



# Magnetic ground state of orthorhombically distorted $\text{CaCoO}_3$ perovskite oxide: GGA and GGA+ $U$ calculations



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## ABSTRACT

Cobalt-based perovskite oxides have been attracted considerable attention due to their fascinating properties, especially entangled magnetic spin structures. Here, we comprehensively study the various magnetic ordering in recently reported orthorhombically distorted  $\text{CaCoO}_3$  perovskite oxide by employing the density functional theory calculations. A strong ferromagnetic coupling due to double exchange interactions between neighbouring Co atoms within the  $\text{CoO}_2$  bilayers is found than the anti-ferromagnetic coupling, which results in ferromagnetic spin ordering as a magnetic ground state with metallic electronic ground state (even Co is in its +4 state) for both exchange-correlation potentials (generalized gradient approximation (GGA) and GGA+ $U$ ). The estimated magnetic transition temperature  $T_C = 116/139$  K for GGA/GGA+ $U$ , which is close to the experimentally observed value of 95 K for helimagnetic ground state.

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## 1. Introduction

3d transition-metal perovskite oxides provide a playground for both functional electronics and spintronic devices, including metal-insulator transitions [1,2], colossal magnetoresistance [3], magnetism [4], superconductivity [5–7], orbital ordering [2,8], and spin ordering [9]. In this respect, cobalt-based perovskite oxides have been paid considerable attention due to appealing physical properties [10–12] and various spin states [13,14,16,23], which strongly depend on the slight symmetry between the crystal field energy and the Hund's rule exchange [17]. For example, it is experimentally observed that  $\text{SrFeO}_3(\text{SrCoO}_3)$  with Fe(Co) in +4 state exhibits anti-ferromagnetic (AFM) helical/ferromagnetic (FM) spin ordering with metallic conductivity at low/room temperature [18–21]. On the other hand, perovskites are showing band insulating (band gap between different kind of orbitals *i.e.*, between *p* and *d*) behaviour, when Co/Fe is in +3 state [22,23]. Hence, one of the critical challenge is the understanding of strong electron correlations in these materials as well as their applicability.

Very recently, Osaka et al. [24] synthesis the Co-based  $\text{CaCoO}_3$  perovskite oxide, which crystallizes in orthorhombically (Ortho.) distorted phase with space group  $Pbnm$  (No. 62). The crystal structure of  $\text{CaCoO}_3$  is very similar to that of the  $\text{GdFeO}_3$ , which is

like that of  $\text{CaFeO}_3$ . From the magnetic susceptibility experiment, the authors found a very small value of negative magnetoresistance at low temperature (95 K), which is incompatible to the simple *G*-type AFM spin ordering and hints to FM or AFM helimagnetic (HM). The authors observed that neighbouring spins of the Co atoms are aligned parallel to each but the magnetic ground state is AFM HM as found in the case of  $\text{SrFeO}_3$ . On the other hand, FM ordering is observed in  $\text{SrCoO}_3$  perovskite oxide due to double exchange interaction [29]. The electronic ground state and spin state of  $\text{Co}^{+4}$  in  $\text{CaCoO}_3$  is incoherent metallic and intermediate ( $e_g^1 t_{2g}^4$ ) with  $S = 3/2$ , respectively, as observed in  $\text{SrCoO}_3$  [26]. In contrast, the specific heat data of  $\text{CaCoO}_3$  shows a very small pseudogap near the Fermi level ( $E_F$ ), which hints to Mott-insulating state of the system instead of metallic. Therefore, need more clarification on the electronic and magnetic ground states of the compound under consideration.

The main purpose of the present work is to investigate the electronic and magnetic ground state of the Ortho. phase of  $\text{CaCoO}_3$  with magnetic transition temperature  $T_C$ , which is estimated by comparing the FM and AFM solutions. The stability of the different spin configurations is taken into account on the basis of total energy calculations.

## 2. Computational methods

Spin-polarized density functional theory calculations within

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full-potential linearized augmented plane-wave methods as implemented in the WIEN2k code [27] are used. For the electronic exchange-correlation functional, the generalized gradient approximation (GGA) as well as GGA+*U*, on-site Coulomb repulsions on the Co 3*d* state, method are applied. Core states are treated fully relativistically, while the scalar relativistic approximation is used for valence states. A  $9 \times 7 \times 9$  *k*-mesh with 100 points in the irreducible wedge of the Brillouin zone is taken into account, which is found to be well converged. Self-consistency is assumed for a total energy convergence of less than  $10^{-5}$  eV. Moreover, a maximum value of the angular momentum of  $l_{\max} = 12$  is employed for the wave function expansion inside the atomic spheres and a plane-wave cutoff of  $R_{\text{MT}}K_{\text{max}} = 8.0$  with  $G_{\text{max}} = 24$  is applied. We have fully optimized the crystal structure of the CaCoO<sub>3</sub> by minimizing the atomic forces upto 5 mRy/a.u.

### 3. Results and discussion

Results of structure relaxation are listed in Table 1 together with experimental data for the Ortho. phase of CaCoO<sub>3</sub> which contains 4 Ca, 4 Co, and 12 O atoms per unit cell. As coordinates of the Ca, Co, and O ions are not fixed by symmetry, therefore, the valence shell examine of the Co atoms in CaCoO<sub>3</sub> points to a large magnetic moment. It is also noted that magnetic exchange coupling between Co atoms is established by O ions because transition metals and O orbitals are strongly hybridized, which forms covalent bonding. Hence, if there is a strong exchange interaction between chemical bonding and magnetic forces, therefore, we have relaxed the atomic coordinates also with high precision.

From Table 1, one can clearly see that the calculated lattice parameters, bond lengths, bond angles, and atomic positions are in good agreement with the experimentally observed values up to  $\sim +0.3\%$  accuracy. First, the structural stability is analyzed by calculating the enthalpy of formation ( $\Delta H_f$ ) of the Orth. distorted phase of CaCoO<sub>3</sub> using the following formula,

$$\Delta H_f^{\text{PbMoO}_3} = E_t^{\text{PbMoO}_3} - E_t^{\text{Pb}} - E_t^{\text{Mo}} - \frac{3}{2}E_t^{\text{O}_2} \quad (1)$$

where  $E_t^{\text{CaCoO}_3}$  is the ground state total energy of the cubic or distorted phase of CaCoO<sub>3</sub>, while  $E_t^{\text{Ca}}$  and  $E_t^{\text{Co}}$  are the ground state total energies of optimized single atom of the Ca and Co, respectively. The last term in Eq. (1) ( $E_t^{\text{O}_2}$ ) represents the total energy of an

oxygen dimer (O<sub>2</sub>), which has been computed by adding the PBE-GGA [28] cohesive energy of an oxygen molecule ( $E_c^{\text{O}_2}$ ) in twice the total energy of a single oxygen atom ( $E_t^{\text{O}}$ ) placed in a large fcc supercell using  $\Gamma$ -point *k*-sampling *i. e.*,

$$E_t^{\text{O}_2} = 2E_t^{\text{O}} + E_c^{\text{O}_2} \quad (2)$$

The estimated GGA  $\Delta H_f$  are listed in Table 1 with un-relaxed (experimental) and relaxed (DFT) parameters per formula unit. The relaxed structure shows more stability than that of un-relaxed one and values of  $\Delta H_f$  presented in Table 1 are very reasonable, which provide a good description for evaluating the energetics in CaCoO<sub>3</sub>.

In order to calculate the magnetic ground state of CaCoO<sub>3</sub>, the FM and three different AFM (A, C, and G) spin ordering are taken into account. In the FM ordering, all the Co atoms are align in one direction and support each other. The AFM ordering contain AFM-A (in-plane FM coupling which coupled anti-ferromagnetically with out-of plane for each bilayer), AFM-C (in-plane and out-of-plane AFM and FM coupling, respectively, for each bilayer), and AFM-G (AFM coupling in-plane and out-of-plane for each bilayer) as shown in Fig. 1. This method allows us to estimate the energetically stable ordering which is computed as  $\Delta E = E_{\text{AFM}} - E_{\text{FM}}$ , where  $\Delta E$  is the magnetic energy difference between AFM and FM spin ordering. Along with this, magnetic transition temperature ( $T_C$ ) is also determine in each case as:

$$T_C = \frac{2/3 \cdot \Delta E}{k_B}, \quad (3)$$

where  $k_B$  is the Boltzmann constant. Our GGA and GGA+*U* simulations predict that total energy of the FM spin ordering is 10/13/14 and 12/14/16 meV per formula unit lower than the AFM A/C/G-type spin states, respectively, see Fig. 2(a). The corresponding  $T_C$  in each case are also plotted in Fig. 2(b). Hence, FM spin ordering is the magnetic ground state of Ortho. CaCoO<sub>3</sub> with estimated  $T_C$  of 116 K/139 K for GGA/GGA+*U* scheme, which is in contrast to the experiment [24] where authors found that the magnetic ground state is AFM HM with  $T_C = 95$  K. We obtained a little deviation from the experiment, which may be attributed to a low accuracy of the parameters. However, in order to ensure that whether the very small  $\Delta E$  between FM and AFM ordering is reliable, we performed additional calculations using a  $12 \times 9 \times 12$  *k*-mesh having 245 points in the irreducible wedge of the Brillouin zone along with increasing total energy convergence to  $10^{-7}$  eV and obtain almost the same energy difference with an accuracy of  $\sim 1.1$  meV. Interestingly, we found that the AFM-A spin ordering is nearly degenerate with the FM phase. Because, spin of the nearest-neighbour Co atoms are aligned ferromagnetically in FM and AFM-A spin ordering. On the other hand, spins of the Co atoms are anti-ferromagnetically aligned in the G and C-type structures. Therefore,  $\Delta E$  is higher in the case of AFM G/C-type spin ordering as compared to AFM A-type ordering. This strong FM coupling in CaCoO<sub>3</sub> can be attributed to double exchange mechanism, which reduces the strength of super exchange coupling in AFM structures as found in the case of SrCoO<sub>3</sub> [29].

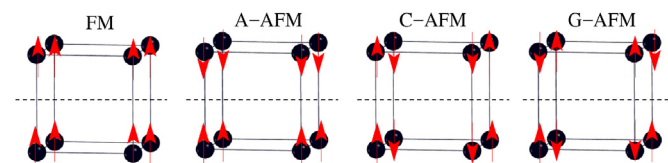


Fig. 1. Schematic diagram of the magnetic orderings considered in the present work. Dashed lines separate adjacent bilayers and only Mo atoms are shown.

Table 1

Experimental and DFT (GGA-PBE) equilibrium lattice parameters (Å), atomic positions, bond lengths (Å), bond angles (degree), and enthalpies of formation  $\Delta H_f$  (eV/atom) of CaCoO<sub>3</sub> perovskites oxide in orthorhombic phase with space group *Pbnm* (No. 62).

	Experiment [24]	DFT
<i>a</i>	5.271	5.429
<i>b</i>	5.295	5.454
<i>c</i>	7.439	7.662
Ca( <i>x,y,z</i> ),site	(0.494,0.463,0.25),4c	(0.509,0.477,0.25),4c
Co( <i>x,y,z</i> ),site	(0.5,0,0),4b	(0.5,0,0),4b
O1( <i>x,y,z</i> ),site	(0.783,0.199,0.034),8d	(0.807,0.205,0.035),8d
O2( <i>x,y,z</i> ),site	(0.064,0.499,0.25),4c	(0.066,0.514,0.25),4c
Ca–O1	2.35–2.61	2.39–2.97
Ca–O2	2.28–2.47	2.32–2.53
Co–O1	1.84–1.98	1.89–2.01
Co–O2	1.89	1.91–1.93
Co–O1–Co	155.6	156.8
Co–O2–Co	159.5	161.3
O1–Co–O1	88.6–91.4	89.6–91.9
O1–Co–O2	88.6–91.4	89.3–92.1
$\Delta H_f$ (un-relx.)	–	–1.834
$\Delta H_f$ (relx.)	–	–1.957

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