

## Nature of Magnetism in $\text{Ca}_3\text{Co}_2\text{O}_6$

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We find using local spin density approximation + Hubbard  $U$  band structure calculations that the novel one-dimensional cobaltate  $\text{Ca}_3\text{Co}_2\text{O}_6$  is not a ferromagnetic half-metal but a Mott insulator. Both the octahedral and the trigonal Co ions are formally trivalent, with the octahedral being in the low-spin and the trigonal in the high-spin state. The inclusion of the spin-orbit coupling leads to the occupation of the minority-spin  $d_2$  orbital for the unusually coordinated trigonal Co, producing a giant orbital moment ( $1.57\mu_B$ ). It also results in an anomalously large magnetocrystalline anisotropy (of order 70 meV), elucidating why the magnetism is highly Ising-like. The role of the oxygen holes, carrying an induced magnetic moment of  $0.13\mu_B$  per oxygen, for the exchange interactions is discussed.

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The one-dimensional (1D) cobaltate  $\text{Ca}_3\text{Co}_2\text{O}_6$  [1] and isostructural  $A_3MM'\text{O}_6$  ( $A$  = alkaline-earth metal;  $M, M'$  = transition metals) compounds [2] attract now considerable attention due to their peculiar crystal structure and very unusual properties. A large number of research activities have been triggered by the discovery of the unconventional magnetic structure with strange magnetization jumps [3–12], reminiscent of quantum tunneling of magnetization in molecular magnets, and also by the observation of the large thermoelectric power and magnetoresistance [13–15].

From a theoretical point of view, the understanding of the  $\text{Ca}_3\text{Co}_2\text{O}_6$  system is far from satisfactory. The crystal structure consists of triangular lattice of  $c$ -axis chains of alternating  $\text{CoO}_6$  octahedra and trigonal prisms sharing common faces [1,3]. Both the spin and valence state of the Co ions in these two positions, i.e.,  $\text{Co}_{\text{oct}}$  and  $\text{Co}_{\text{trig}}$ , respectively, are a matter of controversy. There were several suggestions made [1–16], the most common ones being either the nonmagnetic low-spin (LS,  $S = 0$ )  $\text{Co}_{\text{oct}}^{3+}$  and magnetic high-spin (HS,  $S = 2$ )  $\text{Co}_{\text{trig}}^{3+}$ , or the LS ( $S = 1/2$ )  $\text{Co}_{\text{oct}}^{4+}$  and HS ( $S = 3/2$ )  $\text{Co}_{\text{trig}}^{2+}$ . Recent local-spin-density approximation (LSDA) and generalized gradient approximation (GGA) calculations do not provide clarity: Whangbo *et al.* [17] and Eyert *et al.* [18] support the first alternative, while Vidya *et al.* [19] the second one. To add to the confusion, all those calculations [17–19] predict  $\text{Ca}_3\text{Co}_2\text{O}_6$  to be a metal, in strong disagreement with the experiments [5,13,15]. In fact, it has been even claimed [19] that this material would be the first 1D oxide displaying ferromagnetic half-metallicity (FMHM).

Another problem is the nature of magnetism in this material. In modeling the intriguing magnetic properties, it was always concluded or assumed that the Co chains behave as an Ising system with ferromagnetic (FM) intra-chain exchange [3–10]. The nature of such behavior, however, is completely unclear: the origin of Ising-like behavior was not discussed at all, and attempts to explain

the FM exchange using an ionic superexchange model [20] meet some problems, see below.

In view of these controversies, we carried out a theoretical study of the electronic structure and magnetic properties of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in which we took more explicitly into account the correlated motion of the electrons typical in transition metal oxides. In this work we used the local-spin-density approximation + Hubbard  $U$  (LSDA +  $U$ ) method [21], including also the spin-orbit coupling (SOC). We settle theoretically the issue on the valence (spin) state, and find that  $\text{Ca}_3\text{Co}_2\text{O}_6$  is a Mott or rather charge-transfer insulator [22] already for moderate values of Hubbard  $U$ .

The inclusion of the SOC leads to a series of surprising but experimentally sound results: a giant orbital moment for the HS  $\text{Co}_{\text{trig}}$  ion consistent with the experimentally observed large total magnetic moment, an anomalously large magnetocrystalline anisotropy important to explain the Ising-like properties, and an unusual orbital occupation of the  $\text{Co}_{\text{trig}}$  ion requiring a completely new approach for modeling the exchange interactions.

Our calculations were performed by using the full-potential augmented plane waves plus local orbital method [23]. We took the  $\text{Ca}_3\text{Co}_2\text{O}_6$  structure data determined by neutron diffraction measurements at 40 K [1]. The muffin-tin sphere radii are chosen to be 2.7, 2.0, and 1.6 Bohr for Ca, Co, and O atoms, respectively. The cutoff energy of 16 Ryd is used for plane wave expansion, and  $5 \times 5 \times 5$   $\mathbf{k}$  mesh for integrations over the Brillouin zone. The SOC is included by the second-variational method with scalar relativistic wave functions [23]. The easy magnetization direction is along the  $c$ -axis chains.

We plot in Fig. 1 the LSDA results, which give a FMHM solution, in agreement with previous calculations [17–19]. One should note that the Fermi level is located in a narrow  $\text{Co}_{\text{trig}}$   $3d$  band with no more than 1 eV width, which is consistent with the system being 1D. It is then also natural to expect that already modest electron correlation effects at

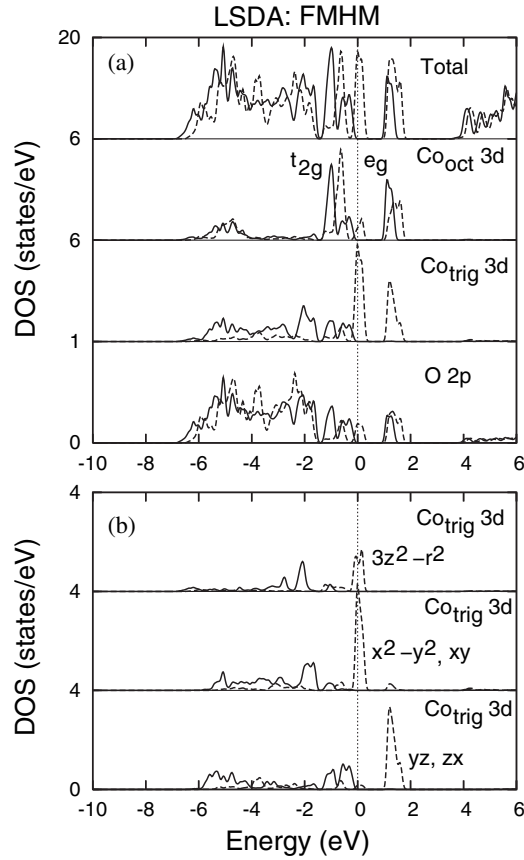


FIG. 1. Density of states (DOS) of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the ferromagnetic half-metallic (FMHM) state from LSDA. The Fermi level is set at zero energy. (a) shows (from upper to lower panels) the total DOS, the  $\text{Co}_{\text{oct}}$  3d,  $\text{Co}_{\text{trig}}$  3d, and O 2p partial DOS. (b) shows the  $\text{Co}_{\text{trig}}$  3d orbitally resolved partial DOS. Solid (dashed) lines depict the spin-up (down) states.

the Co sites will be able to turn this material into a Mott insulator.

Another important point to note from our LSDA results is that for the  $\text{Co}_{\text{trig}}$  ion, the crystal field does not split up the 3d orbitals into the usual  $e_g$  and  $t_{2g}$  levels. Instead, it is found that the  $x^2 - y^2$  is degenerate with the  $xy$ , and the  $yz$  with  $zx$  orbital, as can be seen from Fig. 1(b). In the presence of the SOC, it is then better to use the complex orbitals  $d_0$ ,  $d_2/d_{-2}$ , and  $d_1/d_{-1}$ . Significant from the LSDA is also that the narrow  $d_0$  singlet and  $d_2/d_{-2}$  doublet bands are almost degenerate. Figure 2 sketches the local crystal field energy diagram. This implies that SOC, so far not included in all the LSDA calculations [17–19], could have a substantial effect on the outcome for the predictions on the magnetic properties. An interesting aspect from Fig. 1(b) is the finding that the  $d_1/d_{-1}$  band is split off from the  $d_0$  and  $d_2/d_{-2}$  bands by about 1 eV, i.e., much larger than the SOC energy scale. Therefore, the SOC Hamiltonian can be simplified into just  $\zeta l_z s_z$  by neglecting the  $l_+ s_-$  and  $l_- s_+$  mixing terms. This has far reaching consequences for the magnetocrystalline anisotropy as we will show below.

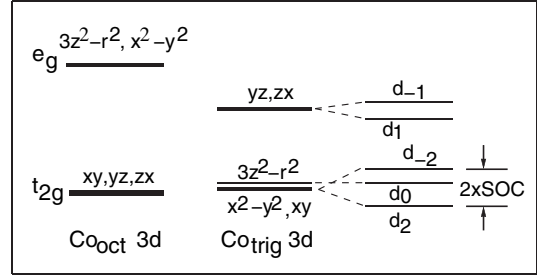


FIG. 2. Local crystal field energy diagram for: (left)  $\text{Co}_{\text{oct}}$  and (right)  $\text{Co}_{\text{trig}}$  without and with spin-orbit coupling.

In Fig. 3 we show our LSDA + U + SOC results [24]. We find that  $\text{Ca}_3\text{Co}_2\text{O}_6$  is an insulator with ferromagnetic chains (FMI), i.e., not a metal, in contrast to the LSDA results [17–19]. We have used  $U = 5$  eV for the Coulomb energy and  $J_H = 0.9$  eV for the Hund exchange parameter. These values are taken from electron spectroscopy measurements [25] and Hartree-Fock calculations [26]. To investigate to what extent the insulating solution is robust against the particular choice of  $U$ , we have calculated and plotted in Fig. 4 (top panel) the band gap as a function of  $U$ . One can observe that a value as small as 2.5 eV is already sufficient to open up a gap. This is consistent with the system being 1D resulting in a small width of the Co 3d

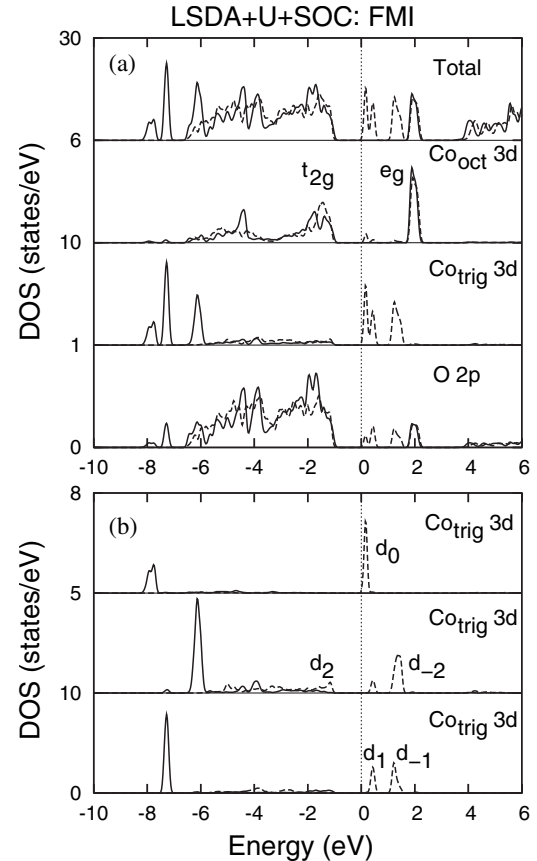


FIG. 3. Density of states (DOS) of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the ferromagnetic insulating (FMI) state from LSDA + U + SOC.

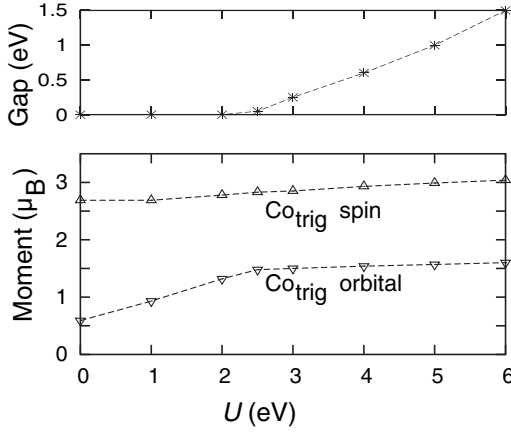


FIG. 4.  $U$  dependence of the insulating gap (top panel), as well as of the spin and orbital contributions to the  $\text{Co}_{\text{trig}}$  magnetic moment (bottom panel).

band. The presence of this gap does not practically depend on the inclusion of SOC and is due to the Hubbard term  $U$ . We therefore can conclude that  $\text{Ca}_3\text{Co}_2\text{O}_6$  is a correlated insulator [22] for any realistic value of  $U$ , i.e., 4–6 eV for  $\text{Co}^{3+}$ .

As far as the valences are concerned, we find from the LSDA +  $U$  + SOC that both the  $\text{Co}_{\text{oct}}$  and  $\text{Co}_{\text{trig}}$  sites have the 3+ valence. The 4+ / 2+ scenario (also FMI) is unstable and lies higher by 84 meV per formula unit (f.u.). The  $\text{Co}_{\text{oct}}$  ion in the 3+ / 3+ ground state is definitely LS: as can be seen from Fig. 3(a), the large  $\text{Co}_{\text{oct}}$   $t_{2g} - e_g$  band gap does not leave any room for a  $3d^6$  state other than the one with  $t_{2g}^6$ , i.e., nonmagnetic. The  $\text{Co}_{\text{trig}}$  ion, on the other hand, is in the HS state ( $S = 2$ ). Very interesting is the orbital occupation for this  $\text{Co}_{\text{trig}}^{3+}$  ion: Fig. 3(b) shows that five electrons occupy all the spin-up  $d_0$ ,  $d_1/d_{-1}$ , and  $d_2/d_{-2}$  orbitals, and that the sixth electron resides in the spin-down  $d_2$  orbital. This is the consequence of the SOC in this very narrow band system with the tiny crystal field splitting between the  $d_0$  and  $d_2/d_{-2}$  levels. When the  $d_{-2}$  orbital is forced to be occupied instead, the increasing total energy allows us to estimate the SOC strength to be about 70 meV. As a result, the orbital contribution to the magnetic moment can be much larger than the  $1\mu_B$  one usually finds for Co or Fe ions in  $O_h$  symmetry. An ionic  $d_2$  state would give an orbital moment of  $2\mu_B$ , but here we find  $1.57\mu_B$  due to covalency

and small distortions of the trigonal prism; see also Table I. Experimentally, Hu *et al.* have recently found using soft-x-ray magnetic circular dichroism that  $\text{Ca}_3\text{Co}_2\text{O}_6$  indeed has an orbital moment which is significantly larger than  $1\mu_B$  [27].

Adding the orbital moment to the  $4\mu_B$  from the  $S = 2$  spin contribution, we end up with the total magnetic moment of about  $5.66\mu_B/\text{f.u.}$ . Experimentally, Maignan *et al.* [9] found from magnetization measurements the saturated total moment close to  $5.0\mu_B$ .

We may speculate that perhaps a small part of the sample ( $\approx 10\%$ ) is somewhat misaligned, which due to the anomalously large magnetocrystalline anisotropy as we will show below, will then not get magnetized. In any case, since it is easier to find experimental reasons why the sample is not fully magnetized rather than “over”-magnetized, it is probably better that the theory slightly overestimates the moment. It would be especially unsatisfactory if one, for example, would ignore the SOC or assume that the sixth electron occupies the  $d_0$  spin-down orbital [28], giving in both cases a total moment of only  $4.0\mu_B$ . In fact, as listed in Table I, we find in our LSDA +  $U$  + SOC calculations that the configuration with the sixth electron forced to occupy the  $d_0$  spin-down orbital is unstable by 71 meV/f.u. as compared to the ground state. Important is that this analysis is also robust against the particular choice of  $U$  made here. Figure 4 (bottom panel) shows that the spin and orbital moments stay constant within  $0.2\mu_B$  as long as the system is an insulator, i.e., when  $U$  is varied between 2.5 and 6 eV.

The occupation of the spin-down  $d_2$  orbital has as a consequence that the orbital and, due to the SOC, also the spin contributions to the magnetic moment, are oriented along the  $z$  direction, i.e., the  $c$  axis. To flip both the spin and orbital moments into the plane perpendicular to the  $c$  axis is impossible, since this would require that the spin-down  $d_1$  and  $d_{-1}$  become partially occupied, and we have seen from the LSDA calculations in Fig. 1(b) that this would cost roughly the crystal field energy ( $\sim 1$  eV). To flip only the spin moment into the plane but keep the orbital moment along the  $c$  axis is also quite difficult, since this would cost the full spin-orbit splitting of about 70 meV. Also a third scenario in which one tries to alter the moment directions by occupying non-spin-orbit-active spin-down  $d_0$  orbital is equally unlikely, since our LSDA +  $U$  + SOC calculations show that this would cost

TABLE I. Calculated electronic state of  $\text{Ca}_3\text{Co}_2\text{O}_6$ ; total-energy difference (meV) per formula unit; moments ( $\mu_B$ ) at each  $\text{Co}_{\text{oct}}$ ,  $\text{Co}_{\text{trig}}$ , and O ion, as well as in the interstitial region and total magnetic moment per formula unit. Both Co sites are trivalent in the solutions listed. The high-spin  $\text{Co}_{\text{trig}}^{3+}$  has either the minority-spin  $d_2$  or  $d_0$  occupied.

	State	$\Delta E$	$\text{Co}_{\text{oct}}^{\text{spin}}$	$\text{Co}_{\text{oct}}^{\text{orb}}$	$\text{Co}_{\text{trig}}^{\text{spin}}$	$\text{Co}_{\text{trig}}^{\text{orb}}$	O	Interstitial	Total
LSDA	FMHM		0.34		2.70		0.13	0.13	4.00
LSDA + $U$ + SOC	FMI( $d_2$ )	0	0.07	0.09	2.99	1.57	0.13	0.13	5.66
LSDA + $U$ + SOC	AFI( $d_2$ )	12	0	0	$\pm 2.99$	$\pm 1.57$	$\pm 0.13$	0	0
LSDA + $U$ + SOC	FMI( $d_0$ )	71	0.002	0.03	2.96	0.10	0.14	0.14	4.13

71 meV, as already mentioned above and in Table I. All this means that the magnetocrystalline anisotropy is exceptionally large, and that all the relevant magnetic degrees of freedom are highly fixed in the  $z$  direction, justifying why the magnetic behavior of  $\text{Ca}_3\text{Co}_2\text{O}_6$  can be well described by Ising models.

In trying to explain the intrachain FM exchange interaction we also have investigated the antiferromagnetic insulating (AFI) scenario. Here we took the chain as an alternation of spin-up and spin-down  $\text{HS-Co}_{\text{trig}}$  ions with  $\text{LS-Co}_{\text{oct}}$  ions in between. Our LSDA + U + SOC calculations find that the AFI solution, having the same spin and orbital moments at the  $\text{HS Co}_{\text{trig}}$  ions as the FMI ground state, lies above the latter by about 12 meV/f.u.; see Table I [29]. As a result, the intrachain FM coupling parameter of each  $\text{HS Co}_{\text{trig}}$  pair can be estimated to be of the order of 1.5 meV (17 K), assuming a simple Heisenberg model with  $S = 2$ . This intrachain exchange parameter is in reasonable agreement with the experimentally observed intrachain Curie temperature of  $24 \pm 2$  K [3–5].

This result seems at first sight to support the ionic superexchange model proposed by Frésard *et al.* [20]. That model used an ansatz for the Co ions which was confirmed by our LSDA + U + SOC, namely,  $\text{LS Co}_{\text{oct}}^{3+}$  and  $\text{HS Co}_{\text{trig}}^{3+}$  with the  $d_0$  orbital half occupied, and found the exchange parameter of about 2 meV, very close to ours. However, that model involved essentially only the  $\text{Co}_{\text{trig}}$  and  $\text{Co}_{\text{oct}}$   $3z^2 - r^2$  ( $d_0$ ) orbitals, in which case the solution should be AF, according to the first Goodenough-Kanamori-Anderson rule [30].

We believe that the intrachain FM interaction is connected with the large contribution of holes on the oxygens. On the basis of general arguments and also our calculations, one finds that the actual charge distribution corresponds rather not to  $\text{Co}^{3+}$ , but to  $\text{Co}^{2+}\underline{L}$  ( $\underline{L}$  = oxygen hole), although the quantum numbers are those of  $\text{Co}^{3+}$ . In this case, two of such oxygen holes from two neighboring  $\text{HS-Co}_{\text{trig}}^{3+}$  form a triplet state at the  $\text{LS-Co}_{\text{oct}}^{3+}$  in between, much the same as two oxygen holes form a triplet state around a metal vacancy in ZnO and CaO [31]. This allows us to gain the full coherent hybridization energy with the empty  $e_g$  states of the  $\text{Co}_{\text{oct}}^{3+}$  ion. An indication for this is the presence of a covalency-induced spin moment in the oxygen of about  $0.13\mu_B$  per ion as well as in the  $\text{LS-Co}_{\text{oct}}^{3+}$  of about  $0.07\mu_B$ ; see Table I. This picture of the origin of the FM intrachain exchange should be confirmed by further studies.

To conclude, we find using LSDA + U + SOC band structure calculations that  $\text{Ca}_3\text{Co}_2\text{O}_6$  is not a ferromagnetic half-metal but a Mott insulator with both the octahedral and the trigonal Co ions being formally trivalent, which settles the valence-state issue. Spin-orbit coupling and unusual coordination of the trigonal Co ion lead to the occupation of the  $d_2$  spin-down orbital, generating a giant orbital moment ( $1.57\mu_B$ ) and an extremely large magneto-

crystalline anisotropy (70 meV), which explains the Ising character of the magnetism of this material. The ferromagnetic intrachain interaction is presumably connected with the effect of oxygen holes in this small charge-transfer gap system. This also leads to an appreciable magnetic moment of  $0.13\mu_B$  on each oxygen.

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