	AFM1	Exp
	Co	x/a	-0.007	-0.007	0.000
		z/c	-0.001	-0.001	0.000
$C_{2}O_{2}$	O_1	x/a	0.357	0.357	0.363
COO_2		z/c	0.091	0.091	0.008
	O_2	x/a	-0.371	-0.371	-0.364
		z/c	-0.092	-0.092	-0.104
	Ca_1	x/a	0.171	0.171	0.182
		z/c	0.265	0.265	0.281
	Ca_2	x/a	0.314	0.313	0.312
		z/c	-0.266	-0.266	-0.273
	Co	x/a	-0.302	-0.304	-0.298
BS		z/c	-0.500	-0.500	-0.495
100	O_1	x/a	-0.302	-0.301	-0.282
		z/c	0.339	0.339	0.338
	O_2	x/a	0.282	0.285	0.183
		z/c	0.500	0.500	0.497
	O_3	x/a	-0.200	-0.199	-0.163
		z/c	-0.340	-0.340	-0.323

Table 3.6: Optimized fractional coordinates within B1WC (RA = 3/2) and experimental data [7].

3.1.2.2 Magnetic properties

As mentionned earlier, our calculations were performed starting from several initial configurations for all Co atoms in both subsystems, as described in Chapter 2, and only FM2 and AFM1 managed to converge. In terms of relative energy between FM2 and AFM1, we got the following result: AFM1 has an energy 62.94 meV lower than FM2, which is consistent with what Asahi *et al* previously found [23] and our previous LDA calculations. Thus, we shall once again focus on the AFM1 structure.

Table 3.7 displays the effective magnetic moments for Co atoms in both CoO_2 and Ca_2CoO_3 subsystems.

With our calculations performed with the B1WC hybrid functional, we obtained effective magnetic moments for Co atoms belonging to the CoO₂ subsystem close to zero. We find an average over the modulus of the individual magnetic moments for Co atoms belonging to the rocksalt-type subsystem close to what Rébola [6] obtained with his DFT+U calculations (around 2.65 $\mu_{\rm B}$). If we perform the average over the modulus of the individual magnetic moments of Co atoms for the whole system, we get $\mu_{tot.}^{ave.} = 1.055 \ \mu_{\rm B}/\text{Co}$, which is quite close to the value measured by Masset *et* al (1.3 $\mu_{\rm B}/\text{Co}$) [4]. Once again, we can argue that the antiferromagnetic ordering and the resulting net magnetic moment in the rocksalt subsystem due to Co atoms (-0.135 $\mu_{\rm B}$) is in line with the ferrimagnetic phase observed below 19 K [3, 20], and one can see that its value increased from our LDA calculation, and this can be attributed to the better treatement of the exchange-correlation energy expected from the hybrid

AFN	Л1	
$\mu_s(\mu_B)$	\mathbf{RS}	$\mu_s(\mu_B)$
0.000	Co1-1	2.870
0.000	Co1-2	2.334
0.000	Co2-1	-2.669
0.001	Co2-2	-2.669
0.001		
0.000		
0.001		-0.034
	$\begin{array}{c} \mu_s(\mu_B) \\ 0.000 \\ 0.000 \\ 0.000 \\ 0.001 \\ 0.001 \\ 0.000 \\ 0.001 \end{array}$	$\begin{array}{c c} \mu_s(\mu_B) & \text{RS} \\ \hline 0.000 & \text{Co1-1} \\ 0.000 & \text{Co1-2} \\ 0.000 & \text{Co2-1} \\ 0.001 & \text{Co2-2} \\ 0.001 \\ \hline 0.000 & \hline \end{array}$

Table 3.7: Individual magnetic moments for Co atoms belonging to the CoO_2 and rocksalt-type subsystem computed with the B1WC functional, with the 3/2 structural approximation.

functional formalism.

3.1.2.3 Electronic properties

In order to gain insight into the transport properties of $Ca_3Co_4O_9$, we plotted the band structure around the Fermi level E_F (figure 3.6 for AFM1), as well as the density of states (figure 3.7). The horizontal dashed line is the Fermi level, the full bands are the occupied states and the dashed bands are the unoccupied states.

The AFM1 band structure displays bands far from E_F that are the same for both spin channels. However, near E_F , the bands disperse differently for each spin channels. The majority spin band structure present a gap of 1.25 eV, whereas the minority spin channel has a band dispersing across E_F (red band in figure 3.6), therefore this B1WC calculation predict a half-metallic behavior. This result is in agreement with Rébola *et al*'s DFT+U calculations. Both spin channels taken into account, it seems that we have a small gap just above the last partly occupied band, which could be related to the gap predicted by Takeuchi *et al* [22]. However, a single band disperse across the Fermi level, therefore, our system is predicted as a conductor, as our LDA calculations predicted.

To further investigate the electronic structure, we plotted partial density of states projected into d orbitals of Co for both subsystems in the same fashion we did in the previous subsection (figure 3.8 and 3.9). The Fermi level E_F is displayed with the vertical dashed lines.

It turns out that the main energetic contributions near the Fermi level are from the 3d orbitals of Co atoms in the CoO₂ subsystem and no contribution of the 3d orbitals of Co atoms in the rocksalt-type subsystem is found, contrary to what is obtained in LDA and which is in agreement both with Takeuchi's experiment [22] and Rébola *et al*'s DFT+U calculations [6]. However, in contrast with Rébola's *et al*'s calculations, we find as near as zero contribution of the *d* orbitals of Co atoms in the CoO₂ subsystem at the exact Fermi energy.

As one can see, the density of states below the Fermi level mainly originates from the t_{2g} bands, while the e_g bands lies about 3.3 eV above the Fermi level and are



Figure 3.6: Electronic band structure of $Ca_3Co_4O_9$ (AFM1) calculated with the B1WC functional for RA = 3/2, for each spin channel.



Figure 3.7: Density of states of $Ca_3Co_4O_9$ (AFM1) calculated with the B1WC functional for RA = 3/2.



Figure 3.8: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the CoO₂ subsystem. Calculations performed within the B1WC functional (AFM1) with RA = 3/2. The blue curves designs the t_{2g} bands.



Figure 3.9: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the rocksalt type subsystem. Calculations performed within the B1WC functional (AFM1) with RA = 3/2.

mainly unoccupied as predicted by the crystal field theory. The t_{2g} bands are close to E_F of about 0.5 eV and therefore should contribute to the transport properties.

As one could notice in the LDA results, the splitting [24] between of the 3*d* orbitals of Co in the CoO₂ as t_{2g} (blue plots in figure 3.8) and e_g orbitals is once again obtained (around 3.6 eV): the d_{xy} and d_{xz} orbitals are almost fully occupied, the d_{yz} is not fully occupied, and the d_{z^2} and $d_{x^2-y^2}$ are mainly unoccupied. The d_{yz} orbital is the one holding the hole involved in the electrical conduction, which could be seen as the a_{1g} orbital obtained from Soret *et al*'s quantum chemistry calculations [24].

3.1.3 B1WC calculations with RA = 5/3

Following our calculations on the approximated commensurate structure with RA = 3/2, in the same fashion Rébola *et al* proceeded [6], we decided to compute the properties of the approximated commensurate crystal with RA = 5/3, still using the B1WC functional for the exchange-correlation. This time, only the antiferromagnetic structure (AFM1) was relaxed since it was observed to be the ground state with the $\frac{3}{2}$ approximant.

3.1.3.1 Crystallographic properties

As we did with our previous calculations, we fully relaxed the lattice, atomic positions and electronic structure. The optimized lattice parameters are given in table 3.8.

	a(Å)	$\mathbf{b}_2(\mathrm{\AA})$	$\mathbf{b}_1(\mathrm{\AA})$	c(Å)	$\beta(^{\circ})$
Exp (300 K) [7]	4.830	2.820	4.560	10.840	98.130
AFM1	4.821	2.756	4.593	10.876	98.12

Table 3.8: Experimental and optimized lattice parameters for each calculations using the B1WC hybrid function with RA = 5/3.

One can see that the optimized values are overall closer to the experimental values. We have errors of -0.01 % on β , -0.18 % on a, -2.27 % on b_2 , 0.72 % on b_1 and 0.33 on c. The biggest errors are still on the b parameters. But these results are much closer to the experimental data than our previous results with the 3/2 approximant.

The optimized fractional coordinates within Miyazaki's model [7] are listed in table 3.6 and are compared to the experimental data. All the values except the fractional coordinates of O_2 in the rocksalt-type subsystem along the **a**-axis and O_1 in the CoO₂ subsystem along the **c**-axis are close to the experimental values. The use of a bigger supercell does not manage to correct the errors we already had with the $\frac{3}{2}$ approximant, which are attributed to Miyazaki *et al*'s model [7] which does not take into account the incommensurate nature of the real system.

3.1.3.2 Magnetic properties

The magnetic moments for each cobalt in both subsystems are given in table 3.10.

If we perform the average over the *modulus* of the individual magnetic moments of Co atoms for the whole system, we get $\mu_{tot.}^{ave.} = 1.013 \ \mu_{\rm B}/{\rm Co}$, which is a bit lower

Subsystem			AFM1	Exp
	Co	x/a	-0.007	0.000
		z/c	-0.001	0.000
$C_{2}O_{2}$	O_1	x/a	0.355	0.363
000_{2}		z/c	0.092	0.008
	O_2	x/a	-0.369	-0.364
		z/c	-0.094	-0.104
	Ca_1	x/a	0.170	0.182
		z/c	0.270	0.281
	Ca_2	x/a	0.313	0.312
		z/c	-0.271	-0.273
	Co	x/a	-0.225	-0.298
BS		z/c	-0.501	-0.495
103	O_1	x/a	-0.302	-0.282
		z/c	0.340	0.338
	O_2	x/a	0.292	0.183
		z/c	0.499	0.497
	O_3	x/a	-0.199	-0.163
		z/c	-0.341	-0.323

Table 3.9: Optimized fractional coordinates within B1WC (RA = 5/3) and experimental data [7].

AFM1			
CoO_2	$\mu_s(\mu_B)$	RS	$\mu_s(\mu_B)$
Co1-1	-0.004	Co1-1	2.330
Co1-2	-0.001	Co1-2	2.830
Co2-1	-0.001	Co2-1	2.830
Co2-2	0.021	Co2-1	-2.285
Co3-1	0.021	Co3-1	-2.285
Co3-2	-0.002	Co3-2	-2.762
Co4-1	-0.002		
Co4-2	0.021		
Co5-1	0.021		
Co5-2	0.789		
Average	0.086		0.110

Table 3.10: Individual magnetic moments for Co atoms belonging to the CoO₂ and rocksalt-type subsystem computed with the B1WC functional, with RA = 5/3.

than what we had with the B1WC - RA = 3/2 calculation, but still close to the value measured by Masset *et al* (1.3 $\mu_{\rm B}/{\rm Co}$) [4]. One can see once again that, in our calculation, all the magnetic properties are held within the rocksalt subsystem, which hold an antiferromagnetic coupling between the Cobalt atoms, but with a non-

zero total effective magnetic moment (0.659 $\mu_{\rm B}$), and thus tends to reproduce the ferrimagnetic state observed in the Ca₂CoO₃ below 19 K [3, 20]. However, the Co in the CoO₂ subsystem have mostly weak effective magnetic moments, which nonetheless improve in magnitude in comparison to our study of the $\frac{3}{2}$ supercell within B1WC. One can notice that a single cobalt possesses a high magnetic moment of 0.789 $\mu_{\rm B}$. This could be explained by the mixed valences Co³⁺ and Co⁴⁺ in the CoO₂ subsystem: as shown in figure 1.15, the Co⁴⁺ ions are holding a single electron in the a_{1g} orbital, which results in a net magnetic moment for this atom. It seems consistent with the mixture of Co³⁺ and Co⁴⁺ proposed by Yang *et al* [19].

3.1.3.3 Electronic properties

In order to gain insight into the influence of the approximant on the electronic structure, we plotted the band structure around the Fermi level E_F (figure 3.10) and the density of states as well (figure 3.11). The horizontal dashed line is the Fermi level, the full bands are the occupied states and the dashed bands are the unoccupied states.

The band structure for the majority spin channel has a gap of about 0.5 eV above the last occupied band, yet the minority spin channel has its last occupied band slightly dispersing across the Fermi level, confirming the half-metallic character of our compound computed with the B1WC functional.

To further investigate the electronic properties of the 5/3 structure, we plotted partial density of states projected into d orbitals of Co for both subsystems in the same fashion we did in the previous subsections (figure 3.12 and 3.13). The Fermi level E_F is displayed with the vertical dashed lines.

The results are similar to what we presented in the previous subsection, except that this time, there is an even stronger contribution of the 3d orbitals of Co from the CoO₂ subsystem which contributes to the Fermi level.

The splitting between the 3*d* orbitals of Co in the CoO₂ as t_{2g} (blue plots in figure 3.12) and e_g orbitals is once again obtained (around 3.6 eV), and we retrieve somehow the population observed in the $\frac{3}{2}$ structure: the d_{xy} and d_{xz} orbitals are fully occupied, the d_{yz} is not fully occupied, and the d_{z^2} and $d_{x^2-y^2}$ are majorly unoccupied. The d_{yz} is holding the hole involved in the electrical conduction, and thus cements the results of Takeuchi *et al* [22],Klie *et al* [17], Soret and Lepetit [24].

3.1.4 DFT calculations : conclusions

We performed a set of LDA calculations (with RA = 3/2), and while the resulting crystallographic and magnetic properties are somewhat close to experimental results in spite of some errors on the individual b_1 and b_2 lattice parameters of the two subsystems, the electronic structure is not in agreement experimental results. Previous LDA calculations [6, 23] yielded the same errors, and we can therefore conclude that the local density approximation fail to yield the correct electronic structure.

Then, using the same structure RA = 3/2, we switched the exchange-correlation functional from LDA to B1WC, allowing us to better treat exchange effects. The crystallographic and magnetic properties obtained from this set of calculations are closer to the experimental observations, and this time the electronic structure is in good



Figure 3.10: Electronic band structure of $Ca_3Co_4O_9$ (AFM1) with RA = 5/3, for each spin channel.



Figure 3.11: Total density of states of $Ca_3Co_4O_9$ (AFM1) obtained with the B1WC functional with RA = 5/3.



Figure 3.12: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the CoO₂ subsystem. Calculations performed within the B1WC functional (AFM1) with RA = 5/3. The blue curves designs the occupied states.



Figure 3.13: Spin-up (positive values) and spin-down (negative values) partial density of states projected into d orbitals of Co atoms in the rocksalt type subsystem. Calculations performed within the B1WC functional (AFM1) with RA = 5/3.

agreement with Takeuchi *et al*'s experiment [22]. The B1WC functional is therefore a good alternative to the Hubbard correction used in DFT+U calculations.

Finally, still using the B1WC hybrid functional, we switched the approximated crystallographic structure from RA = 3/2 to RA = 5/3. This allows us to better treat the crystallographic properties, as the lattice parameters b_1 and b_2 are now closer to their experimental values. In term of magnetic properties, a stronger magnetic moment arises from a cobalt atom in the CoO₂ subsystem, which can be related to the mixed valence observed in that subsystem [19], but the rest of the magnetic moment are relatively close to what has been observed in the RA = 3/2 structure. In terms of electronic properties, we do obtain an even better agreement with Takeuchi *et al* experiment, as more Co-3d states contributes to the density of states around the Fermi level. Therefore, increasing the size of the supercell proves to be a good way to better treat the individual lattice parameters and to give better insight upon the magnetic properties localized in the CoO₂ subsystem.

While we did perform the B1WC calculations both with the RA = 3/2 and RA = 5/3 supercells, we shall also discuss the importance of the incommensurate nature of the compound. Unlike Asahi *et al*, Rébola *et al* approximed different primitive cells for Ca₃Co₄O₉, increasing in volume as the rational approximant get closer to the golden ratio. However, this method is computionally intensive and would require too much time. During our calculations using the $\frac{3}{2}$ approximant, we noticed that translating the rocksalt-type structure of $\frac{1}{4}$ **b** along the **b** direction (**b** being the lattice parameter of the approximated unit cell) gave the same structure as before, but with inversed **a**-axis and **c**-axis as shown in figure 3.14.



Figure 3.14: Our approximated RA = 3/2 supercell, with the rocksalt subsystem untranslated (left) and translated along the **b**-axis of $\frac{b}{4}$ (right).

DFT calculations on this new structure yield the same total energy and the same density of states. Seeing these results, we decided to play with the position of the rocksalt-type subsystem, translating it along the **b** direction, and to study its influence

upon the electronic properties. The calculations were performed using the configuration yielding the lowest energy, AFM1. Taking the optimized structure and fixing it, we successively translated the rocksalt-type subsystem of $\frac{1}{16}$ **b**, $\frac{1}{8}$ **b**, and $\frac{1}{4}$ **b**.

As one can see in figure 3.15, the relative positions of the two subsystems along **b** does not affect much the density of states, and the contributions from the 3d bands of Co stay at the same levels of energy. This would means that the transport properties due to the electronic structure should not depend on the relative positions of the two subsystems along **b**. Rébola also observed that the role of the rational approximant did not affect much the density of states [6]. We can conclude from our calculations that the relative positions of the CoO₂ and rocksalt type subsystems does not affect much the electronic structure of Ca₃Co₄O₉, and the incommensurate character of the compound does not seem to affect the electronic properties.

3.2 Thermoelectric properties

While Ca₃Co₄O₉ generates increasing interest as a thermoelectric compound, there has been to date only a restricted number of experimental characterization of its thermoelectric properties, and even less theoretical studies, the latter being restricted to a characterization of the Seebeck coefficient in the framework of the Heikes formula [6, 23, 24]. Here, we decided to go one step further and the present section is devoted to the first extensive theoretical investigation of the transport and thermoelectric properties of Ca₃Co₄O₉ using Boltzmann transport formalism. As it is rather difficult to obtain the lattice contribution to the thermal conductivity κ_l , we are unable to study the figure of merit $ZT = \frac{S^2 \sigma T}{\kappa_l + \kappa_e}$ from our calculations. Instead, we will focus here on the power factor $S^2 \sigma$, and its individual contributions S and σ .

As the electronic structure with the B1WC functional on the RA = 3/2 proved itself to be consistent already with experiments, we decided to perform calculations with BoltzTraP on this structure and to obtain the thermoelectric properties as a function of temperature and chemical potential.

3.2.1 Seebeck coefficient and power factor with respect to chemical potential

First, we discuss the behavior of the Seebeck coefficient with respect to the chemical potential, at different temperatures (figure 3.16) as well as the Power Factor $S^2\sigma$ (figure 3.17). These quantities are in fact tensors: Ca₃Co₄O₉ is displays strongly anisotropic transports properties [4], related to its layered misfit structure. Hence, the different components of the Seebeck and resistivity tensors are different. As the interesting transport properties are expected to occur along the CoO₂ planes, in the following discussion, we will only focus on the averaged in-plane quantities that are also those that are experimentally measured.

BoltzTraP can only yield the electrical conductivities time the inverse of the relaxation time τ , whereas we have direct access to the Seebeck coefficient, as seen in equations (2.61) and (2.62). In order to estimate the relaxation time, we can fit our calculated restistivity in order to reproduce the experimental value at a given temper-



ature. We did so, using the experimental in-plane resistivity obtained at 300 K by Masset*et al* [4] for an undoped compound. This give us an estimate $\tau \approx 2.86 \times 10^{-16} s$, which we consider constant at our level of approximation in the following discussion.



Figure 3.16: Seebeck coefficient in function of chemical potential at temperatures from 100 K to 600 K.



Figure 3.17: Power factor in function of chemical potential at temperatures from 100 K to 600 K.

The Seebeck coefficient is reported in figure 3.16. Depending on the chemical potential, the temperature dependence of S is can be absolutely different. At the Fermi level ($\mu = E_F$), the Seebeck coefficient is positive as the intrinsic charge carriers are holes.

A better insight upon the thermoelectric performance can be obtained by looking at the power factor (figure 3.17). At the $\mu = E_F$, we have $S^2 \sigma \approx 3 \ \mu \text{Wcm}^{-1}\text{K}^{-2}$ at room temperature, a value that could be even increased to 4.8 $\mu \text{Wm}^{-1}\text{K}^{-2}$ by appropriate hole doping. This is sizeable, although significantly below what can be observed in Bi₂Te₃ ($PF \approx 40-50 \ \mu \text{Wcm}^{-1}\text{K}^{-2}$ at 300 K), one of the best thermoelectric available. Interestingly however in Ca₃Co₄O₉, the global trend in the range [-0.25 eV,+0.85 eV] is that the power factor increases as a function of temperature, which is not the case with Bi₂Te₃ [11]. This behavior combined with the chemical stability of Ca₃Co₄O₉ at high temperatures confirm the potential interest of this compound for pratical applications.

We also notice the presence of a wide peak beyond the Fermi level, which yield even higher values than the ones located below the Fermi level. This highlights that $Ca_3Co_4O_9$, although previously overlooked, could also be a good n-type thermoelectric when appropriately doped with electrons.

3.2.2 Intrinsic $Ca_3Co_4O_9$

Let us now investigate more explicitly the temperature dependence of the transport coefficients. Experimentally, specimens of $Ca_3Co_4O_9$ are synthetized without explicit doping and experimental studies performed since the discovery of $Ca_3Co_4O_9$ focused upon the temperature dependence of the thermoelectric properties, rather than trying to optimize them with doping. As a first attempt we will so compare to experiment looking at the temperature dependence of the Seebeck coefficient and the electrical resistivity calculated for the intrinsic compound.

We did so by investigating the evolution of these coefficients with respect to the temperature at the Fermi level ($\mu = E_F$). First, let us analyze the behavior of the Seebeck coefficient reported in figure 3.18. We have a value of $S = 225 \ \mu \text{VK}^{-1}$ at 300 K which is consistent with precedent calculations performed by Rébola *et al* who obtained, based on their LDA+U results and using the Heikes formula, a Seebeck coefficient of 233 μVK^{-1} [6]. The behavior of our calculated Seebeck coefficient is strikingly similar to prior measurements as one can see in figure 1.10. Unfortunately, the order of magnitude is almost twice as large as what has been measured: all previous experiments found values around 125 μVK^{-1} [2–4].

We also report the temperature dependence of the electrical resistivity at the Fermi level. As one can see in figure 3.19, the highly anisotropic behavior observed by Masset *et al* [4] is well reproduced as the out-of-plane resistivity is at least one order of magnitude larger than the in-plane resistivity (see figure 1.11). However, the computed inplane resistivity ρ_{ab} completely fails to present the anomalous temperature dependence seen in measurements. One could wonder if this is related to the insulating-conducting phase transitions observed below room temperature, and that fails to appear in our theoretical curve. On the other hand, we can question if the as-grown samples used in experimental studies are really intrinsic or if they present self-doping which can affect the chemical potential.

The transport properties happens to be extremelly dependent on the chemical potential, and we have no means to know this parameter for the experiments reported in the litterature. However, the chemical potential is related to the number


Figure 3.18: Seebeck coefficient in function of temperature when $\mu = E_F$.

of charge carriers. From measurements of the Hall resistivity at room temperature $(R_H(300K) \approx 7.6 * 10^{-9} m^3 C^{-1})$ by Limelette *et al* [5] and using the following formula:

$$R_H = \frac{1}{ne} \tag{3.1}$$

where n is the concentration of charge carriers and e the value of a single charge, we estimate the concentration of charge carriers in Limelette et al's sample around $8.22 * 10^{20}$ cm⁻³ at room temperature. Although the result given by this formula is a simple estimate and should not be taken as the exact value⁴. It is two orders of magnitude larger than the calculated concentration of intrinsic charge carriers is $n_{300K}^{E_F} = 5.41 * 10^{18}$ cm⁻³ at room temperature. This strongly support the idea that as-grown crystals are not intrinsic but strongly self-doped with holes. Comparison with experimental data should therefore be perfomed at lower chemical potential holding higher concentrations of holes.

3.2.3 Hole-doped $Ca_3Co_4O_9$

In order to get better insight on how to correctly reproduce the experimental behavior, we decide to look below the Fermi level where concentration of holes is closer to $8.22 * 10^{20} \text{ cm}^{-3}$. If one take a look at figure 3.16, it appears that around $\mu - E_F = -0.062 \text{ eV}$, the Seebeck coefficient at room temperature actually corresponds to the experimental value of 125 μVK^{-1} . At this chemical potential, the concentration of charge carriers

⁴The use of this formula should be taken with caution since the concentration of the charge carriers in oxides is known to be greatly temperature dependent, which is not properly taken into account in this formula. The physics behind this temperature dependence is not yet known and unfortunately no better estimation of the carrier concentration can be achieved to date.



Figure 3.19: Seebeck coefficient in function of temperature when $\mu = E_F$.

at room temperature is equal to $5.19 * 10^{19} \text{ cm}^{-3}$, which is still about one order of magnitude below what we estimated for Limelette *et al*'s sample, but much closer (as said previously, there is a huge uncertainty on this estimated value).

We report the temperature dependence of S at $\mu - E_F = -0.062$ eV to see if it actually behaves as what has been observed experimentally. We do find the value of



Figure 3.20: Seebeck coefficient in function of temperature at different chemical potentials.

 $S = 131 \ \mu \text{VK}^{-1}$ at 300 K, which is consistent with the experimental data. The global behavior of the Seebeck coefficient is still rather similar to the experimental one and

we even manage to retrieve a jump around 25 K. However, the plateau between 100 K and 300 K is less pronounced than what is actually observed. The figure also report the Seebeck coefficient at $\mu - E_F = -0.075$ eV. The concentration of charge carriers at this chemical potential is still equal to 5.19×10^{19} cm⁻³. The temperature dependence of the Seebeck coefficient is the same as the the previous case.

In a similar fashion, we plotted the temperature dependence of the in-plane electrical resistivity ρ_{ab} (figure 3.21). This time, the in-plane resistivity displays a behavior



Figure 3.21: In-plane resistivity as a function of temperature at different chemical potentials.

in much better qualitative agreement with what is observed in experiments, suggesting that the non-monotonic behavior observed experimentally, which was attributed to magnetic and structural phase transitions, can actually be intrinsic to the the ground state phase. Such bold claim would require further investigation in order to be validated.

Although more systematic investigations should be performed, it seems that, by playing with the chemical potential, we can reproduce the global behavior of the power factor. In figures 3.20 and 3.21, one can see that the temperature dependence of the Seebeck coefficient and the in-plane resistivity ρ_{ab} is strongly correlated to the chemical potential, and thus the concentration of charge carriers : at $\mu - E_F = -0.056$ eV $(n_{300K} = 4.44 * 10^{19} \text{ cm}^{-3})$, the behavior of the in-plane resistivity around 0 K is completely inaccurate, despite a number of charge carriers close to what we have at -0.062 eV and -0.075 eV.

3.2.4 Thermoelectric properties - Conclusions

In conclusion, despite the the difficulty to make direct comparisons with experimental data related to the strong dependence upon the concentration of charge carriers and our lack of informations about the specimens used in previous experiments, we managed to qualitatively reproduce, at our level of approximation, the behavior of the Seebeck coefficient and the electrical resistivity with respect to the temperature within Boltzmann transport theory.

We observe that at room temperature, the power factor of Ca₃Co₄O₉ cannot directly compete with Bi₂Te₃ (PF_{Ca₃Co₄O₉ (300K) $\approx 3-4 \,\mu \text{Wcm}^{-1}\text{K}^{-2}$, PF_{Bi₂Te₃}(300K) $\approx 40-50 \,\mu \text{Wcm}^{-1}\text{K}^{-2}$), but is large enough to generate interest: our results predict that the compound can be used both as a p-type and n-type thermoelectric. Moreover, the increasing behavior of the power factor with respect to the temperature allows Ca₃Co₄O₉ to be a good alternative to Bi₂Te₃ for high temperature applications.}

By playing with the chemical potential, we can also observe that the qualitative anomalous behavior of the in-plane resistivity is reproduced, suggesting that it is intrinsic to the ground state phase, whereas previous research groups suggested various phase transitions as the origin of this peculiar behavior.

The next logical step will be to validate these findings on the RA = 5/3 structure.

Conclusions and perspectives

The misfit calcium cobaltite $Ca_3Co_4O_9$ recently appeared as one of the most promising thermoelectric oxide compounds. It is a very complex material and, in spite of recent experimental and theoretical studies, many questions remain open concerning its properties.

In our work we have studied theoretically the properties of $Ca_3Co_4O_9$. We investigated its structural, electronic and magnetic properties within the density functional theory using an original hybrid functional approach. Then, going beyong previous theoretical studies, we characterized its transport and thermoelectric properties within the Boltzmann transport formalism.

Our main results can be summarized as follows:

- 1. The hybrid B1WC approach properly reproduces the electronic properties and constitutes a valuable alternative to the LDA+U method. Within this approach the contribution to the electronic structure at the Fermi level mainly originates from the t_{2g} orbitals of Co in the CoO₂ subsystem, whereas no contribution from the rocksalt subsystem is found, which is in agreement with previous experiments [22]. Within our calculations Ca₃Co₄O₉ appears to be a half-metal in which the CoO₂ subsystem is the conducting layer, similarly to what happens in other misfit compounds such as Na_xCoO₂.
- 2. The essentially antiferromagnetic order found in our B1WC calculations is consistent with the ferrimagnetic phase in the rock-salt subsystem found below 19 K. This ground state was suggested by Asahi *et al* [23] on the basis of LDA calculations which fails in reproducing the electronic structure [22]. It contrasts with Rébola *et al* who performed their calculations on a ferromagnetic structure [6].
- 3. We have shown that the relative position of the CoO_2 and Ca_2CoO_3 subsystems along the incommensurate direction has only weak influence upon the density of states, suggesting that the incommensurate nature of misfit calcium cobaltite does not play a significant role on its electronic properties. In that regard, we agree with Rébola *et al*'s proposal, who reached this conclusion by comparing results on different supercells, whereas Soret and Lepetit [24] argued otherwise.
- 4. For the RA = 3/2 supercell, we managed to model the global behaviors and order of magnitude of the Seebeck coefficient and the electrical resistivity within the Boltzmann transport theory. Our computed transport and thermoelectric properties are in qualitative agreement with experimental data. They suggest that

as-grown Ca₃Co₄O₉ crystals are self-doped with holes. Our calculations suggest that the anomalous behavior of the electrical conductivity in temperature might be intrinsic to the ground state phase of Ca₃Co₄O₉ rather than to a phase transition. We propose that reducing or compensating partly self-doping might increase the thermoelectric properties. Moreover, doping the misfit with electrons might produce even larger thermoelectric properties. This feature, previously overlooked, still significantly increases the potential interest for Ca₃Co₄O₉ on the basis of which it now appears that both good n-type and good p-type thermoelectric properties can be achieved by appropriate doping as required for pratical applications.

This is still a preliminary work and additional checks are still required to complete this study:

- First, the thermoelectric properties should be confirmed at the level of the 5/3 approximant which better reproduce the structure of the real misfit compound. Explicit comparison of the results with what was obtained with the 3/2 approximant is needed to validate our conclusions.
- Second, we should check explicitly the influence of the magnetic order on the thermoelectric properties.
- Third, we should confirm that the relative position of the two subsystems does not significantly affect the thermoelectric properties. Although the electronic density of states look rather insensitive to translation of one subsystem respect to the other thermoelectric properties are dependent upon the derivatives of the band structure so that apparently minor changes could eventually lead to different transport and thermoelectric properties.
- Going further, it might be eventually interesting also to check if it is possible to enhance the thermoelectric properties *via* other methods than doping, playing for instance with epitaxial strain as it could be achieved by growing $Ca_3Co_4O_9$ on an appropriate substrate...

As one can see, there's still a lot to do with calcium cobaltite, and surely, the future will reserve more surprises...

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