Spin state of LaCoO₃: Dependence on CoO₆ octahedra geometry

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(Received 20 April 2004; published 28 February 2005)

The electronic structure of the rhombohedral LaCoO₃ perovskite is calculated for a number of structures with varying CoO₆ octahedra geometry. The calculations are based on the generalized gradient approximation (GGA) to the density functional theory and, in order to describe better the strong electron-electron correlation in Co 3*d* states, the GGA+U method is employed. Depending on the Co-O distance *d* and the Co-O-Co bond angle β , the spin *S* of the cobalt ion is found to correspond either to the intermediate spin state [(IS), *S*=1] or to the low spin state [(LS), *S*=0]. The border line dividing the IS and LS states in the (*d*, β) space is determined. The IS state is more stable than the LS state for structures with longer Co-O distances and more open Co-O-Co angles. The GGA+U results are in agreement with recently observed pressure-induced IS-LS transition.

DOI: 10.1103/PhysRevB.71.054420

PACS number(s): 75.30.Wx, 71.15.Mb

I. INTRODUCTION

At low temperatures the cobaltite LaCoO₃ is nonmagnetic, the Co³⁺ ion being in the low spin (LS) state, so that in the limit of fully localized electrons it corresponds to filled t_{2g} levels and empty e_g states [(LS), $t_{2g}^6 e_g^0$, S=0]. At ≈ 100 K LaCoO₃ undergoes a transition to a magnetic state, the character of which is still under question. Possible states of the Co³⁺ ion, which can give rise to the magnetism, correspond either to the intermediate spin [(IS), $t_{2g}^5 e_g^1$, S=1] or to the high spin [(HS), $t_{2g}^4 e_g^2$, S=2].

In the past the magnetism above 100 K was explained as being caused either by the 1:1 mixture of LS and HS states,¹ or by the HS state in which, however, the antiferromagnetic interactions are also present.² More recently it was pointed out that the IS state of Co^{3+} ion is the most probable source of the magnetism.³⁻⁶

Explanation of the transition from the nonmagnetic to the magnetic state by an *ab initio* calculation of the electronic structure of LaCoO₃ represents a formidable problem. First, the density functional theory (DFT), on which such calculations are usually based, concerns the ground state, i.e., the absolute zero temperature only. The second problem is the strong correlation of the electrons of the magnetic cations in the 3d magnetic oxides. The two methods which are usually applied in DFT-based calculations, the local spin density approximation (LSDA) or the generalized gradient approximation (GGA), often fail to describe correctly systems with strong correlations. A possible way to overcome the above two problems was suggested by Korotin *et al.*⁷ These authors assumed that the spin-state transition in LaCoO₃ is driven by the change of the crystal structure with the temperature, i.e., the entropy part of the free energy was neglected. The temperature evolution of the electronic structure may then be obtained by adopting the crystal structure determined experimentally at different temperatures⁸ and performing the corresponding series of *ab initio* calculations. To account for the strong electron correlations of the 3d electrons of cobalt, the LDA+U approach was used. In order to determine the energy differences between the LS, IS, and HS states Korotin et al.⁷ employed the fixed-spin-moment (FSM) method. In this method the total energy of the system is minimized under the condition that the total spin moment is fixed at a prescribed value. In a qualitative agreement with the experiment the ground state was found to be LS for the low temperature structures. The total energies per formula unit of the IS and HS states were higher by 0.24 eV and 0.65 eV, respectively. When increasing temperature, the energies of the IS and LS states crossed at \sim 150 K and IS became the ground state for higher temperatures. The energy of the HS state was the highest in the whole temperature range. The calculation of the electronic structure of the $La_{1-r}Sr_rCoO_3$ system using GGA without the Hubbard U correction was reported by Ravindran *et al.*⁹ For x=0 the crystal structure corresponding to 4 K was considered and it was found that the LS state had the lowest energy. Using the FSM method the energy of the IS and HS states were higher by 0.025 and 1.124 eV, respectively.

LaCoO₃ crystallizes in the rhombohedral space group $R\bar{3}c$. The structure description involves three parameters: lattice constant *a*, rhombohedral angle α , and oxygen coordinate *x*. These three parameters could also be expressed in terms of the Co-O-Co bond angle β and the geometry of the CoO₆ octahedron: the Co-O bond length *d* and the trigonal distortion characterized by the O-Co-O angle γ . The dependence of the crystal structure on temperature was studied experimentally in Refs. 8 and 10, see Fig. 1(b). In this paper no deviation from the $R\bar{3}c$ symmetry was reported. Note, however, that recently a monoclinic distortion of the structure (space group I2/a) was found by single-crystal x-ray diffraction.¹¹

Pressure-induced IS-LS transition in $LaCoO_3$ at room temperature was reported by Vogt *et al.*¹² The authors measured synchrotron x-ray powder diffraction under pressure up to 8 GPa. They observed a change of the Co-O bond compressibility around 4 GPa [see Fig. 1(a)], which was ascribed to the continuous depopulation of the IS state driven by an increased crystal-field splitting and connected with an effective reduction of the size of the Co³⁺ cation.

In this paper we show that the GGA+U method correctly reproduces the pressure-induced spin transition observed experimentally.¹² Moreover, the phase diagram of the magnetic states vs the crystal structure distortion is determined.



FIG. 1. (a) The dependence of $LaCoO_3$ crystal structure on pressure (Ref. 12) (\blacklozenge) and (b) on temperature. The data were taken from Thornton *et al.* (Ref. 8) (\blacklozenge) and Radaelli *et al.* (Ref. 10) (\Box).

II. METHOD OF CALCULATION

The calculations were made with the WIEN2K program.¹³ This program is based on the DFT and uses the full-potential linearized augmented plane wave (FPLAPW) method with the dual basis set. In the LAPW method the space is divided into atomic spheres and the interstitial region. The electron states are then classified as the core states, which are fully contained in the atomic spheres and the valence states. The valence states are expanded using the basis functions. Each of the basis functions has the form of the plane wave in the interstitial region, while it is an atomiclike function in the atomic spheres. To make possible the treatment of two valence functions with the same orbital number (such as 3p and 4p functions of Co) so-called local orbitals are added to the basis functions.¹⁴ In our calculations the 3p, 3d, 4s, 4p states of Co, 2s, 2p, 3s of O and 5s, 5p, 5d, 6s, 6p, 6d states of La were treated as the valence states. The number n_k of the k points in the irreducible part of the Brillouin zone was 85 and the number n_b of the basis functions was ≈ 100 per atom in the unit cell. (n_b differs somewhat for different k points.) All calculations were spin-polarized, assuming ferromagnetic ordering of the Co spins. For the exchange correlation potential we adopted the GGA form¹⁵ as for the 3d compounds it is superior to the LSDA, as a rule. The radii of the atomic spheres were 2.00, 1.90, and 1.65 a.u. for La, Co, and O, respectively.

Despite the fact that GGA is more suitable than LSDA when applied to inhomogeneous electron systems, in the 3d transition metal oxides the energy gap and the magnetic moments are still underestimated.¹⁶ To improve the description of Co 3d electrons we thus used the LDA+U method as described by Anisimov *et al.*,¹⁷ but with the GGA instead of LSDA exchange-correlation potential. In what follows the method is therefore denoted as GGA+U. The method is no longer truly *ab initio* as the values of the Hubbard parameter

U and the exchange parameter J must be inserted. These can either be taken from experimental or estimated values using the restricted LSDA (GGA) supercell calculation. In Ref. 7 the values U=7.8 eV and J=0.92 eV were found by employing the LSDA supercell procedure.

In the LDA+U-like methods an orbitally dependent potential is introduced for the chosen set of electron states, which in our case are 3d states of Co. The additional potential has an atomic Hartree-Fock form, but with screened Coulomb and exchange interaction parameters. The problem is that the exchange and correlation parameters already contained in the LSDA or GGA should be subtracted. The form of this "double-counting correction" is spherically symmetrical, and it is not clear to which extent its application in the full potential methods is justified, as there is no doublecounting correction for the nonspherical terms in the GGA+U orbital potential. We avoided this problem by using the effective $U_{eff} = U - J$ instead of the parameter U and by putting the nonspherical terms in the orbital potential equal to zero. In what follows the notation $U = U_{eff}$ is used, but it should be kept in mind that we are dealing with the effective U which is smaller than the Hubbard parameter. Using the data of Ref. 7 the LSDA value of U_{eff} equals 6.88 eV. Moreover, as we showed recently,¹⁸ when the GGA instead of the LSDA exchange-correlation potential is used, the value of Ushould be reduced. In what follows the value of the Hubbard parameter $U \equiv U_{eff} = 5.4$ eV was chosen. We checked that the main results obtained, the LS-IS transition, and the phase diagram, are not sensitive to the U value.

Our calculations were carried out without fixing the spin moments. For each structure the GGA calculation was performed first and then the GGA+U was started using the electron density and occupation matrices of the converged GGA.

III. RESULTS AND DISCUSSION

To obtain the temperature dependence of the crystal structure parameters, we made a linear fit to the experimentally determined evolution of the crystal structure as reported in Refs. 8 and 10 [see Fig. 1(b)]. In this way the crystal structures for selected temperatures were reconstructed. This approach represents a rough approximation only, since it neglects, e.g., anomalous thermal lattice expansion observed around the spin transition temperature.^{6,10}

The converged total magnetic moments and the relative total energy per formula unit vs temperature and the corresponding CoO_6 octahedra geometry are displayed in Fig. 2. At high temperatures the GGA calculations converged to a magnetic solution with the magnetic moment decreasing from ~1.5 μ_B at 1000 K to ~1 μ_B at 100 K. Below 100 K the moment decreased suddenly to ~0. After applying the GGA+U the low-temperature structures remained in the LS state (*S*=0), while the magnetic moment of the high-temperature structures was enhanced to 2 μ_B , corresponding to its nominal value in the IS state (*S*=1). Close to the LS-IS transition some of the GGA+U was applied. Thus the IS-LS transition calculated with GGA+U is shifted to



FIG. 2. Temperature dependence of the total relative energy per formula unit calculated by (a) GGA and (b) GGA+U. (c) Magnetic moment vs temperature calculated by GGA (\Box) and GGA+U (\circ). Full (open) symbols correspond to LS (IS) states. Three parameters (β , d, γ) that characterize the local geometry are shown below the temperature axis.

higher temperatures (100-150 K) compared to the GGA (0-100 K).

The ground states calculated by the GGA for the structures determined under pressure in Ref. 12 were all magnetic with the total magnetic moments per formula unit around $1\mu_B$. Switching on the GGA+U enhanced the magnetic moment of the low-pressure structures to $2\mu_B$, while the high pressure structures (\geq 4 GPa) became nonmagnetic, corresponding to the LS state (*S*=0) (see Fig. 3). The IS-LS tran-



FIG. 3. Pressure dependence of the total relative energy (a) GGA and (b) GGA+U calculation. (c) Pressure dependence of the calculated magnetic moments.



FIG. 4. Total relative energy vs volume (a) GGA and (b) GGA+U calculation. Full (open) symbols correspond to LS (IS) states. (c) Magnetic moment vs Co-O-Co bond angle β calculated by GGA (open symbols) and GGA+U (full symbols).

sition calculated by the GGA+U is thus in good agreement with the experiment.¹²

To get a better insight into the mechanisms leading to different magnetic ground states, we determined the dependence of the magnetic state on the LaCoO₃ crystal structure parameters. First several structures without trigonal deformation (γ =90°) were compared with analogous structures having the maximum observed trigonal deformation (γ =91.5°, see Fig. 1). The calculation shows that the effect of the trigonal deformation is rather small, and we decided therefore to calculate the phase diagram in the (d, β) space only.

The dependence of the total energy on volume for several values of d is displayed in Figs. 4(a) and 4(b). The magnetic



FIG. 5. The bond distance Co-O (*d*) vs bond angle Co-O-Co (β) phase diagram of spin state in LaCoO₃. Calculated IS states (Δ), LS states (Δ), and LS state by GGA+U but IS by GGA (∇). Spin states for structure dependence on temperature (LS: \blacksquare ; IS: \Box) and on pressure (LS: \bullet ; IS: \bigcirc). The approximate position of the border line between LS and IS states is plotted as a solid line for GGA +U and a dashed line for GGA.



FIG. 6. Example of DOS calculated by GGA (U=0) for structures with d=1.90 Å. (a) LS state, $\beta=164^{\circ}$; (b) IS state, $\beta=176^{\circ}$.

moment per formula unit as a function of the angle β is shown in Fig. 4(c). It is seen that if d decreases, more openangle β is required for the LS \rightarrow IS transition to occur. The GGA+U method gives an abrupt transition, with the magnetic moment increasing from zero to its IS nominal value $2\mu_B$. The transition as obtained in GGA is smoother, especially for short d, and the magnetic moment is significantly smaller than $2\mu_B$. The resulting (d,β) diagram with calculated structures together with structures observed under varying temperature and pressure is shown in Fig. 5. Three different sets of calculated results are indicated in the diagram: (1) LS state, (2) IS state, and (3) IS state for GGA, but LS for GGA+U. Thus the LS-IS border line is different for GGA and GGA+U, especially for short *d*. Nevertheless, both for GGA and GGA+U the magnetic ground state (IS) is more stable for structures with longer d and more open β . The



FIG. 7. Example of DOS calculated by GGA+U (U=5.4 eV) for structures with d=1.90 Å. (a) LS state, β =164°; (b) IS state, β =176°.

construction of the diagram reduces the complex problem of spin-state equilibria to a dependence on the local parameters d and β . The calculated phase diagram is thus, at least in principle, transferable from the specific case of the rhombohedral LaCoO₃ to related $RCoO_3$ systems (R=rare earth or Y). To do that, at least two obstacles must be overcome. First, the symmetry of $RCoO_3$ is lower (orthorhombic) and the effect of the symmetry reduction should be analyzed. Second, if the transition temperature is high, as such, e.g., in YCoO₃,¹⁹ the role of entropy may become important.

Examples of the densities of states calculated by GGA and GGA+U for structures with d=1.90 Å are displayed in Figs. 6 and 7, respectively. The densities of states (DOS) calculated using the GGA corresponds to a metal for all cases considered. In the LS case all t_{2g} states are occupied and the



FIG. 8. Fit of calculated LS-IS border line calculated by GGA+U (×) to $\cos(\pi-\beta)d^{-3.5}=Ad^{-5}+B$. For a description of other symbols see Fig. 5.

density of states at the Fermi energy E_F is low. In contrast to this, for IS a sharp peak corresponding to the minority spin t_{2g} states is intersected by E_F . With GGA+U the situation is very different; the LS systems are insulators with a gap ~1.5 eV. The states just below E_F correspond to strongly intermixed (almost 1:1) $\operatorname{Co}(t_{2g})$ -O(p) states. The hybridization of the t_{2g} states in an octahedron is usually small. In our case the strong $\operatorname{Co}(t_{2g})$ -O(p) mixing is caused by the selected value of the Hubbard parameter U=5.4 eV. For this U the t_{2g} states are shifted downwards and come in to contact with the oxygen p states. As a consequence the hybridization is strongly enhanced. For the IS case the GGA+U results correspond to a half metal with conduction in the majority spin channel only. The states on E_F are $\operatorname{Co}(e_g)$ strongly hybridized with the oxygen p states.

Note that the IS states calculated using the GGA+U always have a magnetic moment per LaCoO₃ equal to 2 μ_B . This may be understood taking into account that the system is half metallic (Fig. 7), i.e., there is a gap in the DOS of the minority spin electrons. As a consequence the number n_{\downarrow} of the minority spin electrons must be an integral number. The total number of electrons n_{tot} is integral too, and thus the number of the majority spin electrons $n_{\uparrow}=n_{tot}-n_{\downarrow}$ as well as the magnetic moment $\mu_B(n_{\uparrow}-n_{\downarrow})$ are also integers.

In a simple one-electron crystal-field picture for nondistorted CoO₆ octahedra the LS state is stable if the crystalfield splitting is larger than the on site Coulomb repulsion $\Delta_{CF} > \Delta_{U}$, whereas the HS state is stable if $\Delta_{CF} < \Delta_{U}$. The IS state could only be stabilized in distorted octahedra, e.g., by a Jahn-Teller effect. The calculation shows that the IS state may be stabilized also in the nondistorted octahedra due to the strong hybridization of $\text{Co-}e_g$ orbitals with the *p* orbitals of oxygen ligands. The hybridization broadens the *d-p* bands and makes the t_{2g} and e_g bands overlap, as can be seen in figures of DOS (Figs. 6 and 7). The smaller Co-O-Co bond angle decreases the hybridization and narrows the *d-p* bands. The shorter Co-O bond pushes the antibonding e_g orbitals to higher energy, whereas mainly nonbonding t_{2g} are less influenced, and the energy difference between e_g and t_{2g} , which corresponds to Δ_{CF} in the crystal-field approximation, is increased. Both of these effects prevent overlapping t_{2g} and e_g and thus support LS.

The dependence of the level of the orbital overlap W on the bond distance d and angle β in perovskites could be expressed as^{20,21}

$$W \sim \frac{\cos(\pi - \beta)}{d^{3.5}}.$$
 (1)

The crystal-field splitting $\Delta_{\rm CF}$ changes with d^{-5} in the point charge approximation.²² Thus we attempted to fit the IS-LS border line by an equation,

$$\frac{\cos(\pi - \beta)}{d^{3.5}} = \frac{A}{d^5} + B.$$
 (2)

where *d* is in Å, A=3.108, and B=-0.020 56. The formula (2) fits quite well the calculated LS-IS border line (see Fig. 8), and supports the above-mentioned explanation of the spin-state stability dependence on *d* and β , although it cannot comprise the complex DOS structures.

IV. CONCLUSIONS

The electronic structure of LaCoO₃ was calculated by GGA and GGA+U for a number of structures with varying Co-O distances d and Co-O-Co bond angles β . The spin of LaCoO₃ calculated by GGA+U corresponds either to the intermediate spin state (IS, S=1) or to the low spin state (LS, S=0). The IS state is more stable than the LS state for structures with longer Co-O distances and more open Co-O-Co angles.

The magnetic state calculated by GGA+U for structures of $LaCoO_3$ determined recently under pressure by Vogt *et al.*¹² is in agreement with the proposed pressure-induced IS-LS transition.

ACKNOWLEDGMENT

This work was supported by the Project No. A1010214 of the Grant Agency of the AS CR.

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