The influence of the rare earth ions radii on the Low Spin to Intermediate Spin state transition in lanthanide cobaltite perovskites: $\text{LaCoO}_3$ vs. $\text{HoCoO}_3$

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(Dated: October 27, 2018)

Abstract

We present first principles LDA+U calculations of electronic structure and magnetic state for $\text{LaCoO}_3$ and $\text{HoCoO}_3$. Low Spin to Intermediate Spin state transition was found in our calculations using experimental crystallographic data for both materials with a much higher transition temperature for $\text{HoCoO}_3$, which agrees well with the experimental estimations. Low Spin state $t_{2g}^6e_{g}^0$ (non-magnetic) to Intermediate Spin state $t_{2g}^5e_{g}^1$ (magnetic) transition of Co$^{3+}$ ions happens due to the competition between crystal field $t_{2g}$-$e_{g}$ splitting and effective exchange interaction between $3d$ spin-orbitals. We show that the difference in crystal structure parameters for $\text{HoCoO}_3$ and $\text{LaCoO}_3$ due to the smaller ionic radius of Ho ion comparing with La ion results in stronger crystal field splitting for $\text{HoCoO}_3$ (0.09 eV $\approx$ 1000 K larger than for $\text{LaCoO}_3$) and hence tip the balance between the Low Spin and Intermediate Spin states to the non-magnetic solution in $\text{HoCoO}_3$.

PACS numbers: 78.70.Dm, 71.25.Tn
I. INTRODUCTION

In lanthanum cobaltite LaCoO$_3$ there is a temperature induced transition from a non-magnetic to a magnetic state, which has attracted considerable interest last years [1]. In the ground state of LaCoO$_3$ there is no magnetic moment on Co ions. At low temperature the magnetic susceptibility increases exponentially with temperature, exhibiting a maximum near 100 K. While initially this maximum was ascribed to a transition from a Low Spin non-magnetic ground state ($t^{6}_{2g}$, $S=0$) to a High Spin state ($t^{4}_{2g}e^{2}_{g}$, $S=2$), later a new scenario involving Intermediate Spin state ($t^{5}_{2g}e^{1}_{g}$, $S=1$) has been proposed. Using the results of LDA+U, Korotin et al. [2] explained stabilization of Intermediate Spin state over High Spin state due to the large hybridization between Co-3$d$ ($e_g$) and O-2$p$ orbitals.

\[ \Delta_{cf} \]

\[ \Delta_{ex} \]

FIG. 1: Scheme of energy levels for Low Spin state of Co$^{3+}$ ions in LaCoO$_3$.

The physical reason for this transition is a competition between crystal-field energy $\Delta_{cf}$ ($t_{2g}$-$e_g$ energy splitting) and intra-atomic (Hund) exchange energy $\Delta_{ex}$ (Fig. 1). In the ground state $\Delta_{cf}$ is only slightly larger then $\Delta_{ex}$ so that the energy of the excited magnetic state of Co ion is relatively small and with increasing of temperature its population increases resulting in an increase of magnetic susceptibility. When La ions are substituted in perovskite cobaltites by other rare earth elements with smaller ionic radii, magnetic properties show significant changes. For NdCoO$_3$ material $^{59}$Co Knight shift measurements [3] showed that Co ions remain to be in the Low Spin state up to 580 K, where the gradual metal-insulator transition is observed. High-temperature diffraction study of lanthanide cobaltite perovskites LnCoO$_3$ (Ln=Nd, Gd, Dy and Ho) [4] led its authors to conclusion, that "at room temperature all cobalt ions are in the Low Spin state regardless of the Ln atomic number" and only as temperature increases to 1000 K "the possible electronic phase transi-
tion can be suggested”. Magnetic and electric measurements for \( \mathrm{Ho}_{1-x}\mathrm{Ca}_x\mathrm{CoO}_3 \) system showed that “there is no apparent transition between Low Spin and High Spin of Co\(^{3+}\) ions in 300-900 K temperature range”. All these data show that Low Spin state of Co\(^{3+}\) ions in lanthanide cobaltite perovskites with smaller rare earth ions becomes more stable comparing with LaCoO\(_3\) and transition temperature increases dramatically. In the present work we have investigated relative stability of Low Spin and Intermediate Spin states of Co\(^{3+}\) ions in LaCoO\(_3\) and HoCoO\(_3\) as a function of experimental crystal structure parameters measured at different temperatures. We have found that, indeed, while for LaCoO\(_3\) transition temperature value (defined as the temperature, where calculated total energy of Low Spin solution becomes higher than the energy of Intermediate Spin solution) is 140 K, for HoCoO\(_3\) this value is 1070 K. The physical reason for this is decreasing of Co-O bond length due to the chemical pressure happening with substitution of La ions by smaller Ho ions and hence increasing of the crystal field \( t_{2g}-e_g \) energy splitting value thus stabilizing Low Spin state. Such conclusion is supported by the results of the recent diffraction experiments under pressure for LaCoO\(_3\) [6], which were interpreted as “pressure-induced Intermediate-to-Low Spin-state transition”.

II. CRYSTAL STRUCTURE

LaCoO\(_3\) crystallizes in the rhombohedrally distorted cubic perovskite structure [7, 8]. According to the latest crystallographic data by Radaelli et al. [8] the space group of this compound is \( \mathrm{R}\overline{3}c \) for all measured temperatures and has two formula units in the unit cell. Main structural motif of this compound is a nearly perfect CoO\(_6\) octahedron. The rhombohedral distortion of the parent cubic perovskite structure can be described by deformation along the body diagonal so that the angle of the Co-O-Co bond has changed form 180° to \(~163°\) (Fig. 2).

HoCoO\(_3\) has orthorhombically distorted perovskite crystal structure (prototype GdFeO\(_3\), space group \( \mathrm{Pbnm} \)) [4] (Fig. 2), which contains four formula units in the unit cell. Like for LaCoO\(_3\) the main crystallographic motif form CoO\(_6\) octahedra, which are rotated in \( ab \)-plane and tilted in respect to \( c \)-axis. Due to smaller ionic radius of Ho ion comparing with La ion, distortion from the cubic perovskite structure is stronger for HoCoO\(_3\) than for LaCoO\(_3\) and the angles of the Co-O-Co bond have values 149° (in \( ab \)-plane) and 152° (along \( c \)-axis).
FIG. 2: The rhombohedral crystal structure of LaCoO$_3$ (left) and the orthorhombic crystal structure of HoCoO$_3$ (right). Co: large spheres; O: small spheres.

In addition to the strong bending of the Co-O-Co bond the average length of the Co-O bond is decreased with substitution of La by Ho (1.934 Å and 1.921 Å at 300 K [4, 8]). Such decrease can be understood as a result of chemical pressure, induced by the smaller ionic radius of Ho ion comparing with La ion.

The crystal structure parameters as a function of temperature were measured for LaCoO$_3$ in [8] and for HoCoO$_3$ in [4]. It was demonstrated in [2] that LDA+U calculations can reproduce a Low Spin-Intermediate Spin transition for LaCoO$_3$ using temperature dependent crystal structure as an input. We used the same procedure for HoCoO$_3$ in order to find if a small decrease of Co-O bond length due to the chemical pressure can results in stabilization of the Low Spin state.

Five 3d-orbitals are separated into triply degenerate $t_{2g}$ and doubly degenerate $e_g$ subsets only in cubic symmetry lattice. The rhombohedral crystal structure of LaCoO$_3$ and the orthorhombic crystal structure of HoCoO$_3$ have lower symmetry than cubic as a whole but CoO$_6$ octahedra are only slightly distorted in those compounds. In local coordinate system centered on Co ion with the axes directed to the oxygen ions $t_{2g}$-$e_g$ orbitals are still well defined. In the following we have used such defined orbitals for analysis of the calculated electronic structure.
III. LDA BAND STRUCTURE

The standard L(S)DA (Local (Spin) Density Approximation \cite{9, 10}) based methods cannot describe magnetic state for LaCoO$_3$ without taking into account Coulomb interaction between 3$d$ electrons as it was demonstrated in \cite{2}. However analysis of the LDA results is instructive for understanding of the basic electronic structure of lanthanide cobaltite perovskites.

We used LMTO method \cite{11} to perform calculations of electronic structure for LaCoO$_3$ and HoCoO$_3$. The results are presented in Fig. 3. The radii of the muffin-tin spheres in LaCoO$_3$ for 5 K structure were $R_{\text{La}}$=3.76 a.u., $R_{\text{Co}}$=2.49 a.u., and $R_{\text{O}}$=2.0 a.u. With temperature increasing $R_{\text{Co}}$ and $R_{\text{O}}$ were increased proportionally to Co-O distance for a given temperature. In HoCoO$_3$ for lowest temperature (300 K) crystal structure $R_{\text{Co}}$ and $R_{\text{O}}$ were taken as the corresponding values for LaCoO$_3$ scaled in proportion of Co-O distances in LaCoO$_3$ and HoCoO$_3$. Then $R_{\text{Co}}$ and $R_{\text{O}}$ were increased proportionally to the change of the Co-O distance in HoCoO$_3$ for a given temperature. $R_{\text{La}}$ was adjusted to fill completely the volume of the unit cell. In the orbital basis set the following states were included: Co(4$s$,4$p$,3$d$), O(3$s$,2$p$), La,Ho(6$s$,6$p$,5$d$,4$f$). Partially filled 4$f$ states of Ho were treated as a pseudo-core states.

Figure 3 (left panel) shows in details LDA calculated electronic band structure of LaCoO$_3$. On the top of the figure total density of states (DOS) is shown. There are three distinguishable sets of bands: completely filled O-$p$ bands, partially filled Co-$d$ bands and empty La-$f$ bands. The bands in the energy range from -7 eV to -1.5 eV originate mainly from O-2$p$ states but have a significant admixture from Co-3$d$ states. Between 0 eV and 2 eV there are empty La-4$f$ bands. The two groups of bands presented in the third panel, which extend from -1.5 eV to 0 eV and from 0 eV to 2.0 eV, are the Co-3$d$ states. Also a substantial O-2$p$ contributions are apparent in this energy range. Co-3$d$ states, due to the octahedral symmetry as we discussed above, are formed by completely occupied $t_{2g}$ states and empty $e_g$ states with a “pseudo-gap” between them. The partial densities of states for $t_{2g}$ and $e_g$ states are presented in the fourth and fifth panels of Fig. 3 correspondingly. We have calculated centers of gravity and standard deviations of partial $t_{2g}$ and $e_g$ DOS (shown in Fig. 3) in order to determine the value of crystal field splitting between $t_{2g}$ and $e_g$ states. It was found that $t_{2g}$ states are 1.93 eV lower than $e_g$. Also $t_{2g}$ band is much more narrow.
FIG. 3: DOS of LaCoO$_3$ (left) and HoCoO$_3$ (right) calculated within the LDA. Top panel: total DOS; second from top panel - partial O-2p DOS; Last three panels: partial Co-3d, Co-3d ($t_{2g}$) and Co-3d ($e_g$) DOS. For partial Co-3d ($t_{2g}$) and Co-3d ($e_g$) DOS centers of gravities C and standard deviation $\sigma$ of corresponding Co 3d orbitals are shown. The Fermi level is zero energy.

than $e_g$.

LDA band structure obtained for HoCoO$_3$ is shown in Fig. 3 (right panel). In general it is very similar to LaCoO$_3$ bands (except for the absence of 4$f$ band because Ho-4$f$ states were treated as a pseudo-core). The important difference from LaCoO$_3$ is relative positions of $t_{2g}$ and $e_g$ bands of Co-3$d$ shell. As one can see from last two panels of Fig. 3 (right side), $t_{2g}$ states are 2.04 eV lower than $e_g$ comparing with 1.93 eV for LaCoO$_3$ and also $e_g$ band is more narrow (standard deviation $\sigma$ is 1.45 comparing with 1.59 for LaCoO$_3$). The higher position of $e_g$ states and the smaller width of the corresponding band result in opening of a small energy gap $\approx 0.07$ eV.

Those results can be well understood from the difference in crystal structure of two compounds. The values of Co-O-Co bond angles deviate from 180° much more in HoCoO$_3$ than in LaCoO$_3$. That leads to a weaker $d$-$p$-$d$ hybridization and hence to a more narrow
Co-3d ($e_g$) band.

In addition to Co-O-Co bond bending, substitution of La ion on a smaller Ho ion lead to the compression of Co-O bond lengths. Decreased value of Co-O bond length in HoCoO$_3$ comparing with LaCoO$_3$ results in the increased value of hybridization strength between O-2p states and Co-3d states and hence to the increasing of $t_{2g}$-$e_g$ energy splitting of Co-3d states.

For the problem of Low Spin to Intermediate Spin state transition the most important is increasing of the $t_{2g}$-$e_g$ energy splitting value. As magnetic transition in cobaltites is determined by the competition between crystal field and exchange energies, this result can dramatically increase excitation energy to the magnetic state and hence increase transition temperature for HoCoO$_3$ comparing with LaCoO$_3$.

One can estimate the change of excitation to magnetic state energy as equal to the change in the value of $t_{2g}$-$e_g$ energy splitting: 2.04-1.93=0.09 eV≈1000K. This value must be connected to the transition temperature difference. We will show below, that this crude estimate agrees surprisingly well with the results of our LDA+U calculations.

IV. LDA+U RESULTS

In the present work we used a general rotationally invariant formulation of LDA+U approach instead of the old version used in [2]. The main idea of the LDA+U approach [12, 13] is to add to the LSDA functional the term $E^U$ corresponding to the mean-field approximation of the Coulomb interaction in multiband Hubbard model (Hartree-Fock approximation)

$$E^{LDA+U}[\rho^\sigma(\mathbf{r}), \{n^\sigma\}] = E^{LSDA}[\rho^\sigma(\mathbf{r})] + E^U[\{n^\sigma\}] - E_{dc}[\{n^\sigma\}],$$

(1)

$\rho^\sigma(\mathbf{r})$ is the charge density for spin-$\sigma$ electrons, $E^{LSDA}[\rho^\sigma(\mathbf{r})]$ is the standard LSDA (Local Spin-Density Approximation) functional and Coulomb interaction term $E^U$ is a functional of the occupation matrix $n^\sigma$:

$$n^\sigma_{inlm,nlm'} = \frac{-1}{\pi} \int_{E_F}^{E} \text{Im} G^\sigma_{inlm,inlm'}(E)dE.$$ 

(2)

Here $G^\sigma_{inlm,inlm'}(E) = \langle inlm\sigma | (E - \hat{H})^{-1} | inlm'\sigma \rangle$ are the elements of the Green function matrix in the basis of $d$-orbitals | inlm$\sigma$ ($i$ denotes the cite, $n$ the main quantum number,
$l$- orbital quantum number, $m$- magnetic number and $\sigma$- spin index)

$$
E^U[{n^\sigma}] = \frac{1}{2} \sum_{m,\sigma} \{ \langle m, m' | V_{ee} | m', m'' \rangle n_{mm}^\sigma n_{m'm'm''}^\sigma + 
(\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{m'm'm''}^\sigma n_{m'm'm''}^\sigma \},
$$

(3)

where $V_{ee}$ are the screened Coulomb interactions among the $d$ electrons. Finally, the last term in Eq. (1) corrects for double counting and is given by

$$
E_{dc}[{n^\sigma}] = \frac{1}{2} UN(N - 1) - \frac{1}{2} J[N^\uparrow(N^\uparrow - 1) + N^\downarrow(N^\downarrow - 1)],
$$

(4)

with $N^\sigma = Tr(n_{m'm'}^\sigma)$ and $N = N^\uparrow + N^\downarrow$. $U$ and $J$ are screened Coulomb and exchange parameters [14, 15].

In addition to the usual LSDA potential, an effective single-particle potential to be used in the effective single-particle Hamiltonian has the form:

$$
\hat{H} = \hat{H}_{LSDA} + \sum_{mm'} | inlm\sigma\rangle V_{mm'}^\sigma \langle inlm'\sigma |,
$$

(5)

$$
V_{mm'}^\sigma = \sum_{m'm'm''} \{ \langle m, m'' | V_{ee} | m', m''' \rangle n_{m'm'm''}^\sigma +
(\langle m, m'' | V_{ee} | m', m''' \rangle - \langle m, m'' | V_{ee} | m''', m' \rangle) n_{m'm'm''}^\sigma n_{m'm'm''}^\sigma \} -
$$

$$
U(N - \frac{1}{2}) + J(N^\sigma - \frac{1}{2}).
$$

(6)

The matrix elements of Coulomb interaction can be expressed in terms of complex spherical harmonics and effective Slater integrals $F^k$ [17] as

$$
\langle m, m'' | V_{ee} | m', m''' \rangle = \sum_{k=0}^{2l} a_k(m, m', m'', m''') F^k,
$$

(7)

and

$$
a_k(m, m', m'', m''') = \frac{4\pi}{2k + 1} \sum_{q=-k}^{k} \langle lm | Y_{kq} | lm' \rangle \langle lm'' | Y_{kq}^* | lm''' \rangle.
$$

For $d$ electrons one needs $F^0$, $F^2$ and $F^4$ and these can be linked to the Coulomb and Stoner parameters $U$ and $J$ obtained from the LSDA-supercell procedures via $U = F^0$ and $J = (F^2 + F^4)/14$, while the ratio $F^2/F^4$ is to a good accuracy a constant $\sim 0.625$ for the $3d$ elements [16, 18] (for $f$ electrons the corresponding expression is $J = (286F^2 + 195F^4 +$
The Coulomb parameter $U$ is calculated as a second derivative of the total energy (or the first derivative of the corresponding eigenvalue) in respect to the occupancy of localized orbitals of the central atom in a supercell with fixed occupancies on all other atoms [14].

Coulomb interaction parameters $U=7.80$ eV and $J=0.99$ eV used in our LDA+U calculations were computed in [2] by the constrained LDA approach [14]. The main effect of LDA+U potential correction [6] is the energy splitting between occupied and empty states in such a way that the former are pushed down and the latter up comparing with LDA. In the result magnetic state solution, which does not exist in LSDA, becomes stable in LDA+U and by comparing the relative energy of two solutions, non-magnetic and magnetic, one can find the ground state of the system.

We have investigated two solutions for both compounds for all crystal structure param-
eters corresponding to the temperatures 5-300 K for LaCoO$_3$ and 300-1080 K for HoCoO$_3$. The Low Spin state solutions (Fig. 4) are very similar to LDA results (Fig. 3). The main effect of LDA+U correction is higher position of the empty Co-3$d$ ($e_g$) states and the opposite effect on the occupied Co-3$d$ ($t_{2g}$) states and hence opening of a sizable energy gap (0.7 eV for LaCoO$_3$ and 1.3 eV for HoCoO$_3$).

![Graph](image)

**FIG. 5:** DOS of LaCoO$_3$ (left) and HoCoO$_3$ (right) calculated within the LDA+U approach for Intermediate Spin state $t_{2g}^5e_g^1$ of Co ion. Top panel: total DOS; second from top panel: partial O-2$p$ DOS; Last three panels: partial Co-3$d$, Co-3$d$ ($t_{2g}$) and Co-3$d$ ($e_g$) DOS correspondingly. The Fermi level is zero energy.

On the other hand the Intermediate Spin state solutions (Fig. 5) are very different from LDA. At first a peak above Fermi energy appears for minority spin Co-3$d$ ($t_{2g}$) states corresponding to a hole in $t_{2g}$ shell and at second the majority spin Co-3$d$ ($e_g$) band becomes half-filled ($t_{2g}^5e_g^1$ configuration). The magnetic moment values on Co ions are equal to 2.2 $\mu_B$ for LaCoO$_3$ and 2.17 $\mu_B$ for HoCoO$_3$. The Intermediate State solution gave metallic state in contrast to the semiconductor properties of LaCoO$_3$. In [2] this contradiction was explained by the possibility of orbital ordering of the partially filled $e_g$-orbitals of Co$^{3+}$ ions in
Intermediate State and opening an energy gap in the orbitally ordered state. Recently the evidence for orbital order in LaCoO$_3$ was found in diffraction experiments [19].

The most interesting are results for total energy values of Low Spin and Intermediate Spin solutions. In Fig. 6 those energies are plotted as a function of the temperature (temperature is taken into account in our calculations only via experimental crystal structure parameters). For LaCoO$_3$ at 5 K the total energy difference between Low Spin and Intermediate Spin states is only 37 meV and (by interpolation) becomes zero at 140 K. For room temperature (300 K) Low Spin state is higher in energy than Intermediate Spin on 45 meV.

For HoCoO$_3$ the situation is very different. At room temperature there is a very large total energy difference between Low Spin and Intermediate Spin states (200 meV) and only at 1080 K Intermediate Spin state becomes lower in energy than Low Spin. The interpolated value of T, where energies of Low Spin and Intermediate Spin are equal is 1070 K.

One can identify the temperatures, where lines for Low Spin and Intermediate Spin states cross in Fig. 6 as magnetic transition temperatures. The value for LaCoO$_3$ equal to 140 K agrees very well with the 100 K maximum in experimental susceptibility curve [1]. The calculated magnetic transition temperature for HoCoO$_3$ equal to 1070 K also agrees with the results of [4], where authors conclude that “at room temperature all cobalt ions are in the Low Spin state” and only as temperature increases to 1000 K “the possible electronic phase transition can be suggested”.

FIG. 6: Comparison of total energy per Co ion of Intermediate Spin state $t_{5g}^5e_g^1$ (full line, circles) and Low Spin state $t_{5g}^6e_g^0$ (dashed line, diamonds) solutions for LaCoO$_3$ (left) and HoCoO$_3$ (right) calculated with the LDA+U approach as a functions of temperature. The temperature of transition (calculated as the temperature where two lines cross) is $\sim 140$ K for LaCoO$_3$ and $\sim 1070$ K for HoCoO$_3$. 
V. CONCLUSION

Comparative study of electronic structure and magnetic properties of LaCoO$_3$ and HoCoO$_3$ was done using LDA and LDA+U approaches. The chemical pressure induced by substitution of La ions by smaller Ho ions leads to the bending of Co-O-Co bond angles and compression of Co-O bond length that in its turn increases the value of crystal field splitting in HoCoO$_3$. Total energy calculations for Low Spin and Intermediate Spin states demonstrated that this increase results in stabilization of non-magnetic solution in HoCoO$_3$ and hence increasing of transition temperature from 140 K (LaCoO$_3$) to 1070 K (HoCoO$_3$). Calculated transition temperatures agree well with the experimental estimations.

Acknowledgments

The work was supported by the INTAS project No.01-0278 and the Russian Foundation for Basic Research through grants RFFI-01-02-17063 (VA, IN, MK) and RFFI-03-02-06026, the grant of Ural Branch of the Russian Academy of Sciences for Young Scientists, Grant of the President of Russia for Young Scientists MK-95.2003.02 (IN).

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