Ising Magnetism and Ferroelectricity in Ca_3CoMnO_6

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The origin of both the Ising chain magnetism and ferroelectricity in Ca_3CoMnO_6 is studied by *ab initio* electronic structure calculations and x-ray absorption spectroscopy. We find that Ca_3CoMnO_6 has alternate trigonal prismatic Co^{2+} and octahedral Mn^{4+} sites in the spin chain. Both the Co^{2+} and Mn^{4+} are in the high-spin state. In addition, the Co^{2+} has a huge orbital moment of $1.7\mu_B$ which is responsible for the significant Ising magnetism. The centrosymmetric crystal structure known so far is calculated to be unstable with respect to exchange striction in the experimentally observed ↑↑↓↓ antiferromagnetic structure for the Ising chain. The calculated inequivalence of the Co-Mn distances accounts for the ferroelectricity.

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Among a variety of multiferroic materials discovered so far [1,2], the ferroelectric Ising chain magnet Ca_3CoMnO_6 is quite unique, because the ferroelectricity (FE) is driven by exchange striction in a collinear Ising spin chain consisting of charge ordered transition-metal ions [3]. The spin chain has alternate trigonal prismatic and octahedral sites [3,4]. A special ↑↑↓↓ antiferromagnetic (AF) structure is detected in Ca_3CoMnO_6 below $T_N \approx 13$ K by neutron diffraction. However, the measured magnetic moment of $0.66\mu_B$/Co and $1.93\mu_B$/Mn is much smaller than the expected one of the normal high-spin (HS) Co^{2+} ($S = 3/2$) and Mn^{4+} ($S = 3/2$). This led Choi *et al.* to the conclusion that the Co^{2+} is (surprisingly) in a low-spin (LS) state [3]. In contrast, the effective magnetic moment of $\mu_{\rm eff} = 5.8$–$6.0\mu_B$ per formula unit (f.u.), extracted from magnetic susceptibility measurements above T_N [4,5], suggests that both Co^{2+} and Mn^{4+} are in a HS state. Thus there is an apparent discrepancy between those data, and the problem concerning the spin state of, in particular, Co^{2+} ions seems to be still unsolved. Another important question is to understand the nature of the Ising magnetism and of the resulting exchange striction, which are apparently crucial for the appearance of FE in Ca_3CoMnO_6. To this end, we carried out *ab initio* electronic structure calculations and x-ray absorption spectroscopy (XAS). We address the important issues including the Co/Mn site preference, their charge, spin and orbital states, the origin of the Ising magnetism, and the exchange striction.

Our *ab initio* calculations were performed by using the full-potential augmented plane waves plus the local orbital method (WIEN2K code) [6]. We took the experimental centrosymmetric structure data of the rhombohedral lattice (R-$3c$) which have in a hexagonal setting the lattice constant $a = 9.1314$ Å and $c = 10.5817$ Å [4,7]. The calculations were done for different magnetic structures (↑↓↑↓ , ↑↑↓↓ , ↑↓↓↓ , and ↑↑↑↑ orderings in the Co-Mn-Co-Mn chains). To study the exchange striction effect, we investigated the effect of internal atomic relaxation allowing the inversion symmetry to be broken in the ↑↑↓↓ spin chain, as discussed below. The muffin-tin sphere radii are chosen to be 2.4, 2.1 and 1.4 Bohr for Ca, Co/Mn and O atoms, respectively. The cutoff energy of 16 Ryd is used for plane wave expansion, and $5 \times 5 \times 5$ **k** mesh for integrations over the Brillouin zone. To account for the strong electron correlations, GGA + U (the generalized gradient approximation [8] plus Hubbard U) calculations [9] were performed. The values $U = 5$ (4) eV for the Co (Mn) $3d$ electrons (with a common Hund exchange of 0.9 eV) are used, according to the calculations using a local-orbital basis [10]. Note also that the choice of U value in the range of 2–7 eV does not affect the conclusion made in this Letter. The spin-orbit coupling (SOC) turns out to be crucial and it is included by the second-variational method with scalar relativistic wave functions [6].

It is quite common that an octahedral Co^{3+} ion is in a LS ground state. This may suggest that the small moment of $0.66\mu_B$/Co in Ca_3CoMnO_6 could be due to the Co/Mn site disorder, i.e., an appreciable presence of the octahedral LS Co^{3+}. To probe the Co/Mn site preference, we computed two structures either with the trigonal Co ($Co_{\rm trig}$) and octahedral Mn ($Mn_{\rm oct}$) or vice versa. The total energy results show that the former structure is more stable than the later by 0.33 eV/f.u. in GGA and more significantly, by 1.60 eV/f.u. in GGA + U + SOC. The energetically favorable structure has the HS trigonal Co^{2+} and the HS octahedral Mn^{4+}, while the unfavorable one indeed has the LS octahedral Co^{3+} and the HS trigonal Mn^{3+}. We plot in Fig. 1 the GGA and GGA + U + SOC calculated density of states (DOSs) only for the favorable structure. The sharp

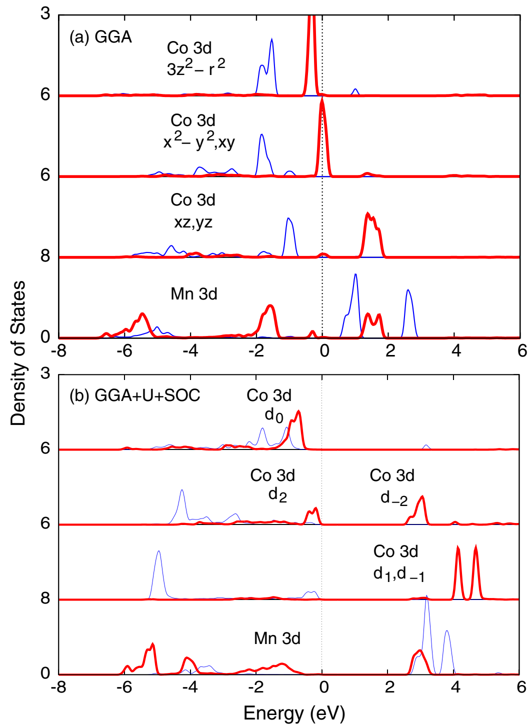

FIG. 1 (color online). Density of states calculated by GGA (a) and GGA + U + SOC (b) for the ↑↓↑↓ spin structure of Ca_3CoMnO_6 with the trigonal Co and octahedral Mn. It practically coincides with that for ↑↑↓↓ . The thin blue (bold red) curves refer to the majority (minority) spin. The Fermi level is set at zero energy. In (a) the Mn^{4+}_{oct} has a closed t^3_{2g} shell centered at −1.5 eV, together with the e_g bonding state around −5.5 eV. The Co_{trig} is in the high-spin 2+ state with the nearly degenerate $3z^2 - r^2$ (d_0), $x^2 - y^2$ and xy ($d_{\pm 2}$) levels. In (b) the ($x^2 - y^2$, xy) doublet splits due to the spin-orbit coupling, and the Hubbard U yields an insulating ground state with the minority-spin $d_0 d_2$ occupation.

DOS peak at the Fermi level, coming from the degenerate $x^2 - y^2$ and xy ($d_{\pm 2}$) levels of the trigonal Co^{2+} minority-spin d electrons, vanishes when going from the GGA to GGA + U + SOC solutions. This explains why, by opening a sizable gap of 2.4 eV, the GGA + U + SOC strongly favors the structure with the Co^{2+}_{trig} and Mn^{4+}_{oct}. The HS Co^{2+} (Mn^{4+}) has a calculated spin moment of 2.64 (2.70)μ_B, both staying constant within 0.2μ_B for U = 2–7 eV.

Having established the $Co^{2+}_{trig}/Mn^{4+}_{oct}$ site preference from the above total-energy calculations, we turn to our XAS measurements to confirm it. The room temperature Co-$L_{2,3}$ and Mn-$L_{2,3}$ XAS spectra of Ca_3CoMnO_6 were collected at the ID08 beam line of the European Synchrotron Radiation Facility (ESRF) in Grenoble with a resolution of 0.25 eV at Co-L_3 (at 780 eV). The sharp peak at 777.8 eV of the Co-L_3 edge of single crystalline CoO and at 640 eV of the Mn-L_3 of single crystalline MnO were used for energy calibration. The spectra were recorded using the total electron yield method by measuring the sample drain current in a chamber with a base pressure of 2 × 10^{-10} mbar. Clean sample areas were obtained by cleaving the polycrystals *in situ*.

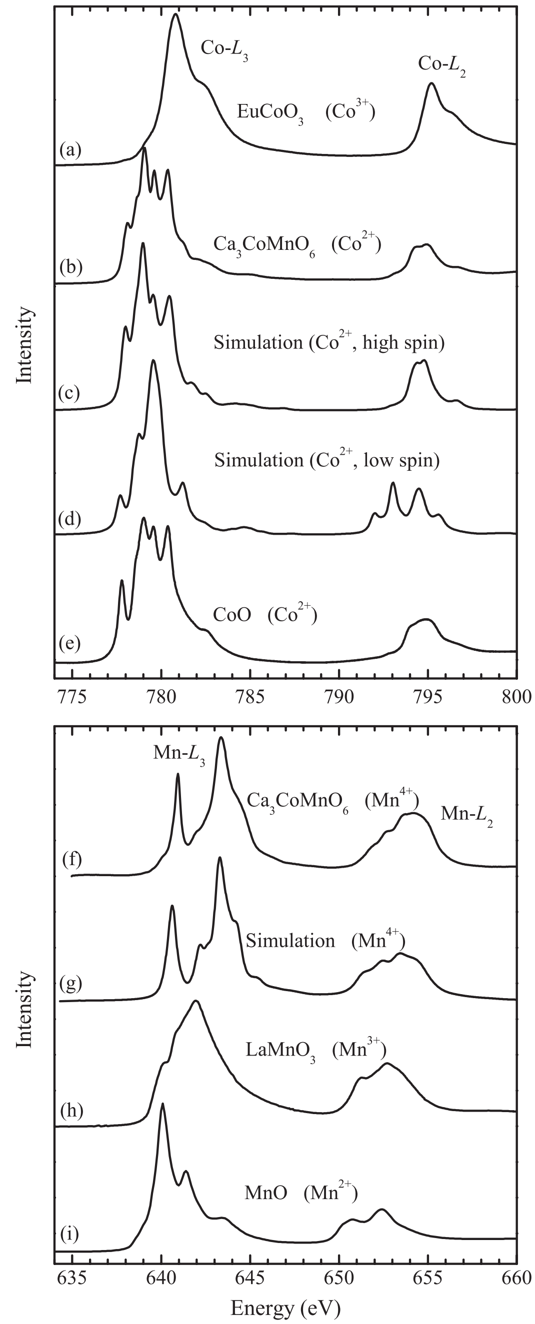

FIG. 2. The experimental and simulated x-ray absorption spectra of Ca_3CoMnO_6 at the Co-$L_{2,3}$ (upper panel) and the Mn-$L_{2,3}$ (lower panel) edges, together with the experimental spectra of the references CoO, $EuCoO_3$, MnO, and $LaMnO_3$. Ca_3CoMnO_6 turns out to have the high-spin trigonal Co^{2+} and octahedral Mn^{4+}.

It is important to note that XAS spectra are highly sensitive to the valence state: an increase of the valence state of the transition metal ion by one causes a shift of the XAS $L_{2,3}$ spectra by one or more eV towards higher energies [11,12]. In Fig. 2 (upper panel) we see a shift of the center of gravity of the Co-L_3 white line to higher photon energies by about 1.5 eV in going from the divalent CoO to the trivalent $EuCoO_3$. The energy position of the Co line in Ca_3CoMnO_6 is the same as in CoO, indicating a Co^{2+} state. Also, a gradual shift of the center of gravity of the Mn-L_3 white line to higher energies from MnO via $LaMnO_3$ to Ca_3CoMnO_6 (lower panel in Fig. 2) evidences the increase of the Mn valence state from 2+ via 3+ to 4 + . In fact the Mn-$L_{2,3}$ edges of Ca_3CoMnO_6 lie at the same energy position as in $SrMnO_3$, $LaMn_{0.5}Co_{0.5}O_3$ [12], and $LaMn_{0.5}Ni_{0.5}O_3$ [13], all of which have the Mn^{4+} state. Thus, our XAS results confirm the Co^{2+}-Mn^{4+} state.

To extract more detailed information concerning the charge and spin states from the Co-$L_{2,3}$ and the Mn-$L_{2,3}$ XAS spectra, we have carried out simulations of the XAS spectra using the well-proven configuration-interaction cluster model [14–16]. We studied a trigonal prism CoO_6 (an octahedral MnO_6) cluster, including the full atomic multiplet theory and the local effects of the solid. Thus our model calculations account for the intra-atomic $3d$-$3d$ and $2p$-$3d$ Coulomb interactions, the atomic $2p$ and $3d$ spin-orbit couplings, the O $2p$-Co $3d$ hybridization, and the proper local crystal-field parameters. The calculated Co-$L_{2,3}$ XAS spectrum for the HS Co^{2+} [curve (c) in Fig. 2] with the ionic trigonal crystal-field interaction $\Delta_{10}^{\text{ionic}} = 0.75$ eV reproduces the experimental spectrum [curve (b)] very well [17]. In order to stabilize a LS state which was concluded by Choi *et al.* [3], we would have to increase the $\Delta_{10}^{\text{ionic}}$ by nearly 3 times (2.8 eV), and the calculated spectrum for this case [curve (d) in Fig. 2] strongly disagrees with the experimental one [curve (b)].

In the lower panel of Fig. 2, one can see that the line shapes of the experimental Mn spectrum [curve (f)] are well reproduced by the simulation [curve (g)] with a Mn^{4+} (t_{2g}^3) configuration in a local O_h symmetry.

Thus, our *ab initio* calculations and XAS experiments have firmly established that the spin-chain magnet Ca_3CoMnO_6 has the HS Co^{2+}_{trig} and HS Mn^{4+}_{oct}, and that there is no appreciable presence of the LS-Co^{3+}_{oct}/HS-Mn^{3+}_{trig}. Obviously, the magnetic moment of $0.66\mu_B$/Co measured by neutron diffraction [3] below $T_N \approx 13$ K is much smaller than our theoretical value [the total calculated moment being about $4.3\mu_B$/Co with the spin (orbital) contribution of 2.6 $(1.7)\mu_B$, see more below] and than the value of $\mu_{\text{eff}} = 5.8$–$6.0\mu_B$ obtained from the high-temperature magnetic susceptibility [4,5]. This may be partially due to strong fluctuations in quasi-one-dimensional chains, with frustrated interchain interactions. Another important factor may be a close proximity of different types of magnetic orderings (see below). This question deserves further study.

As seen in Fig. 1(a), the trigonal Co^{2+} has the nearly degenerate $3z^2 - r^2$ and $(x^2 - y^2, xy)$ levels. Because of the in-plane character of both the $x^2 - y^2$ and xy orbitals, their strong Coulomb repulsion prevents their double occupation in the minority-spin channel. Therefore, the minority-spin $3z^2 - r^2$ orbital is fully occupied and the minority-spin $x^2 - y^2$ and xy are half-filled for the HS Co^{2+} ions. Because of the quasi-one-dimensional character along the c-axis chain, a naive $x^2 - y^2/xy$ planar orbital ordering does not gain any energy (compared with either an $x^2 - y^2/x^2 - y^2$ or xy/xy orbital ordering), as proven by our *ab initio* calculations. In contrast, an efficient way to gain the energy is SOC. When the SOC is included, the $(x^2 - y^2, xy)$ doublet splits into d_2 and d_{-2}, and the gain of the full SOC energy is calculated to be about 70 meV. As a result, a huge orbital magnetic moment of $1.7\mu_B$ is generated at the HS Co^{2+}_{trig} sites with the minority-spin d_0d_2 occupation [Fig. 1(b)], and the SOC firmly fixes the total magnetization (with parallel spin and orbital contributions) along the c-axis chain direction. Note that the orbital moment stays constant within $0.1\mu_B$ in our GGA + U + SOC calculations for $U = 2$–7 eV. Therefore, the peculiar trigonal crystal field and the SOC are responsible for the significant Ising character of Ca_3CoMnO_6; cf. similar situation in the isostructural Ca_3CoRhO_6 [19].

Having established the picture about the Co/Mn site preference, their charge, spin and orbital states, and the significant Ising magnetism, we turn now to the discussion on the intrachain magnetism and the exchange striction leading to ferroelectricity. Since a centrosymmetric structure of Ca_3CoMnO_6 does not carry ferroelectricity, we now look at whether the symmetry can be lowered by allowing for atomic displacements within the *experimentally observed* [3] ↑↑↓↓ magnetic structure of the Co-Mn-Co-Mn Ising spin chain: the Co-Mn bonds would be inequivalent in such a noncentrosymmetric structure leading to chain dimerization, and this will give rise to ferroelectricity. We calculated using GGA + U + SOC the total energy of the system by first shifting the Co ions along the chain making Co-Mn distances unequal (alternating) [20]. The results are shown in Fig. 3. We see that indeed the lattice in the ↑↑↓↓ structure would relax to a state with alternating Co-Mn distances (the difference being 0.012 Å), which means the appearance of FE in the system, cf. [21–24]. The calculated

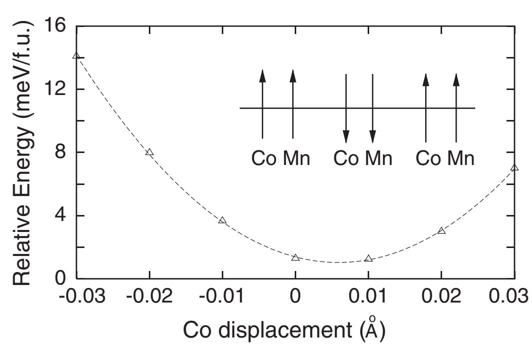

FIG. 3. Relative energy as function of the Co displacements calculated by GGA + U + SOC for the experimental lattice. Triangles stand for the data points, which are fitted into a parabolic curve. The energy minimum shows the Co displacement of 0.006 Å, which leads to alternate short-long-short-long Co-Mn distances (the difference being 0.012 Å) in the Co↑ -Mn↑ -Co↓ -Mn↓ chain as depicted schematically in the inset.

spin and orbital moments remain unchanged. Furthermore, a triclinic lattice ($P1$) was tested to study a likely breaking of the threefold rotation symmetry. A structural relaxation using GGA + U + SOC (with the Co ions fixed at the above optimized position) confirms the small FE distortion of the Co-Mn chains and gives also a small distortion of the Co-O (Mn-O) bonds [only about 0.01 Å out of 2.15 Å (1.92 Å) in bond length]. We would like to point out that those small distortions are not inconsistent with the experiment [7] since they are so small that they would require a special effort for their detection.

We note that in the GGA + U + SOC calculations the ↑↑↓↓ and ↑↓↑↓ magnetic structures for the Co-Mn-Co-Mn spin chain are the two lowest-energy states, with the former being higher in energy. The energy difference is 15 meV/f.u. for the experimentally detected crystal structure [4] and is reduced to 7 meV/f.u. for the relaxed triclinic lattice ($P1$). At the moment it is not clear how to stabilize the experimentally observed ↑↑↓↓ magnetic structure [3] in the GGA + U + SOC calculations. Since the energy difference is rather small and the intrachain exchange interactions rather weak, we speculate that the couplings between the chains may play an important role. The present calculations assumed a simple ferromagnetic interchain interaction, but it is known that there are AF interchain couplings in the isostructural $Ca_3Co_2O_6$ [25] and Ca_3CoRhO_6 [26] compounds with strengths not much smaller than the intrachain ones. These finite AF interchain couplings bring about magnetic frustration, and one needs to investigate a large set of intrachain and interchain magnetic structures in order to explain theoretically the magnetic ground state of Ca_3CoMnO_6.

In summary, we find the site preference of the high-spin trigonal Co^{2+} and the octahedral Mn^{4+} in the Ising chain magnet Ca_3CoMnO_6, using the *ab initio* calculations and x-ray absorption spectroscopy. The Co^{2+} has the very stable minority-spin d_0d_2 occupation due to the peculiar trigonal crystal field, interorbital Coulomb repulsion and the spin-orbit coupling. Thus, a huge orbital moment of $1.7\mu_B$ is predicted and the significant Ising magnetism is well accounted for. Moreover, our calculations indeed found that a structural relaxation due to the exchange striction decreases the energy of the experimentally observed ↑↑↓↓ magnetic ordering and leads to the observed ferroelectricity. However, the mechanism of the full stabilization of the ↑↑↓↓ structure as the ground state calls for a further study.

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[17] Parameters (in eV). Co: $U_{3d3d} = 5$, $U_{2p3d} = 6.5$, $\Delta = 4$, $\Delta_{10}^{\text{ionic}} = 0.75$ (HS), $\Delta_{10}^{\text{ionic}} = 2.8$ (LS), $\Delta_{20}^{\text{ionic}} = -0.1$, $V_{\text{mix}}^{\text{ionic}} = 0.15$. Hybridization from Harrison's rules (Ref. [18]). Mn: $U_{3d3d} = 5$, $U_{2p3d} = 6$, $\Delta = -3$, $\Delta_{10Dq} = 2$, $V_{pd\sigma} = -1.6$. The Slater integrals were reduced to 80% (for Co) and 70% (for Mn) of their Hartree-Fock value.
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