Ising magnetism and ferroelectricity in Ca₃CoMnO₆

Hua Wu,¹ T. Burnus,¹ Z. Hu,¹ C. Martin,² A. Maignan,² J. C. Cezar,³ A. Tanaka,⁴ N. B. Brookes,³ D. I. Khomskii,¹ and L. H. Tjeng¹

¹H. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany
²Laboratoire CRISMAT, UMR 6508 CNRS ENSICAEN, 14050 Caen, France
³European Synchrotron Radiation Facility, Boîte Postale 220, 38043 Grenoble Cédex, France
⁴Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

(Dated: December 4, 2008)

The origin of both the Ising chain magnetism and ferroelectricity in Ca₃CoMnO₆ is studied by ab initio electronic structure calculations and x-ray absorption spectroscopy. We find that Ca₃CoMnO₆ has the alternate trigonal prismatic Co²⁺ and octahedral Mn⁴⁺ sites in the spin chain. Both the Co²⁺ and Mn⁴⁺ are in the high spin state. In addition, the Co²⁺ has a huge orbital moment of 1.7 μB 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.

PACS numbers: 71.20.-b, 78.70.Dm, 71.70.-d, 71.27.+a

Among a variety of multiferroic materials discovered so far [1,2], ferroelectric Ising chain magnet Ca₃CoMnO₆ is quite unique, because the ferroelectricity (FE) is driven by exchange striction in a collinear Ising spin chain consisting of the charge ordered transition-metal ions [3]. The spin chain has the alternate trigonal prismatic and octahedral sites [3,4]. Special ↑↑↓↓ antiferromagnetic (AF) structure is detected in Ca₃CoMnO₆ below Tₘ=13 K by neutron diffraction. However, the measured magnetic moment of 0.66 μB/Co and 1.93 μB/Mn is much smaller than the expected one of the normal high-spin (HS) Co²⁺ (S=3/2) and Mn⁴⁺ (S=3/2). This led Choi et al. to a conclusion that the Co²⁺ is (surprisingly) in a low-spin (LS) state [3]. In contrast, the effective magnetic moment of μ_eff=5.8-6.0 μB per formula unit (f.u.), extracted from magnetic susceptibility measurements above Tₘ=13 K [3,5], suggests that both Co²⁺ and Mn⁴⁺ are in a HS state. Thus there is an apparent controversy between those data, and the problem concerning the spin state of, in particular, Co²⁺ 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 Ca₃CoMnO₆. 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/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 local orbital method (Wien2k code) [6]. We took the experimental centrosymmetric structure data of the rhombohedral lattice (R-3c) which has 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 cut-off energy of 16 Ryd is used for plane wave expansion, and 5×5×5 k-mesh for integrations over Brillouin zone. To account for the strong electron correlations, GGA+U (the generalized gradient approximation [8] plus Hubbard U) calculations [9] were performed. U=5.0 (4.0) 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 choices of U value in the range of 2-7 eV do 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 Co³⁺ ion is in a LS ground state. This may suggest that the small moment of 0.66 μB/Co in Ca₃CoMnO₆ could be due to the Co/Mn site disorder, i.e., an appreciable presence of the octahedral LS Co³⁺. To probe the Co/Mn site preference, we computed two structures either with the trigonal Co (Co_trig) and octahedral Mn (Mn_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 Co²⁺ and the HS octahedral Mn⁴⁺, while the unfavorable one indeed has the LS octahedral Co³⁺ and the HS trigonal Mn³⁺. We plot in Fig. 1 the GGA and GGA+U+SOC calculated density of states (DOS) only for the favorable structure. The sharp DOS peak at the Fermi level, coming from the degenerate x²−
y^2 and xy (d_{\pm2}) 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+} and Mn^{3+} HS Co^{2+} (Mn^{4+}) has a calculated spin moment of 2.64 (2.70) \mu_B, both staying constant within 0.2 \mu_B for U=2-7 eV.

Having established the Co^{2+}/Mn^{4+} 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 of Ca_{3}CoMnO_{6} were collected at the ID08 beamline 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 \times 10^{-10} mbar. Clean sample areas were obtained by cleaving the polycrystals in situ.

Important is 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_{3}CoMnO_{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_{3}CoMnO_{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$_3$CoMnO$_6$ lie at the same energy position as in SrMnO$_3$, LaMn$_{0.5}$Co$_{0.5}$O$_3$, and LaMn$_3$Ni$_3$O$_3$, 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. 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 3$d$–3$d$ and 2$p$–3$d$ Coulomb interactions, the atomic 2$p$ and 3$d$ spin-orbit couplings, the O $2p$–Co 3$d$ 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 $\Delta_{\text{ionic}}^{\mu}=0.75$ eV reproduces the experimental spectrum [curve (b)] very well. In order to stabilize a LS state which was concluded by Choi et al., we would have to increase the $\Delta_{\text{ionic}}^{\mu}$ 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 lineshapes of the experimental Mn spectrum [curve (f)] are well reproduced by the simulation [curve (g)] with a Mn$^{4+}$ ($t^3_{2g}$) configuration in a local $O_h$ symmetry.

Thus, our ab initio calculations and XAS experiments have firmly established that the spin-chain magnet Ca$_3$CoMnO$_6$ has the HS Co$^{2+}$ and HS Mn$^{4+}$, and that there is no appreciable presence of the LS-Co$^{3+}$/HS-Mn$^{3+}$. Obviously, the magnetic moment of 0.66 $\mu_B$/Co measured by neutron diffraction below $T_N\approx13$ 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. 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. Due to 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. Due to 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 $x^2-y^2/xy$ or $xy/xy$ orbital ordering), as proved 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 $d_h^2$ and $d_g$, 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$^{2+}$ 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$_3$CoMnO$_6$; cf. similar situation in the isostructural Ca$_3$CoRhO$_6$.

Having established the picture about the Co/Mn site preference, their charge/spin/orbital states and the significant Ising magnetism, we turn now to the discussion on the intra-chain magnetism and the exchange striction leading to ferroelectricity. Since a centrosymmetric structure of Ca$_3$CoMnO$_6$ does not carry ferroelectricity, we now look whether the symmetry can be lowered by allowing for atomic displacements within the experimentally observed magnetic structure of the Co-Mn-Co Ising spin chain: the Co-Mn bonds would be inequivalent in such a non-centrosymmetric 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 firstly shifting the Co ions along the Co-Mn distances unequal (alternating) $\approx2$–$7$ eV. The results are shown in Fig. 3. We see that indeed the lattice in $\uparrow\uparrow\downarrow\downarrow$ structure would relax to a state with alternating Co-Mn distances (the difference being 0.012 $\AA$), which means the appearance of FE in the system, cf. $\uparrow\uparrow\downarrow\downarrow$. The calculated spin and orbital moments remain unchanged. Furthermore, a triclinic lattice ($P1$) was tested to study a likely breaking of the 3-fold 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.
We note that in the GGA+U+SOC calculations the $\uparrow\uparrow\downarrow\downarrow$ and $\uparrow\downarrow\uparrow\downarrow$ 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 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 $\uparrow\uparrow\downarrow\downarrow$ magnetic structure 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 $\text{Ca}_3\text{Co}_2\text{O}_6$[23] and $\text{Ca}_3\text{CoRhO}_6$[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 intra- and interchain magnetic structures in order to explain theoretically the magnetic ground state of $\text{Ca}_3\text{CoMnO}_6$.

In summary, we find the site preference of the high-spin trigonal $\text{Co}^{2+}$ and the octahedral $\text{Mn}^{4+}$ in the Ising chain magnet $\text{Ca}_3\text{CoMnO}_6$, using the ab initio calculations and x-ray absorption spectroscopy. The $\text{Co}^{2+}$ has the very stable minority-spin $d_0d_2$ occupation due to the peculiar trigonal crystal field, inter-orbital Coulomb repulsion and the spin-orbit coupling. Thus, a huge orbital momentum 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 $\uparrow\uparrow\downarrow\downarrow$ magnetic ordering and leads to the observed ferroelectricity. However, the mechanism of the full stabilization of the $\uparrow\uparrow\downarrow\downarrow$ structure as the ground state calls for a further study.

We are grateful to V. Kiryukhin and S. W. Cheong for informing us of their unpublished structural data. This research was supported by the Deutsche Forschungsgemeinschaft through SFB 608.

[1] S. W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).
[2] D. I. Khomskii, J. Magn. Magn. Mater. 306, 1 (2006).
[3] Y. J. Choi, H. T. Yi, S. Lee, Q. Huang, V. Kiryukhin, and S. W. Cheong, Phys. Rev. Lett. 100, 047601 (2008).
[4] V. G. Zubkov, G. V. Bazuev, A. P. Tyutyunnik, and I. F. Berger, J. Solid State Chem. 160, 293 (2001).
[5] S. Rayaprol, K. Sengupta, and E. V. Sampathkumaran, Solid State Commun. 128, 79 (2003).
[6] P. Blaha, K. Schwarz, C. Madsen, D. Kvasnicka, and J. Luitz, Wien2k package, http://www.wien2k.at
[7] V. Kiryukhin and S. W. Cheong (private communication). Their neutron diffraction measurements at 1.4 K gave practically coinciding structure data with the room-temperature data in Ref. [4]. No symmetry lower than the $R$-3c was observed, and the ferroelectric distortion is too small to be detected.
[8] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
[9] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyžyk, and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993).
[10] W. E. Pickett, S. C. Erwin, and E. C. Ethridge, Phys. Rev. B 58, 1201 (1998).
[11] C. Mitra, Z. Hu, P. Raychaudhuri, S. Wirth, S. I. Csizsar, H. H. Hsieh, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B 67, 092404 (2003).
[12] T. Burnus, Z. Hu, H. H. Hsieh, V. L. J. Joly, P. A. Joy, M. W. Haverkort, H. Wu, A. Tanaka, H.-J. Lin, C. T. Chen, and L. H. Tjeng, Phys. Rev. B 77, 125124 (2008).
[13] M. C. Sánchez, J. García, J. Blasco, G. Subías, and J. Perez-Cacho, Phys. Rev. B 65, 144409 (2002).
[14] A. Tanaka and T. Jo, J. Phys. Soc. Jpn. 63, 2788 (1994).
[15] F. M. F. de Groot, J. Electron Spectrosc. Rel. Phenom. 67, 529 (1994).
[16] See the “Theo Thole Memorial Issue”, J. Electron Spectrosc. Rel. Phenom. 86, 1 (1997).
[17] Parameters (in eV). Co: $U_{3d3d}=5$, $U_{2p3d}=6.5$, $\Delta = 4$, $\Delta_{\text{ionic}} = 0.75$ (HS), $\Delta_{\text{ionic}} = 2.8$ (LS), $\Delta_{\text{ionic}}^{\text{p}} = -0.1$, $\Delta_{\text{ionic}}^{\text{p}} = 0.15$. Hybirdization from Harrison’s rules (Ref. [19]). Mn: $U_{3d3d}=5$, $U_{2p3d}=6$, $\Delta = -3$, $\Delta_{\text{CP}} = 2$, $V_{\text{dd}} = -1.6$. The Slater integrals were reduced to 80% (for Co) and 70% (for Mn) of their Hartree-Fock value.
[18] W. A. Harrison, Electronic Structure and the Properties of Solids, Dover (1989).
[19] H. Wu, Z. Hu, D. I. Khomskii, and L. H. Tjeng, Phys. Rev. B 75, 245118 (2007).
[20] Co ions are in the relatively open trigonal prisms, compared with Mn in the octahedra. Thus, Co is more susceptible to the exchange striction, as proved by the structural relaxation.
[21] D. V. Efremov, J. van den Brink, and D. I. Khomskii, Nature Materials 3, 853 (2004).
[22] S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko, and E. Dagotto, Phys. Rev. Lett. 99, 227201 (2007).
[23] H. J. Xiang, S. H. Wei, M. H. Whangbo, and J. L. F. Da Silva, Phys. Rev. Lett. 101, 037209 (2008).
[24] J. van den Brink, and D. I. Khomskii, J. Phys.: Condens. Matter, in press, (cond-mat/arXiv:0803.2964).
[25] H. Kageyama, K. Yoshimura, K. Kosuge, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. 66, 1607 (1997).
[26] S. Niitaka, K. Yoshimura, K. Kosuge, M. Nishi, and K. Kakurai, Phys. Rev. Lett. 87, 177202 (2001).