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Influence of rare-earth ion radii on the low-spin to intermediate-spin state transition in lanthanide cobaltite perovskites: $LaCoO_3$ versus $HoCoO_3$

I. A. Nekrasov,[1] S. V. Streltsov,[1,2] M. A. Korotin,[1] and V. I. Anisimov[1]
[1]*Institute of Metal Physics, Russian Academy of Sciences-Ural Division, 620219 Yekaterinburg GSP-170, Russia*
[2]*Department of Theoretical Physics and Applied Mathematics, Ural State Technical University, 620002 Yekaterinburg Mira 19, Russia*

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We present first-principles (local-density approximation) LDA+U calculations of electronic structure and magnetic state for $LaCoO_3$ and $HoCoO_3$. 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 $HoCoO_3$, which agrees well with the experimental estimations. Low-spin state $t_{2g}^6e_g^0$ (nonmagnetic) 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 $HoCoO_3$ and $LaCoO_3$ due to the smaller ionic radius of Ho ion comparing with La ion results in stronger crystal-field splitting for $HoCoO_3$ ($0.09\ \mathrm{eV} \approx 1000$ K larger than for $LaCoO_3$) and hence tips the balance between the low-spin and intermediate-spin states to the nonmagnetic solution in $HoCoO_3$.

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I. INTRODUCTION

In lanthanum cobaltite $LaCoO_3$ there is a temperature-induced transition from a nonmagnetic to magnetic state, which has attracted considerable interest in the past 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 nonmagnetic ground state ($t_{2g}^6, S=0$) to a high-spin state ($t_{2g}^4e_g^2, S=2$), later a new scenario involving intermediate-spin state ($t_{2g}^5e_g^1, S=1$) has been proposed. Using the results of (local-density approximation) LDA+U, Korotin *et al.*[2] explained stabilization of intermediate-spin state over high-spin state due to the large hybridization between Co-$3d$ (e_g) and O-$2p$ orbitals.

The physical reason for this transition is a competition between crystal-field energy Δ_{cf} (t_{2g}-e_g energy splitting) and intraatomic (Hund) exchange energy Δ_{ex} (Fig. 1). In the ground state Δ_{cf} is only slightly larger than Δ_{ex} so that the energy of the excited magnetic state of Co ion is relatively small and with increasing 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 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[4] $LnCoO_3$ (Ln=Nd, Gd, Dy, and Ho) led its authors to the 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 transition can be suggested." Magnetic and electric measurements for $Ho_{1-x}Ca_xCoO_3$ system[5] 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 the low-spin state of Co^{3+} ions in lanthanide cobaltite perovskites with smaller rare-earth ions becomes more stable comparing with $LaCoO_3$ and the transition temperature increases dramatically. In the present work we have investigated relative stability of low-spin and intermediate-spin (IS) 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 the decrease of Co-O bond length due to the chemical pressure occurring with substitution of La ions by smaller Ho ions and hence the increase of the crystal-field t_{2g}-e_g energy splitting value, thus stabilizing the 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 crystallo-

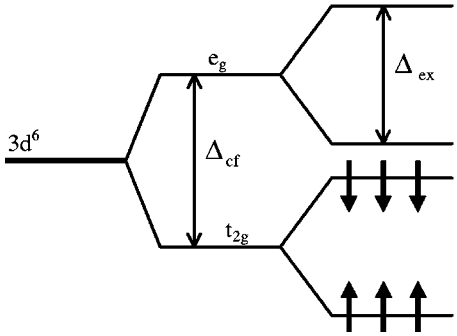

FIG. 1. Scheme of energy levels for low-spin state of Co^{3+} ions in $LaCoO_3$.

TABLE I. Structural parameters and Co-O bond length of $LaCoO_3$ as a function of temperature by Radaelli and Cheong (Ref. 8). The space group is $R\overline{3}c$. The atomic positions are La $6a(0,0,1/4)$, Co $6b(0,0,0)$, and O $18e(x,0,1/4)$.

Temperature (K)	5	50	100	125	150	200	300
a (Å)	5.42625(5)	5.42784(6)	5.43317(5)	5.43530(5)	5.43733(5)	5.44108(5)	5.44864(3)
c (Å)	12.991(1)	12.999(1)	13.022(1)	13.033(1)	13.044(1)	13.064(1)	13.1035(9)
O x	0.55265(8)	0.55277(8)	0.55260(8)	0.55216(8)	0.55200(8)	0.55134(8)	0.55132(8)
Co-O (Å)	1.92544(7)	1.92627(7)	1.92854(7)	1.92922(6)	1.93007(6)	1.93141(6)	1.93452(6)

graphic data by Radaelli and Cheong,[8] the space group the unit cell of this compound is $R\overline{3}c$ for all measured temperatures and has two formula units. Corresponding lattice constants and atomic positions as a function of temperature reported in Ref. 8 are presented in Table I. 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 from 180° to $\sim$163° (Fig. 2).

$HoCoO_3$ has orthorhombically distorted perovskite crystal structure [prototype $GdFeO_3$, space group $Pbnm$ (Ref. 4)] (Fig. 2), which contains four formula units in the unit cell. Corresponding lattice constants and atomic positions as a function of temperature reported in Ref. 4 are presented in Table II. For the temperature 1098 K in the paper[4] only a, b, and c lattice parameters but no atomic positions were reported. Because of that in our further calculations for the temperature 1098 K we used the experimental lattice constants but atomic positions for the temperature 995 K. Like for $LaCoO_3$ the main crystallographic motif form CoO_6 octahedra, which are rotated in the ab plane and tilted with respect to the c axis. Due to smaller ionic radius of Ho ion compared 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 the ab plane) and 152° (along the c axis).

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 (Refs. 8 and 4)]. Such decrease can be understood as a result of chemical pressure, induced by the smaller ionic radius of Ho ion compared with La ion.

It was demonstrated in Ref. 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 result in stabilization of the low-spin (LS) 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 ELECTRONIC STRUCTURE

The standard L(S)DA [local-(spin-) density approximation[9,10]] based methods can not describe magnetic state for $LaCoO_3$ without taking into account Coulomb interaction between $3d$ electrons as it was demonstrated in Ref. 2. However analysis of the LDA results is instructive for understanding the basic electronic structure of lanthanide cobaltite perovskites.

We used scalar relativistic linear muffin-tin orbital method in orthogonal representation within the atomic sphere approximation[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 $R_{La} = 3.76$ a.u., $R_{Co} = 2.49$ a.u., and $R_O = 2.0$ a.u. With increasing temperature R_{Co} and R_O were increased proportionally to Co-O distance for a given tempera-

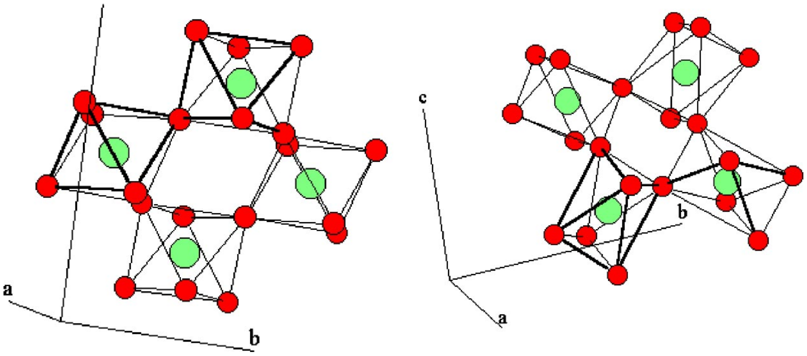

FIG. 2. The rhombohedral crystal structure of $LaCoO_3$ (left) and the orthorhombic crystal structure of $HoCoO_3$ (right). Co, large spheres; O, small spheres.

TABLE II. Structural parameters and averaged Co-O bond length of $HoCoO_3$ as a function of temperature by Liu and Prewitt (Ref. 4). The space group is $Pbnm$. The atomic positions are Co $4b(0,1/2,0)$, Ho and O(1) $4c(x,y,1/4)$, O(2) $8d(x,y,z)$.

Temperature (K)	300	584	892	995	1098
a (Å)	5.1420(2)	5.1618(3)	5.2129(3)	5.2292(3)	5.2426(4)
b (Å)	5.4142(2)	5.4245(2)	5.5049(3)	5.5286(3)	5.5463(4)
c (Å)	7.3731(3)	7.3972(5)	7.4491(4)	7.4689(4)	7.4880(5)
x	0.9792(8)	0.9791(8)	0.9798(11)	0.9784(17)	[a]
Ho y	0.0618(5)	0.0615(5)	0.0612(5)	0.0612(6)	[a]
x	0.0950(79)	0.0925(78)	0.0948(99)	0.0912(95)	[a]
O(1) y	0.4716(82)	0.4725(84)	0.4711(66)	0.4760(76)	[a]
x	0.7054(59)	0.7060(58)	0.7076(70)	0.7032(86)	[a]
O(2) y	0.2950(58)	0.2950(57)	0.2923(55)	0.2934(57)	[a]
z	0.0452(54)	0.0451(54)	0.0472(57)	0.0456(59)	[a]
Ave. Co-O (Å)	1.921	1.923	1.946	1.953	1.961

[a] In the paper (Ref. 4) atomic positions for 1098 K are not presented.

ture. In $HoCoO_3$ for lowest-temperature (300 K) crystal structure R_{Co} and R_O were taken as the corresponding values for $LaCoO_3$ scaled in proportion to Co-O distances in $LaCoO_3$ and averaged Co-O distances in $HoCoO_3$. In $HoCoO_3$ radii of both crystallographically inequivalent oxygens O(1) and O(2) (see Table II) were assumed to be the same. Then R_{Co} and R_O were increased proportionally to the change of the averaged Co-O distance in $HoCoO_3$ for a given temperature. R_{La} was adjusted to fill completely the volume of the unit cell. In the orbital basis set the following states were included: Co$(4s,4p,3d)$, O$(3s,2p)$, La,Ho$(6s,6p,5d,4f)$. Partially filled $4f$ states of Ho were treated as "frozen" ones. This is possible because Ho-$4f$ states are localized and not physically relevant in the system. Due to the rather large value of on-site Coulomb interaction U (of the order of 10 eV) for Ho-$4f$ orbitals the correspond-

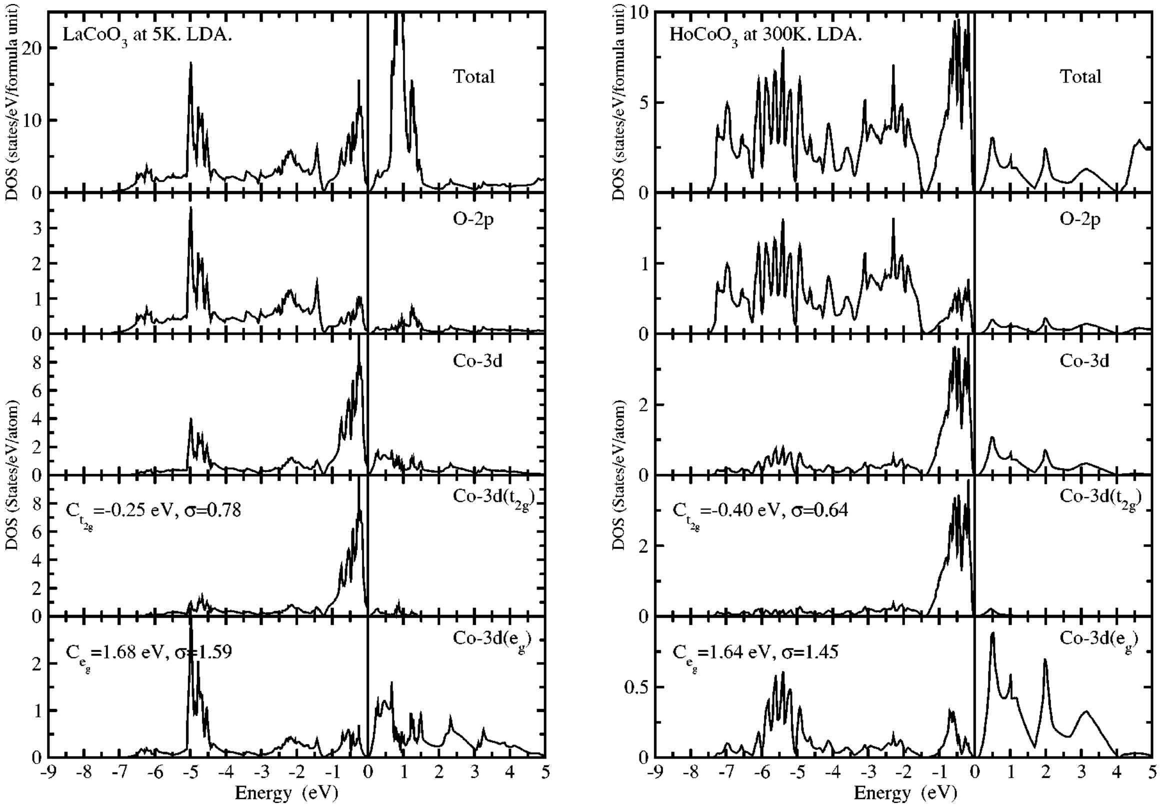

FIG. 3. DOS of $LaCoO_3$ (left) and $HoCoO_3$ (right) calculated within the LDA. Top panel, total DOS; second from top panel, partial O-$2p$ DOS; last three panels, partial Co-$3d$, Co-$3d$ (t_{2g}), and Co-$3d$ (e_g) DOS's. For partial Co-$3d$ (t_{2g}) and Co-$3d$ (e_g) DOS centers of gravities C and standard deviation σ of corresponding Co $3d$ orbitals are shown. The Fermi level is zero energy.

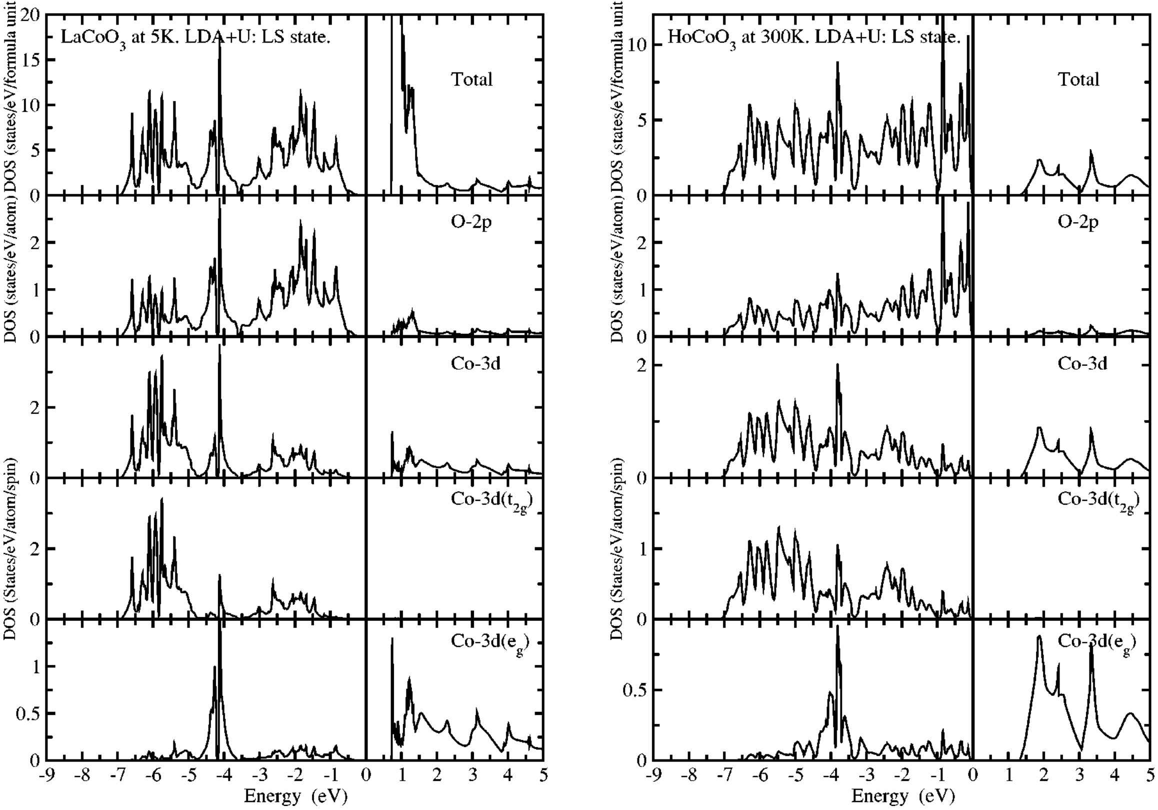

FIG. 4. DOS of $LaCoO_3$ (left) and $HoCoO_3$ (right) calculated within the LDA+U approach for the low-spin state $t_{2g}^6 e_g^0$ of Co ion. Top panel, total DOS; second from top panel, partial O-2p DOS; last three panels: partial Co-3d, Co-3d (t_{2g}), and Co-3d (e_g) DOS correspondingly. The Fermi level is zero energy.

ing states will be located approximately at ±5 eV around the Fermi level. For all calculations were used 27 irreducible k-points.

Figure 3 (left panel) shows in detail LDA calculated electronic 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-2p states but have a significant admixture from Co-3d states. Between 0 eV and 2 eV there are empty La-4f 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-3d states. Also substantial O-2p contributions are apparent in this energy range. Co-3d 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's (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 on 1.93 eV lower than e_g. Also t_{2g} band is much more narrow than e_g.

LDA electronic 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 4f band because Ho-4f states were treated as a frozen ones). The important difference from $LaCoO_3$ is relative positions of t_{2g} and e_g bands of Co-3d shell. As one can see from the last two panels of Fig. 3 (right side), t_{2g} states are on 2.04 eV lower than e_g compared with 1.93 eV for $LaCoO_3$ and also e_g band is more narrow (standard deviation σ is 1.45 compared with 1.59 for $LaCoO_3$). The higher position of e_g states and the smaller width of the corresponding band results in the opening of a small energy gap ≈ 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 leads 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 increase of t_{2g}-e_g energy splitting of Co-3d states.

Thus we have competition between Co-O-Co bond bending (decrease of Co-O hybridization in Ho vs La compound) and Co-O bond-length compression (increase of Co-O hybridization in Ho vs La compound). Our presented results show that the latter has a stronger effect and is responsible for the low-spin state to intermediate-spin state transition.

For the problem of low-spin to intermediate-spin state

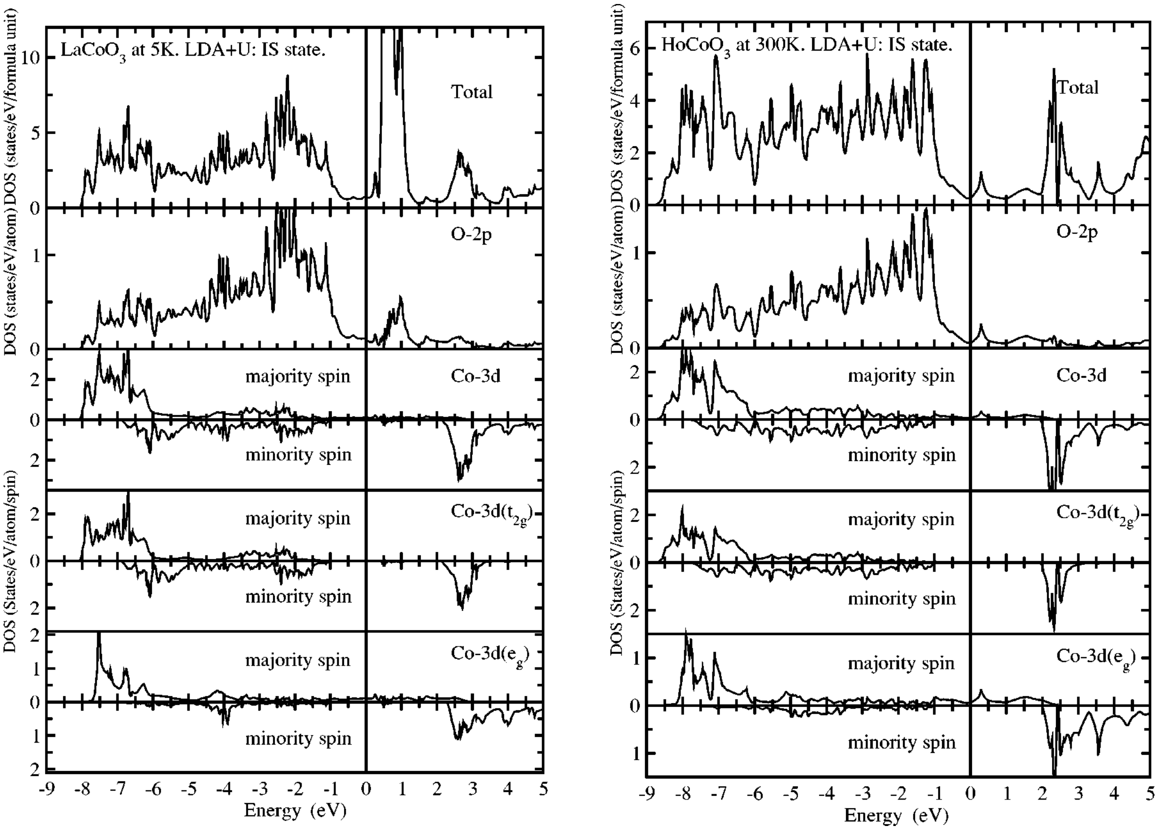

FIG. 5. DOS of LaCoO$_3$ (left) and HoCoO$_3$ (right) calculated within the LDA+U approach for intermediate-spin state $t_{2g}^5 e_g^1$ of Co ion. Top panel, total DOS; second from top panel, partial O-2p DOS; last three panels, partial Co-3d, Co-3d (t_{2g}) and Co-3d (e_g) DOS correspondingly. The Fermi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

transition the most important is the increase of the t_{2g}-e_g energy splitting value. Since 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$_3$ compared 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≈1000 K. 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 described elsewhere[12] instead of the simpler version[13] used in Ref. 2.

Coulomb interaction parameters $U=7.80$ eV and $J=0.99$ eV used in our LDA+U calculations were computed in Ref. 2 by the constrained LDA approach.[14] The main effect of LDA+U potential correction is the energy splitting between occupied and empty states in a such way that the former are pushed down and the latter up compared 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, nonmagnetic and magnetic, one can find the ground state of the system.[15–18]

We have investigated two solutions for both compounds for all crystal structure parameters 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-3d (e_g) states and the opposite effect on the occupied Co-3d (t_{2g}) states and hence opening of a sizable energy gap (0.7 eV for LaCoO$_3$ and 1.3 eV for HoCoO$_3$).

On the other hand, the intermediate-spin state solutions (Fig. 5) are very different from LDA. At first a peak above the Fermi energy appears for minority-spin Co-3d (t_{2g}) states corresponding to a hole in t_{2g} shell and at second majority-spin Co-3d (e_g) band becomes half filled ($t_{2g}^5 e_g^1$ configuration). The magnetic-moment values on Co ions are equal to 2.2μ_B for LaCoO$_3$ and 2.17μ_B for HoCoO$_3$. The intermediate-spin state solution gave metallic state in contrast to the semiconductor properties of LaCoO$_3$. In Ref. 2 this contradiction was explained by the possibility of orbital ordering of the partially filled e_g orbitals of Co^{3+} ions in intermediate-spin 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 (tempera-

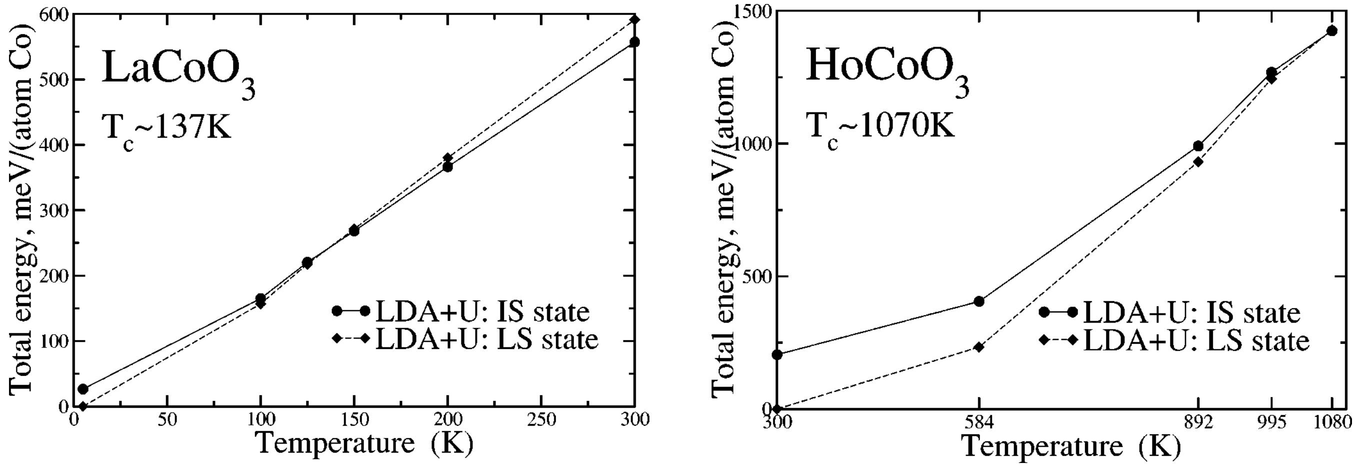

FIG. 6. Comparison of total energy per Co ion of intermediate spin-state $t_{2g}^5 e_g^1$ (full line, circles) and low-spin state $t_{2g}^6 e_g^0$ (dashed line, diamonds) solutions for $LaCoO_3$ (left) and $HoCoO_3$ (right) calculated with the LDA+U approach as a functions of temperature. The temperature of transition (calculated as the temperature where two lines cross) is ~137 K for $LaCoO_3$ and ~1070 K for $HoCoO_3$. Drawn lines are for guiding the eyes.

ture 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 137 K. For room temperature (300 K) the low-spin state is higher in energy than the 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 1070 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 the experimental susceptibility curve.[1] The calculated magnetic transition temperature for $HoCoO_3$ equal to 1070 K also agrees with the results of Ref. 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."

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, which in 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 nonmagnetic solution in $HoCoO_3$ and hence in the increase of transition temperature from 137 K ($LaCoO_3$) to 1070 K ($HoCoO_3$). Calculated transition temperatures agree well with the experimental estimations.

ACKNOWLEDGMENTS

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[1] For a short review on experimental and theoretical aspects of $LaCoO_3$ problem see M. Imada, A. Fujimori, and Y. Tokura, Rev. Mod. Phys. **70**, 1039 (1998), pp. 1235–1239.

[2] M.A. Korotin, S.Yu. Ezhov, I.V. Solovyev, V.I. Anisimov, D.I. Khomskii, and G.A. Sawatzky, Phys. Rev. B **54**, 5309 (1996).

[3] M. Itoh and J. Hashimoto, Physica C **341-348**, 2141 (2000).

[4] X. Liu and C.T. Prewitt, J. Phys. Chem. Solids **52**, 441 (1991).

[5] Y.S. Im, K.H. Ryu, K.H. Kim, C.H. Yo, J. Phys. Chem. Solids **58**, 2079 (1997).

[6] T. Vogt, J.A. Hriljac, N.C. Hyatt, and P. Woodward, Phys. Rev. B **67**, 140401 (2003).

[7] G. Thornton, B.C. Tofield, and A.W. Hewat, J. Solid State Chem. **61**, 301 (1986).

[8] P.G. Radaelli and S.-W. Cheong, Phys. Rev. B **66**, 094408 (2002).

[9] W. Kohn and L.J. Sham, Phys. Rev. A **140**, 1133 (1965); L.J. Sham and W. Kohn, Phys. Rev. **145**, 561 (1966).

[10] L. Hedin and B. Lundqvist, J. Phys. C **4**, 2064 (1971); U. von Barth and L. Hedin, *ibid.* **5**, 1629 (1972).

[11] O.K. Andersen, Phys. Rev. B **12**, 3060 (1975); O. Gunnarsson, O. Jepsen, and O.K. Andersen, Phys. Rev. B **27**, 7144 (1983).

[12] V.I. Anisimov, F. Aryasetiawan, and A.I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).
[13] V.I. Anisimov, J. Zaanen, and O.K. Andersen, Phys. Rev. B **44**, 943 (1991).
[14] O. Gunnarsson, O.K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B **39**, 1708 (1989).
[15] V.I. Anisimov and O. Gunnarsson, Phys. Rev. B **43**, 7570 (1991).
[16] V.I. Anisimov, I.V. Solovyev, M.A. Korotin, M.T. Czyżyk, and G.A. Sawatzky, Phys. Rev. B **48**, 16929 (1993).
[17] B.R. Judd, *Operator Techniques in Atomic Spectroscopy* (McGraw-Hill, New York, 1963).
[18] F.M.F. de Groot, J.C. Fuggle, B.T. Thole, and G.A. Sawatzky, Phys. Rev. B **42**, 5459 (1990).
[19] G. Maris, Y. Ren, V. Volotchaev, C. Zobel, T. Lorentz, and T.T.M. Palstra, Phys. Rev. B **67**, 224423 (2003).