

## Tailor-Made Electronic and Magnetic Properties in One-Dimensional Pure and Y-Substituted $\text{Ca}_3\text{Co}_2\text{O}_6$

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Full-potential density-functional calculations show that the electronic structure of one-dimensional ferrimagnetic  $\text{Ca}_3\text{Co}_2\text{O}_6$  varies from metal to half metal to insulator as its magnetic ordering changes from the ferrimagnetic through the ferromagnetic to the paramagnetic state. The present Letter is the first to establish the occurrence of half metallicity in one-dimensional oxides. Moreover, the electronic and magnetic properties of this material can be tuned by substitution of Y for Ca, as shown by our detailed study on  $\text{Ca}_{3-x}\text{Y}_x\text{Co}_2\text{O}_6$  ( $x = 0, 0.3, 0.75, \text{ and } 1$ ). The Co ions are in two different valence states [ $\text{Co}^{4+}$  (low-spin) and  $\text{Co}^{2+}$  (high-spin)], and hence the occurrence of charge ordering in addition to spin ordering is established. For specific Y concentrations we predict a rarely seen combination of ferromagnetic and insulating behavior.

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Inorganic structures with one-dimensional (1D) atomic arrangements are in the limelight because of their unique electronic and magnetic properties [1]. Investigations into the nature of the magnetism in these materials have proved particularly rewarding because of the combination of highly anisotropic structures and phenomena such as ferromagnetism (F), antiferromagnetism (AF), and more complex magnetic behavior [2]. Low-dimensional materials are currently in the focus because of their technological significance. For example, magnetoresistance effects have been evidenced in layered Bi-based cobaltites [3,4] and a high figure of merit for the conversion of thermoelectric energy is found [5] in the two-dimensional  $\text{Ca}_3\text{Co}_4\text{O}_9$ .

A large number of oxides have been synthesized with 1D structures [6]. However, most of their physical properties and the theoretical interpretations about them remain largely unexplored because of their complex crystal and magnetic structures. The present exploration based on density-functional full-potential calculations is expected to open up new avenues where new materials of fundamental and technological significance can be found. In this Letter we report the first *ab initio* results on electronic structure and magnetic properties of pure and Y-substituted 1D  $\text{Ca}_3\text{Co}_2\text{O}_6$ . We show that  $\text{Ca}_3\text{Co}_2\text{O}_6$  transforms into a half-metallic ferromagnet by application of magnetic fields as well as by substituting Y for Ca. When the concentration of Y increases, the system prefers to be an F insulator.

$\text{Ca}_3\text{Co}_2\text{O}_6$  belongs to the  $A'_3\text{ABO}_6$  class ( $A' = \text{Ca, Sr}$ ,  $A = \text{Co, Ni, Cu, Zn}$ ,  $B = \text{Co, Ir, Pt}$ ) with  $\text{Sr}_3\text{NiIrO}_6$ -type structure [7]. The structure consists of parallel Co-O chains separated by  $\text{Ca}^{2+}$  ions. The chains are built by

alternating face-sharing  $\text{CoO}_6$  octahedra and trigonal prisms along the hexagonal  $c$  axis. The resulting short metal-metal intrachain distance ( $2.59 \text{ \AA}$ ) [compared to the interchain distance ( $5.24 \text{ \AA}$ )] reinforces the 1D character of the structure along the  $c$  axis. Each Co chain is surrounded by six chains constituting a hexagonal pattern in the basal plane.  $\text{Ca}_3\text{Co}_2\text{O}_6$  behaves as a planar Ising-like Heisenberg AF triangular lattice where each chain acts as if it carries a single localized spin. Magnetic studies show F-type intrachain ordering ( $T_{C1} = 24 \text{ K}$ ) with AF-interchain coupling ( $T_{C2} = 10 \text{ K}$ ) [8]. For every two F-aligned Co chains, there is one AF-aligned chain giving a resultant ferrimagnetic (Ferri) structure. A low-temperature neutron-diffraction examination [9] has shown that  $\text{Ca}_3\text{Co}_2\text{O}_6$  possesses a long-range Ferri order below 10 K.

The different possible oxidation states of cobalt in cobalt oxides together with its various spin configurations such as low spin (LS), intermediate spin, and high spin (HS) are responsible for various phenomena such as temperature-/hole-doping-induced spin-state transitions in  $\text{LaCoO}_3$  [10], giant magnetoresistance in  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ , and insulator-to-metal transition as well as magnetoresistance properties in  $\text{LnBaCo}_2\text{O}_{5.5}$  [11]. Although the magnetic properties of  $\text{Ca}_3\text{Co}_2\text{O}_6$  have been clarified to some extent [8,9], the exact electronic state of the Co ions remains controversial. Kageyama *et al.* [12] proposed  $\text{Co}^{3+}$  for both Co1 and Co2 with Co1 being nonmagnetic and Co2 carrying an effective moment of  $1\mu_B$ . The three models proposed for the Co-spin states by Aasland *et al.* [8] do not completely fit the observed magnetic moments and high-field magnetization data. In this Letter we attempt to settle the

controversy over the valence and spin state of the Co ions in  $\text{Ca}_3\text{Co}_2\text{O}_6$ .

$\text{Ca}_3\text{Co}_2\text{O}_6$  is described in the space group  $R\bar{3}c$  with  $a = 9.079$  and  $c = 10.381$  Å [7]. For the paramagnetic (P) and F calculations, we have considered the rhombohedral unit cell (consisting of 22 atoms). For the Ferri case we have taken into account a hexagonal supercell (consisting of 66 atoms) as shown in Fig. 1. Structural parameters for  $\text{Ca}_{3-x}\text{Y}_x\text{Co}_2\text{O}_6$  are taken from low-temperature neutron-diffraction data [13], but for  $\text{Ca}_2\text{YCo}_2\text{O}_6$ , we obtained the structural parameters [14] by force and stress minimization in the F state using the projected augmented wave implementation of the Vienna *ab initio* simulation package (VASP) [15] as experimental data are hitherto not available. The virtual crystal approximation (VCA) has been applied for calculating the total energies for Y-substituted  $\text{Ca}_3\text{Co}_2\text{O}_6$  systems. VCA has been quite successful in explaining magnetic properties of cobaltates [16]; hence its use in the present study seems justified. However, for  $\text{Ca}_2\text{YCo}_2\text{O}_6$  we considered an explicit supercell with periodic replacement of Ca by Y.

The full-potential linear muffin-tin orbital (LMTO) calculations [17] presented in this Letter are all electron, and no shape approximation to the charge density or potential has been used. The basis set is comprised of augmented linear muffin-tin orbitals [18]. The spherical-harmonic expansion of the charge density, potential, and basis functions were carried out up to  $\ell = 6$ . The calculations are based on the generalized-gradient-corrected (GGA) density-functional theory (DFT) as proposed by Perdew *et al.* [19]. The spin-orbit coupling term is included directly in the Hamiltonian matrix elements for the part inside the muffin-tin spheres; hence for spin-polarized cases the size of the secular matrix is doubled. The basis set included Ca  $4s, 4p, 3d$ ; Co  $4s, 4p, 3d$ ; O  $2s, 2p, 3d$ ; and Y  $4p, 4d, 5s$  states. For the total-energy study the  $\mathbf{k}$ -space integration is done using the special point method with 90  $\mathbf{k}$  points in the irreducible part of the first

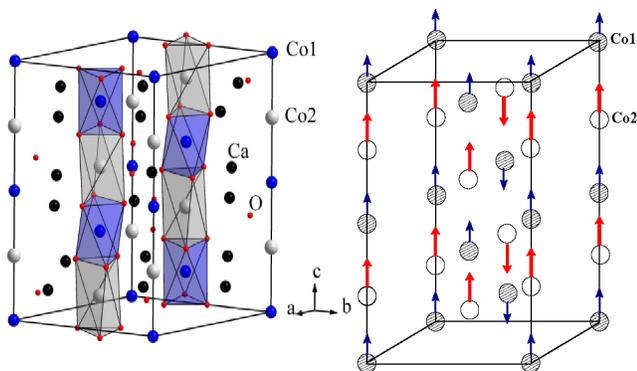


FIG. 1 (color online). Left: crystal structure of one-dimensional  $\text{Ca}_3\text{Co}_2\text{O}_6$ . Right: schematic representation of ferrimagnetic ordering in hexagonal  $\text{Ca}_3\text{Co}_2\text{O}_6$ , consisting of 66 atoms per unit cell; only Co ions are shown. (Note that the Ferri arrangement involves two F and one AF aligned chains.)

Brillouin zone. As the experimental [8] magnetization studies on  $\text{Ca}_3\text{Co}_2\text{O}_6$  show that the easy magnetization axis is along  $c$ , we have chosen  $[001]$  as the magnetization axis for all our spin-polarized calculations. The density of states (DOS) was calculated using the linear tetrahedron technique. Since the effect of strong electron-electron interactions for transition-metal oxides have been discussed in the past, we have also used the LDA +  $U$  method (LDA is local-density approximation). The inclusion of the Coulomb correlation effect through the LDA +  $U$  method does not improve the results indicating that the usual DFT calculations are sufficient to describe the properties of these materials. Because of space limitation we have not included the results of the LDA +  $U$  calculations.

We list the calculated total energy for undoped and electron-doped samples in Table I.  $\text{Ca}_3\text{Co}_2\text{O}_6$  stabilizes in the Ferri state in perfect agreement with experimental findings [8,9]. The F state in which all Co moments are aligned parallel with respect to each other is 114 meV higher in energy than the Ferri state. According to experimental magnetization measurements the magnetic field required for the Ferri-to-F transition is 2.2 T. The exchange splitting increases the band energy (component of total energy) and helps to stabilize the Ferri phase. The gain in band energy is 514 meV/f.u. for the Ferri case compared with the P state. When we include other contributions to the total energy, the Ferri phase is 673 meV/f.u. lower in energy than the P phase. Hence the P phase represents an energetically unfavorable configuration even though it is found to be insulating. From Table I it is clear that when electrons are doped into the system, the F state is stabilized.

A finite DOS (Fig. 2) is present at the Fermi level ( $E_F$ ) in both spin channels in the Ferri phase implying a metallic character. This finding is consistent with the experimental conductivity study [11]. Our partial DOS analysis shows that the states in the vicinity of  $E_F$  are mainly contributed by Co  $d$  states. With Ferri ordering these  $d$  states are considerably delocalized, so electrons are transferred within and between the chains resulting in metallic behavior.

The second panel of Fig. 2 shows the total DOS of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the F state. A finite DOS is present in the up-spin channel at  $E_F$ , whereas an energy gap of 0.09 eV opens up in the down-spin channel, resulting in

TABLE I. Total energy (relative to the lowest energy state in meV/f.u.) in  $\text{Ca}_{3-x}\text{Y}_x\text{Co}_2\text{O}_6$  for the P, F, and Ferri phases using FLMTO including GGA and spin-orbit coupling.

Composition	P	F	Ferri
$\text{Ca}_3\text{Co}_2\text{O}_6$	673	114	0
$\text{Ca}_{2.7}\text{Y}_{0.3}\text{Co}_2\text{O}_6$	693	0	224
$\text{Ca}_{2.25}\text{Y}_{0.75}\text{Co}_2\text{O}_6$	1027	0	481
$\text{Ca}_2\text{YCo}_2\text{O}_6$	753	0	352

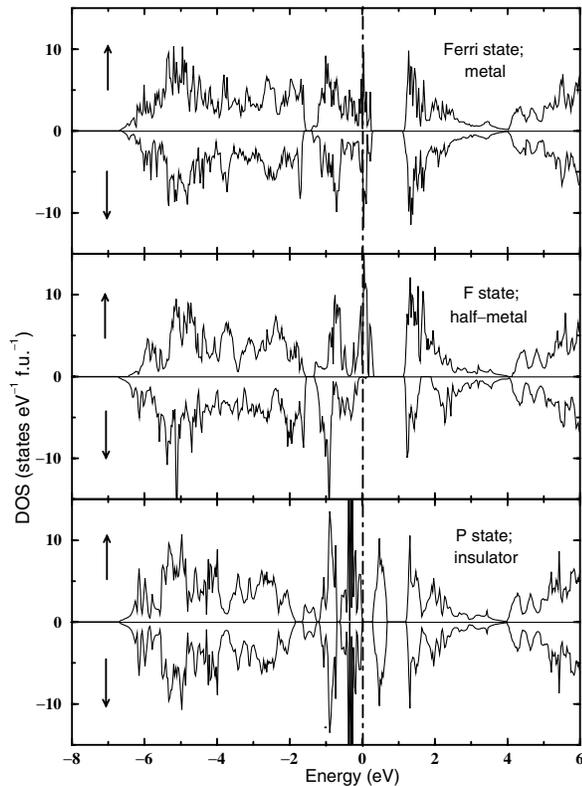


FIG. 2. Total DOS for  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the Ferri, F, and P states.

half-metallic character. Half-metallic ferromagnetic (HMF) oxides attract much attention due to their potential applications in magnetoelectronic [20] and magneto-optical recording devices. *The present Letter is, to the best of our knowledge, the first to point out the occurrence of HMF behavior in 1D oxides.* The strong covalent bonding between Co and O apart from the exchange splitting contributes to the half-metallic (HM) nature. When the long-range magnetic ordering disappears (viz. in the P state), an energy gap opens up in both spin channels with a magnitude of 0.3 eV resulting in an insulator. The DOS analysis shows that relatively many nonbonding 3d electrons from Co exist just below  $E_F$  in the P case, reducing its stability over Ferri and F cases.

Table I shows that the Ferri-to-F transition can be achieved by electron doping (substituting Y for Ca) in addition to the application of magnetic field. However, it is to be noted that a spin-glass behavior or noncollinear magnetism has not been considered in our calculations, though triangular lattice formation is often found to induce such complicated magnetic states.

The total DOS of Y-substituted  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the F ground state is shown in Fig. 3.  $\text{Ca}_{2.7}\text{Y}_{0.3}\text{Co}_2\text{O}_6$  and  $\text{Ca}_{2.25}\text{Y}_{0.75}\text{Co}_2\text{O}_6$  are found to exhibit HM properties with an energy gap in the down-spin channel of 0.156 and 0.375 eV, respectively. If the down-spin channel has not been perturbed by the added electrons, the total magnetic moment is expected to increase. But in contrast, additional states appear around  $-2$  eV in the down-spin

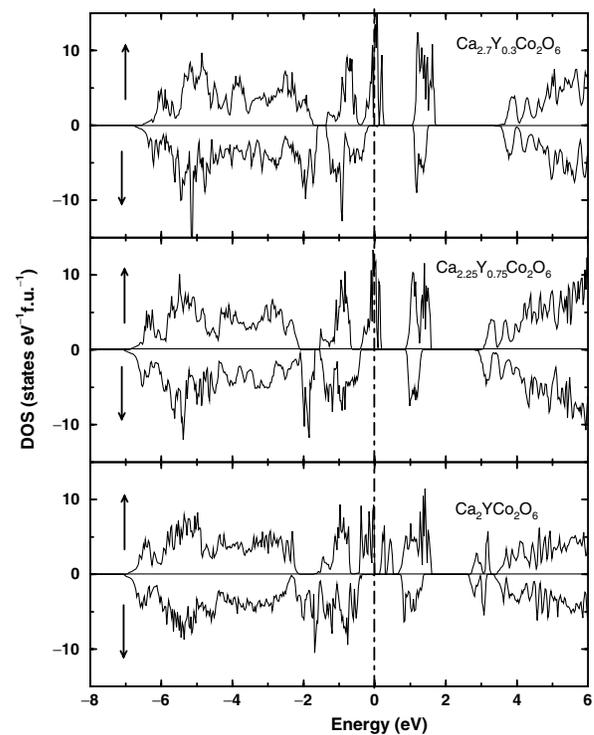


FIG. 3. Total DOS of Y-doped  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the F ground state configurations.

channel of Y-substituted  $\text{Ca}_3\text{Co}_2\text{O}_6$  (see Fig. 3), and hence the magnetic moments decrease. As the electrons become more localized, the HMF situation occurs. A rigid-band analysis shows that if we replace one Ca atom by one Y per formula unit, an insulating material with F ordering should be realized—a combination of material properties that is rarely encountered. Hence we have performed total-energy calculations for  $\text{Ca}_2\text{YCo}_2\text{O}_6$  also in P, F, and Ferri configurations. From Table I it is seen that this material indeed prefers F ordering and from Fig. 3 it is clear that it shows an insulating electronic structure with a band gap of 0.139 eV (0.467 eV according to our LDA +  $U$  calculation), consistent with the rigid-band analysis. Efforts are being made to synthesize this phase [13] which may prove to be the first example of an F insulator in this type of 1D oxide.

Let us now turn our attention to the valence and spin states of Co. Different spin configurations for the crystallographically different Co ions are expected [21] as a consequence of the larger crystal field for octahedral Co1 than for trigonal prismatic Co2. The calculated magnetic moments listed in Table II are found to be in very good agreement with available low-temperature neutron-diffraction and magnetization data. By taking into consideration the magnetic moments at the Co sites, the octahedral and trigonal prismatic crystal fields, and the calculated site- and orbital-projected DOS features (not shown), we conclude that Co1 is indeed  $\text{Co}^{4+}$  in the LS ( $d^5; t_{2g}^5 e_g^0$ ) state and Co2 is  $\text{Co}^{2+}$  in the HS ( $d^7; t_{2g}^5 e_g^2$ ) state. The charge density and electron localization

TABLE II. Calculated magnetic moment (in  $\mu_B$  per Co atom) for  $\text{Ca}_{3-x}\text{Y}_x\text{Co}_2\text{O}_6$  in the F and Ferri states. Total refers to the total magnetic moment per formula unit.

Composition	F			Ferri			Experimental		
	Co1	Co2	Total	Co1	Co2	Total	Co1	Co2	Total
$\text{Ca}_3\text{Co}_2\text{O}_6$	0.179	2.638	3.639	0.169	2.632	1.209	0.08 <sup>a</sup>	3.00 <sup>a</sup>	1.3 <sup>a</sup>
$\text{Ca}_{2.7}\text{Y}_{0.3}\text{Co}_2\text{O}_6$	0.171	2.614	3.521	0.161	2.607	1.172	0.15 <sup>b</sup>	2.41 <sup>b</sup>	...
$\text{Ca}_{2.25}\text{Y}_{0.75}\text{Co}_2\text{O}_6$	0.124	2.488	3.216	0.116	2.485	1.070	...	...	...
$\text{Ca}_2\text{YCo}_2\text{O}_6$	0.065	2.407	2.992	0.138	2.369	0.985	...	...	...

<sup>a</sup>Low-temperature neutron-diffraction data, Ref. [8]. <sup>b</sup>Low-temperature neutron-diffraction data, Ref. [13].

function show weak metallic interaction between the Co atoms and strong covalent interaction between Co and O. Because of the latter feature, a finite moment (around  $0.1\mu_B$ ) is found at the O sites. Also, due to this hybridization between Co and O the magnetic moments at Co are smaller than the ideal spin-only values.

In  $\text{Ca}_2\text{YCo}_2\text{O}_6$ , the additional electron contributed by Y is expected (see the decreasing trend in magnetic moment values in Table II) to go to Co1 and convert this ion into LS, nonmagnetic  $\text{Co}^{3+}$  ( $t_{2g}^6 e_g^0$ ). However, the detailed charge-density analysis shows that the extra electrons mainly go into interstitial regions and are otherwise uniformly distributed on all constituents. It is indeed the strong Co-O bonding interaction which is responsible for the almost vanishing magnetic moment at the Co1 site rather than a valence transition. As equal amounts of Co ions are in two different valence and spin states with localized  $3d$  electrons, ladder-type charge and spin ordering must be present in these materials.

In conclusion, for the first time we have shown the occurrence of HMF and insulating F behavior in fairly complex one-dimensional oxides using accurate density-functional full-potential methods. The metallic Ferri state is found to be the ground state for  $\text{Ca}_3\text{Co}_2\text{O}_6$  in accordance with experiments. Various proposals have been made for spin states of Co such as (i) Co1:LS  $\text{Co}^{3+}$ ; Co2: HS  $\text{Co}^{3+}$ , (ii) Co1: LS  $\text{Co}^{4+}$ ; Co2: HS  $\text{Co}^{2+}$ , and (iii) Co1: LS  $\text{Co}^{2+}$  and  $\text{Co}^{4+}$ ; Co2: HS  $\text{Co}^{3+}$ . By analyzing electronic structure with various tools we conclude that Co1 corresponds to LS  $\text{Co}^{4+}$  and Co2 to HS  $\text{Co}^{2+}$ . We have shown that tailor-made electronic and magnetic properties can be obtained in 1D oxides by magnetic field or electron doping. We predict a seldom observed combination of material properties, namely, a ferromagnetic insulator. Because of the complexity in the crystal and magnetic structures of the considered phases, more studies may reveal new features.

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