

Electronic structure of iron-doped misfit-layered calcium cobaltite



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ABSTRACT

The electronic structures of the undoped and Fe-doped misfit-layered calcium cobaltite are calculated using the first-principles calculations under DFT + U scheme. The calculated density of states (DOS) of the undoped sample is in a good agreement with the past theoretical calculation and experiments. The Fermi level falls at nearly the top of the valence band of the CoO₂ sublattice. The obtained magnetization could also very well explain the previous experiments. With Fe doping, two obvious changes in the DOS can be observed. Firstly, the Fermi energy has shifted to the higher level value and intercepted at the edge of the valence band where the slope is maximum. This characteristic enhances the thermopower of the system. The second change is the additional states ~0.1 eV above the Fermi level coming from the states of Fe atoms. These states are interpreted as a source of charge reservoir providing holes for electrical conduction in the CoO₂ layer. The electronic structures of the Fe-doped case show very good agreement with the previous thermoelectric measurements. The thermopower, calculated using Boltzmann transport theory, is significantly enhanced in the Fe-doped system compared to the undoped one.

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1. Introduction

Thermoelectric materials can directly convert heat into electricity. Good thermoelectric materials should possess high electrical conductivity (σ), low thermal conductivity (κ) and large Seebeck coefficient (thermopower, S). Thermopower is the ratio between the generated voltage at both ends of the sample (ΔV) and the applied the temperature difference (ΔT), i.e. $S = \Delta V / \Delta T$. A dimensionless figure-of-merit (ZT), defined as $ZT = S^2 \sigma T / \kappa$, is generally used to determine the efficiency of any thermoelectric material. Conventionally, such properties are optimized in intermetallic compounds, e.g. Bi₂Te₃, PbTe or SiGe [1]. Oxide materials have been extensively researched as potential materials for thermoelectric applications in recent years since a discovery of a large thermopower in NaCo₂O₄ single crystals [2]. Amongst p-type thermoelectric oxide, calcium cobaltite (Ca₃Co₄O₉) is one of the most promising thermoelectric materials. It possesses a combination of relatively high σ and S and low κ , with ZT comparable to conventional materials [3]. Moreover, this material exhibits a number of interesting properties such as strongly correlated properties [4], anisotropic magnetic properties [5,6], unconventional Hall effect

[7], or even giant dielectric behaviour [8]. A number of structural investigations of this material have been conducted [9–12]. It has been shown that Ca₃Co₄O₉ is in fact a simplification of the actual composition of [Ca₂CoO₃]_n[CoO₂], where n is close to the golden ratio (1.618). Its structure consists of two sublattices: a rocksalt (RS)-type Ca₂CoO₃ layer and a CdI₂-type CoO₂ layer, stacking alternatively along the c axis. The lattice parameters in the a and c directions for both layers are equal but are incommensurate in the b direction.

Transport properties of Ca₃Co₄O₉ (CCO) were reported to be highly anisotropic with the ab -plane σ and S much larger than those in the c -axis direction [5,13]. Such experimental results are believed to be a result of the in-plane conduction of the CoO₂ layer which was confirmed by the XPS study [14]. In spite of a number of successful experiments to explain transport and thermoelectric properties of CCO, very few computational calculations have been carried out. For electronic structure calculation, there have been only the works done by Asahi et al. [15], Rebola et al. [16] and Tang et al. [13]. Asahi et al. carried out the first-principles calculations of CCO using density functional theory (DFT) and presented the densities of states (DOS) and the band structure [15]. They also estimated the thermopower from their calculation using the modified Heikes formula [17]. However, their calculation contradicted the experimental results because they showed that the thermopower and transport properties are the contribution from the RS layer. Rebola

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et al. solved this problem by using DFT + U formalism in their calculation to account for the highly correlated properties of CCO [16]. Their results showed that with DFT + U the DOS has been modified such that the electron contribution near Fermi level was mostly limited to the CoO_2 layer, in an agreement with the experiment [14]. On the other hand, Tang et al. calculated the band structure of CCO and explained the anisotropic S as a difference in Fermi surface in each direction [13].

For thermoelectric application, it is important to maximize ZT of thermoelectric materials. One way to increase the ZT of CCO is to dope it with other elements. Partial substitution of Co with other transition metals has been employed to improve thermoelectric properties [18–26]. Particularly, experimental results showed that the thermoelectric properties of CCO doped with Fe (CCO–Fe) were significantly improved [22,23,27]. Unlike other elemental doping, Fe doping can enhance both σ and S simultaneously [22,23,27]. Up to date, there has not been any computational study for the effect of doping on the electronic structure of CCO. Hence it is interesting to investigate this CCO–Fe system from the theoretical and technological points of view. In this article, we present the results of our study on the DOS of CCO–Fe. The calculated electronic structures of both CCO and CCO–Fe are discussed in terms of the transport, thermoelectric and magnetic properties.

2. Computational methods and details

A crystal structure model of CCO was constructed starting with the data from the experimental values [10]. The lattice parameters of the monoclinic structure unit cell were $a = 4.8381 \text{ \AA}$, $b_1 = 4.5347 \text{ \AA}$, $c = 10.8558 \text{ \AA}$, $\beta = 98.1136^\circ$. The misfit ratio of 1.618 between the CoO_2 layer and the RS layer makes the real unit cell too large for our computational resource. Instead, we built a relatively small unit cell with the $\text{CoO}_2/\text{Ca}_2\text{CoO}_3$ ratio of 5/3. The reduction of the unit cell size was justified based on the work done by Rebola et al. which showed that the 5/3 approximant was sufficient in modeling the essential electronic properties of CCO [16]. Furthermore, the aim of this work is to investigate the effect of Fe substitution for Co on the electronic structure. To limit the concentration of Fe solute atoms in our model (so that it can be compared with experimental data) the unit cell size of CCO was double in the a direction. In other words, the formula of our model crystal structure of CCO can be written as $\text{Ca}_{24}\text{Co}_{32}\text{O}_{76}$ or $[\text{Ca}_2\text{CoO}_3]_{12}[\text{CoO}_2]_{20}$ as shown in Fig. 1.

To investigate the ground state crystal structures, the spin polarized density functional theory embedded in the Vienna Ab initio Simulation Package (VASP) [28] was carried out. Moreover, the LDA + U scheme [29,30] with $U = 5 \text{ eV}$ and $J = 1 \text{ eV}$ [16] was chosen for all calculations. All Co atoms were set in the ferromagnetic alignment. To test the ground state of the magnetic moment of Co atoms, the initial magnetic moment of Co was set to be 1.3 or 4.0 μ_B . With the Projector Augmented Wave (PAW) approach [31], the valence states for all potentials we used were 3s, 3p and 4s for Ca, 3d and 4s for Co, 3p, 3d and 4s for Fe, and 2s and 2p for O. The 500 eV of energy cutoff and $12 \times 4 \times 6$ of \mathbf{k} -points generated by the Monkhorst–Pack scheme were employed for both relax and static calculations [32]. During structural relaxation process, the conjugate-gradient algorithm was employed to determine the ground state configuration. Force acting on each ion was calculated by the Hellmann–Feynman theorem.

To determine the electronic structure of the Fe-doped CCO, we replaced one Co atom in the RS layer with an Fe atom. In fact, there are two Co sites in the CCO system, in RS or CoO_2 . Our previous works have shown that Fe atoms are preferential to stay in the RS site [20,33]. This was also confirmed by the other research group [34]. Thus, we built the model crystal structure of CCO–Fe as $\text{Ca}_{24}\text{Co}_{31}\text{Fe}_1\text{O}_{76}$ or $[\text{Ca}_2\text{Co}_{0.917}\text{Fe}_{0.083}\text{O}_3]_{12}[\text{CoO}_2]_{20}$ (Fig. 1). After Fe substitution, we re-optimized the structure using the same procedure. In order to compare the electronic structure of the CCO and CCO–Fe systems, the same values of U and J (5 and 1 eV, respectively) for the Fe atom were selected. To investigate the most preferable spin configuration of Fe, the initial magnetic moments of Fe were set as 1.3 or 4.0 μ_B . In the present work, the BoltzTraP code based on semi-classical Boltzmann transport theory was used for determining the thermoelectric properties of the CCO and CCO–Fe systems.

3. Results and discussion

We focus this work on the electronic structure of the CCO structure doped with Fe. In this section, we firstly present our calculation for the undoped CCO and compared with the previous investigations. Next, we present the result for the CCO–Fe. In both sections, the contribution from the electronic structure to the transport, thermoelectric and magnetic properties is discussed.

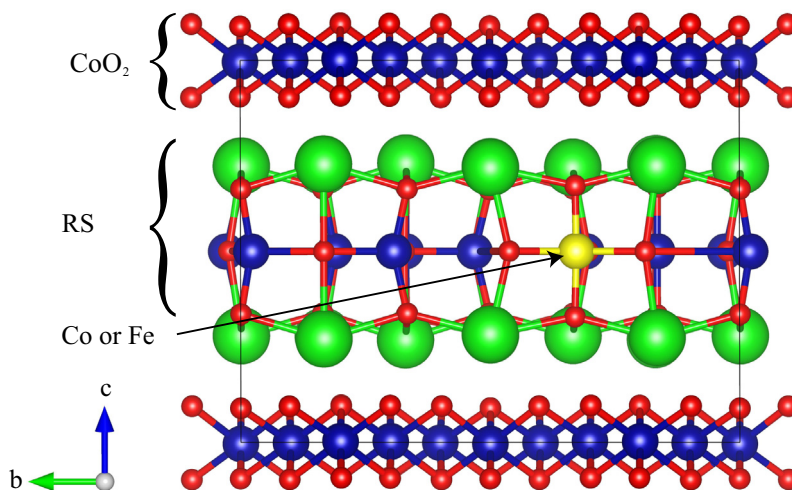


Fig. 1. The model of the unit cell of $\text{Ca}_{24}\text{Co}_{32}\text{O}_{76}$ ($[\text{Ca}_2\text{CoO}_3]_{12}[\text{CoO}_2]_{20}$) or $\text{Ca}_{24}\text{Co}_{31}\text{Fe}_1\text{O}_{76}$ ($[\text{Ca}_2\text{Co}_{0.917}\text{Fe}_{0.083}\text{O}_3]_{12}[\text{CoO}_2]_{20}$). The green, blue, and red spheres represent Ca, Co, and O atoms, respectively. The yellow sphere is either Co or Fe. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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