# Valence, spin, and orbital state of Co ions in one-dimensional $Ca_3Co_2O_6$: An x-ray absorption and magnetic circular dichroism study

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We have investigated the valence, spin, and orbital state of the Co ions in the one-dimensional cobaltate $Ca_3Co_2O_6$ using x-ray absorption and x-ray magnetic circular dichroism at the Co-$L_{2,3}$ edges. The Co ions at both the octahedral $Co_{oct}$ and trigonal $Co_{trig}$ sites are found to be in a 3+ state. From the analysis of the dichroism we established a low-spin state for the $Co_{oct}$ and a high-spin state with an anomalously large orbital moment of $1.7\mu_B$ at the $Co^{3+}_{trig}$ ions. This large orbital moment along the *c*-axis chain and the unusually large magnetocrystalline anisotropy can be traced back to the double occupancy of the $d_2$ orbital in trigonal crystal field.

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The one-dimensional $Ca_3Co_2O_6$ has attracted great interest in recent years due to the observation of the stair-step jumps in the magnetization at regular intervals of the applied magnetic field.[1–9] The rhombohedral structure of this compound consists of $[Co_2O_6]_\infty$ chains running along the *c* axis of the hexagonal unit cell.[10] In each chain, $CoO_6$ octahedra alternate with $CoO_6$ trigonal prisms. The magnetism is Ising-like and directed along the Co chains with large magnetic moments of $4.8\mu_B$ per formula unit.[11,12] The intrachain coupling is ferromagnetic with a spin-freeze at $T_{SF}=7$ K, and the chains couple antiferromagnetically with a Néel temperature of $T_N=25$ K.[11]

Based on density-functional-theory calculations, Vidya *et al.* claimed a low-spin (LS) $Co^{4+}_{oct}$ and a high-spin (HS) $Co^{2+}_{trig}$ state for $Ca_3Co_2O_6$.[13] However, other experimental and theoretical works have proposed a $Co^{3+}$ valence state at both the octahedral and trigonal Co sites, with the $Co_{oct}$ LS ($S=0$) and the $Co_{trig}$ HS ($S=2$) state.[14–18] The Ising character of the magnetism is also subject of discussion. Dai and co-workers found from their band structure calculations that the spin-orbit-inactive $d_0$ orbital lies lowest of all $Co_{trig}$ crystal-field levels,[17,19] and had to invoke excited states in their attempt to explain the Ising magnetism. Wu *et al.*[18] on the other hand, calculated that it is the spin-orbit-active $d_2$ orbital which lies lowest, giving a very different picture for the Ising magnetism.

In this paper we have applied soft-x-ray absorption spectroscopy (XAS) and magnetic circular dichroism (XMCD) at the Co-$L_{2,3}$ edges to resolve the Co valence, spin and orbital state issue in $Ca_3Co_2O_6$. We have also carried out detailed configuration-interaction cluster calculations to analyze the spectra. We found that the Co ions are all in the 3+ state, that the $Co_{oct}$ are nonmagnetic, and that the $Co^{3+}_{trig}$ carry a $1.7\mu_B$ orbital moment. We clarify the orbital occupation issue and the origin of the Ising magnetism.

The $Ca_3Co_2O_6$ single crystals were grown by heating a mixture of $Ca_3Co_4O_9$ and $K_2CO_3$ in a weight ratio of 1:7 at 950 °C for 50 h in an alumina crucible in air. The cooling was performed in two steps, first down to 930 °C at a rate of 10 °C/h and then down to room temperature at 100 °C/h.[8] The Co-$L_{2,3}$ XAS spectra of $Ca_3Co_2O_6$ and of CoO and $EuCoO_3$ (Ref. 20) as references were recorded at the Dragon beamline of the National Synchrotron Radiation Research Center (NSRRC) in Taiwan with an energy resolution of 0.3 eV. The first sharp peak at 777 eV of photonenergy at the Co-$L_3$ edge of CoO was used for energy calibration, which enabled us to achieve better than 0.05 eV accuracy in the relative energy alignment. The XMCD spectra were collected at the ID08 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble with a resolution of 0.25 eV and a degree of circular polarization close to 100% in a magnetic field of 5.5 Tesla with the sample kept at approximately 15–20 K, using a dedicated superconducting magnet setup from Oxford Instruments. The Poynting vector of the photons and the magnetic field were both parallel to the *c* axis. The single-domain $Ca_3Co_2O_6$ crystal used for the XMCD experiment was needle-shaped with a dimension of $0.2\times0.2\times10$ mm$^3$ for $a\times b\times c$. Clean sample areas were obtained by cleaving the crystals *in situ* in chambers with base pressures in the low $10^{-10}$ mbar range. The Co $L_{2,3}$ spectra were recorded using the total-electron-yield method (TEY).

Figure 1 shows the Co-$L_{2,3}$ XAS spectrum of $Ca_3Co_2O_6$ together with that of CoO and $EuCoO_3$. CoO serves here as a 2+ reference and $EuCoO_3$ as a LS 3+ reference.[20] One can see first of all that the 2+ spectrum (CoO) contains peaks

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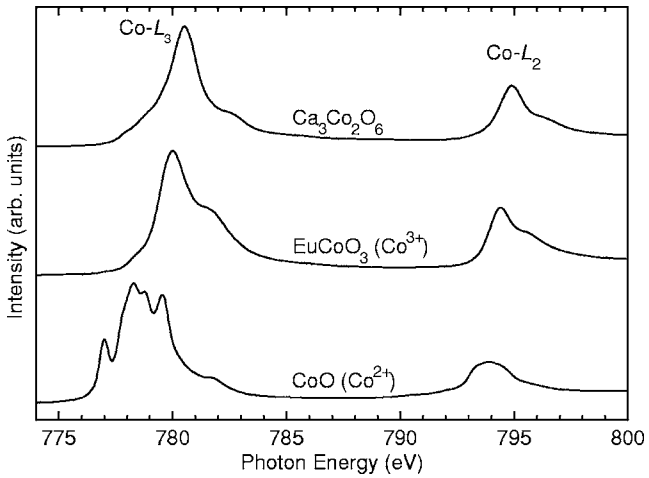


FIG. 1. Co-$L_{2,3}$ XAS spectra of $Ca_3Co_2O_6$, CoO, and $EuCoO_3$.

that are 2 or more eV lower in energy than the main peak of the 3+ spectrum ($EuCoO_3$). It is well known that x-ray absorption spectra at the transition-metal $L_{2,3}$ edges are highly sensitive to the valence state. An increase of the valence of the metal ion by one results in a shift of the $L_{2,3}$ XAS spectra to higher energies by 1 eV or more.[21] This shift is due to a final state effect in the x-ray absorption process. The energy difference between a $3d^n$ ($3d^7$ for $Co^{2+}$) and a $3d^{n-1}$ ($3d^6$ for $Co^{3+}$) configuration is $\Delta E = E(2p^6 3d^{n-1} \rightarrow 2p^5 3d^n) - E(2p^6 3d^n \rightarrow 2p^5 3d^{n+1}) \approx U_{pd} - U_{dd} \approx 1-2$ eV, where $U_{dd}$ is the Coulomb repulsion energy between two $3d$ electrons and $U_{pd}$ the one between a $3d$ electron and the $2p$ core hole.

One can observe from Fig. 1 that the $Ca_3Co_2O_6$ spectrum has no features at the low-energy side, which otherwise could have indicated the presence of $Co^{2+}$ species as in CoO. Instead, the spectrum has a much closer resemblance to that of $Co^{3+}$, as in $EuCoO_3$. This means that one can safely rule out the $Co^{2+}/Co^{4+}$ scenario.[13] In other words, the XAS experiment reveals unambiguously that both the $Co_{oct}$ and the $Co_{trig}$ ions are in the 3+ valence state. This result supports the analysis of the Co $2p$ core-level x-ray photoemission spectra[15] and band-structure calculations.[16,18]

In order to resolve the spin-state issue, we now resort to XMCD. The top part (a) of Fig. 2 depicts Co-$L_{2,3}$ XAS spectra taken with circularly polarized light with the photon spin parallel (red solid line, $\mu^+$) and antiparallel (black dashed line, $\mu^-$) aligned to the magnetic field. The quantization axis $z$ has been chosen to be parallel to the $c$ axis, which is the easy magnetization axis.[3] One can clearly observe large differences between the spectra using these two alignments. The difference spectrum, i.e., the XMCD spectrum, is also shown (blue dash-dotted line, $\mu^+ - \mu^-$). Using the well-known XMCD sum rule developed by Thole *et al.*,[22]

$$L_z = \frac{4}{3} \frac{\int [\mu^+(E) - \mu^-(E)] dE}{\int [\mu^+(E) + \mu^-(E)] dE} (10 - N_e), \qquad (1)$$

where $N_e$ is the number of the Co $d$ electrons, we can extract directly the orbital ($L_z$) contribution to the magnetic moment

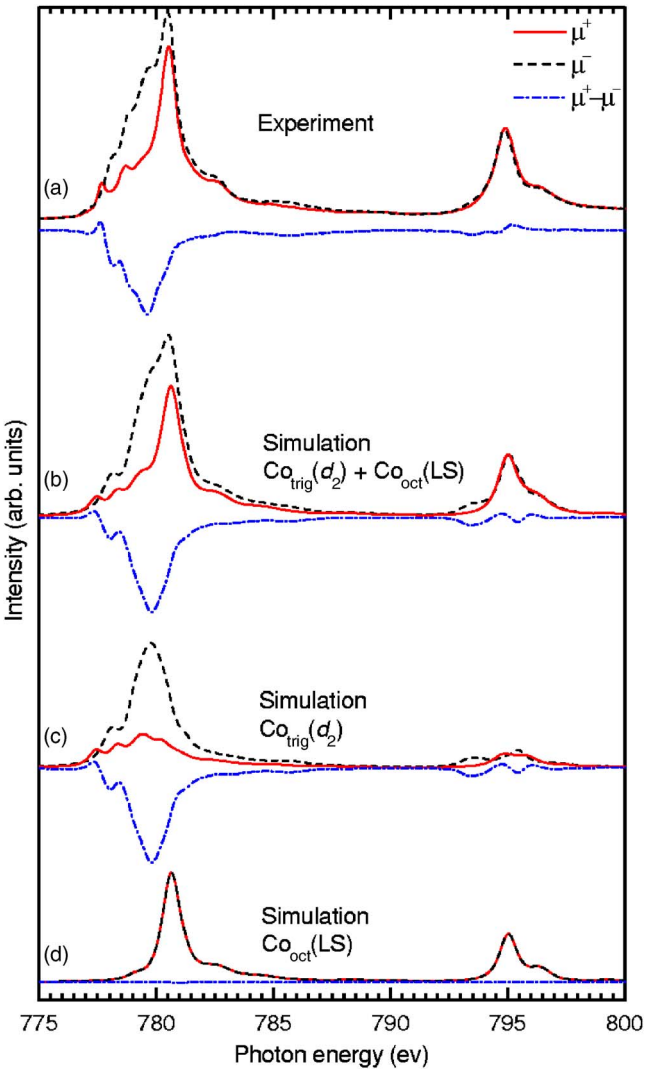


FIG. 2. (Color online) (a) Measured soft-x-ray absorption spectra with parallel ($\mu^+$, red solid line) and antiparallel ($\mu^-$, black dashed line) alignment between photon spin and magnetic field, together with the difference spectrum ($\mu^+ - \mu^-$, blue dashed-dotted line). (b) Simulated sum spectra assuming a doubly occupied $d_2$ orbital for the $Co_{trig}$ and low-spin (LS) $Co_{oct}$ ions; (c) and (d) Contribution of the $Co_{trig}$ and $Co_{oct}$ ions to the simulated sum spectra.

without the need to do detailed modeling. Assuming an average Co $3d$ occupation number of about $N_e = 6.5$ electrons (estimated for a HS $Co^{3+}$ oxide[23] and also to be justified below by cluster calculations) we find a value of $1.2\mu_B$ for the $L_z$, which is a very large number indicating that the ground state is strongly spin-orbit active.

To extract more detailed information concerning the spin and orbital states from the Co-$L_{2,3}$ XAS spectra, we have carried out simulations for the XMCD spectra using the well-proved configuration-interaction (CI) cluster model.[24–26] The method uses for each Co site a $CoO_6$ cluster that includes the full atomic multiplet theory and the local effects of the solid. It accounts 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. In the configuration-interaction cluster calcula-

tion we describe the ground state by the configurations

$$\Psi = \alpha_6|d^6\rangle + \alpha_7|d^7\underline{L}\rangle + \alpha_8|d^8\underline{L}^2\rangle + \alpha_9|d^9\underline{L}^3\rangle, \quad (2)$$

where $\underline{L}$ denotes a ligand hole and $\Sigma_{i=6}^{9}\alpha_i^2=1$.[27,28] The transition-metal electron occupation is then given by

$$N_e = 6\alpha_6^2 + 7\alpha_7^2 + 8\alpha_8^2 + 9\alpha_9^2. \quad (3)$$

The simulations have been carried out using the program XTLS 8.3.[24]

In octahedral symmetry the $3d$ orbitals split up in the well-known $e_g$ and $t_{2g}$ levels; the splitting is given by $10Dq$. In a trigonal prismatic environment, however, it is found that the $x^2$-$y^2$ is degenerate with the $xy$, and the $yz$ with $zx$ orbital.[17,18] In the presence of the spin-orbit coupling, it is then better to use the complex orbitals $d_0$, $d_2/d_{-2}$, and $d_1/d_{-1}$. Band structure calculations indicate that the $d_1/d_{-1}$ band is split off from the $d_0$ and $d_2/d_{-2}$ bands by about 1 eV, while the $d_0$ and $d_2/d_{-2}$ bands are almost degenerate.[17,18] Critical for the magnetism and for the line shape of the simulated spectra are the crystal field parameter $10Dq$ for the $Co_{oct}O_6$ cluster and the crystal field parameter for the splitting between the nearly degenerate $d_0$ and $d_2$ orbitals of the $Co_{trig}O_6$ cluster. $10Dq$ needs to be critically tuned since this is set to determine whether $Co_{oct}$-$O_6$ cluster is in the LS or HS state.[29] The trigonal prism crystal field has also to be fine-tuned since it determines whether the $d_2$ or the $d_0$ lies lowest, and thus the magnitude of the orbital moment and strength of the magnetocrystalline anisotropy as we will show below. Tuning of these parameters will be done by establishing which of the simulated spectra reproduce the experimentally observed ones.

As a starting point, we make the assumption that the $Co_{oct}$ ion is in the LS state, based on the observation that the average $Co_{oct}$-O bond length of 1.916 Å in this material[10] is shorter than the 1.925 Å in $LaCoO_3$ at 5 K, which is known to be LS.[30] With such a short length, the Co ion is subjected to a large enough $10Dq$, sufficient to stabilize the nonmagnetic LS state[29,30] for $Co_{oct}^{3+}$ ions in $Ca_3Co_2O_6$. With this starting point, the magnetism and the XMCD signal must originate from the $Co_{trig}$ ions. This is quite plausible since with the extremely large $Co_{trig}$-O average bond length of 2.062 Å,[10] which is much larger than 1.961 Å for $LaCoO_3$ at 1000 K,[30] one can expect that the crystal field is small enough to stabilize the HS state.[29] Based on the observation that the orbital contribution to the magnetic moment is extremely large, we take the $d_2$ *ansatz* for the $Co_{trig}$ and not the $d_0$. In the CI calculation, the parameters for the multipole part of the Coulomb interactions were given by the Hartree-Fock values, while the monopole parts ($U_{dd}$, $U_{pd}$) were estimated from photoemission experiments on $Co^{3+}$ materials.[31] The one-electron parameters such as the O $2p$-Co $3d$ charge-transfer energies and integrals were estimated from band-structure results.[17–19] The charge-transfer energy is given by $\Delta=E(d^7\underline{L})-E(d^6)=1.5$ eV, the $d$-$d$ Coulomb repulsion by $U_{dd}=5.5$ eV and of $p$-$d$ of the excited Co by $U_{pd}=7.0$ eV; the Slater integrals have been reduced to 80% of their Hartree-Fock value. An exchange field of $H_{ex}=3$ meV has been used. For the $Co_{trig}$ ions the ionic crystal splittings are $\Delta E^{ionic}_{d_1/d_2}=0.9$ eV and $\Delta E^{ionic}_{d_0/d_2}=0.05$ eV taken from band-structure calculation,[18] the hybridization is $V^{hyb}_{d_1}=1.88$ eV, $V^{hyb}_{d_0}=1.28$ eV, and $V^{hyb}_{d_2}=1.25$ eV. For $Co_{oct}$ ions $pd\sigma=-1.44$ eV and $pd\pi=0.63$ eV was used. With this set of parameters we have found a LS-HS transition for $Co_{oct}$ at $10Dq=0.65$ eV. Here we used $10Dq=0.8$ eV, based on band-structure calculation, which is the same value as for $EuCoO_3$ known as a LS $Co^{3+}$ oxide.[20]

The results of these simulations are given by curves (b) in Fig. 2, together with a breakdown into the separate contributions of the $Co_{trig}$ [curves (c)] and $Co_{oct}$ [curves (d)] ions. One can clearly observe that the simulations [curves (b)] reproduce the experimental spectra quite well. All major and minor peaks in the individual experimental XAS ($\mu^+$, $\mu^-$) and XMCD ($\mu^+-\mu^-$) spectra [curves (a)] are present in the simulations [curves (b)]. It is almost needless to remark that the entire simulated XMCD signal is coming from the HS $Co_{trig}$ ions [curves (c)], since we started with a nonmagnetic LS $Co_{oct}$ [curves (d)]. In the simulation, we find $S_z=1.8\mu_B$ and $L_z=1.7\mu_B$, giving a total magnetic moment of $2S_z+L_z=5.3\mu_B$ per formula unit. Due to strong hybridization between Co $3d$ and O $2p$, the $3d$ occupation numbers of the $Co_{trig}$ ions and the $Co_{oct}$ are 6.3 and 6.8, respectively, giving on average 6.5 electrons as used for the sum rules. The calculated total moment from the simulation compares reasonably well with the $4.8\mu_B$ value from direct magnetization measurements.[6,12] Yet, the simulated $L_z$ value ($1.7\mu_B$) is appreciably larger than the one derived from the experiment using the XMCD sum rule ($1.2\mu_B$). However, looking more closely at the simulated and experimental XMCD spectra, we can clearly see that the XMCD spectra have very similar line shapes and that the distinction is mainly in the amplitude, i.e., a matter of scaling. This indicates that the discrepancy in the $L_z$ determination might be caused by the fact that the sample is not fully magnetized in our experiment. According to magnetization measurements one can only achieve 90% of the saturation magnetization at 5.5 T.[12] In addition, slight misalignment of the sample together with the high magnetocrystalline anisotropy may account for some further reduction of the experimental value.

Having established that the $d_2$/LS scenario for the $Co_{trig}/Co_{oct}$ ions explains well the experimental spectra, we now investigate the sensitivity of our analysis. For this we change the *ansatz* for the $Co_{trig}$ ion: we now set the $d_0$ orbital to be energetically lower than the $d_2$.[32] The result is shown in Fig. 3, in which the simulated XMCD spectrum (b) is compared with the experimental one (a). One can unambiguously recognize large discrepancies in the line shapes, not only in the $L_3$ region (777–785 eV), where the simulated XMCD signal has much less amplitude, but also in the $L_2$ (792–797 eV), where now an XMCD signal is calculated while it is practically absent in the experiment. Using the XMCD sum rule,[22] we can relate these discrepancies also directly to the fact that the $d_0$ *ansatz* essentially does not carry an orbital moment.

The success of the cluster method for the analysis of both the high-energy spectroscopies and the ground-state magnetic moments provides confidence for its use to investigate the magnetocrystalline anisotropy in this material. We have

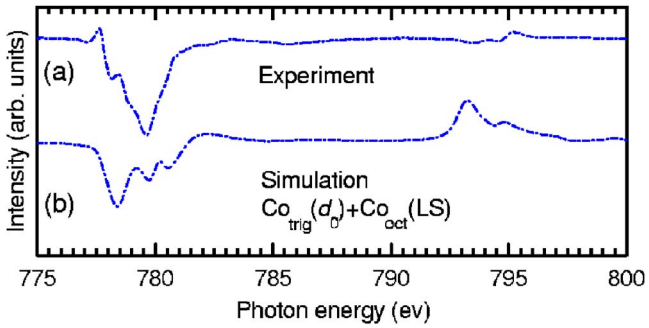


FIG. 3. (Color online) (a) Measured soft-x-ray magnetic circular dichroism spectrum (XMCD, $\mu^+ - \mu^-$); (b) simulated XMCD spectrum assuming a doubly occupied $d_0$ orbital for the $Co_{trig}$ and low-spin (LS) $Co_{oct}$ ions.

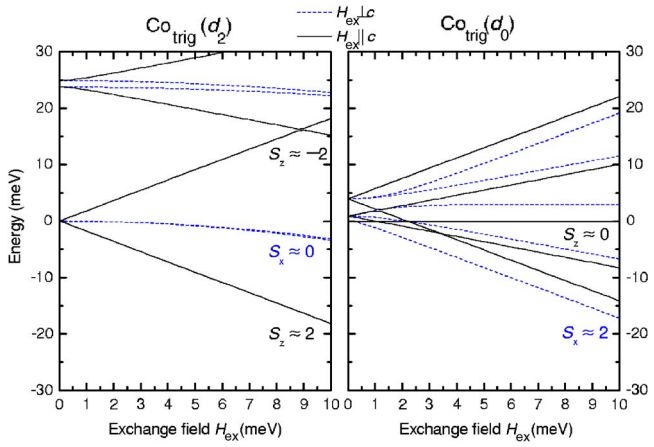


FIG. 4. (Color online) Total-energy level diagram for the $Co_{trig}$ ion as a function of the exchange field $H_{ex}$ along the $z$ direction ($c$ axis, solid black lines) and along the $x$ direction (perpendicular to the $c$ axis, dashed blue lines), with (left-hand panel) the $d_2$ and (right-hand panel) the $d_0$ orbital doubly occupied.

calculated the total energy of the $Co_{trig}O_6$ cluster as a function of the exchange field $H_{ex}$, directed either along the $z$ axis (the $c$ axis or the one-dimensional chain) or along the $x$ axis (perpendicular to the $c$ axis). The results for the $d_2$ *ansatz* are plotted in the left-hand panel of Fig. 4. It is evident that the lowest state gains energy when $H_{ex}$ is along $z$ and very little to nothing for $H_{ex}$ along $x$. This demonstrates directly that the magnetocrystalline anisotropy should be large and directed along the $z$, consistent with the experimental observation that the magnetization parallel to $c$ is almost sixfold of the one perpendicular to $c$ (at 12 K and 5.5 T)[3] and with the Ising nature of the magnetism. We note that the lowest curve in the figure shows an energy gain with a rate twice that of $H_{ex}$ (along $z$), meaning that $S_z$ is close to $2\mu_B$, which in turn is consistent with the HS ($S=2$) nature of the $Co_{trig}$ ion.

We have also analyzed the magnetocrystalline anisotropy of the $Co_{trig}O_6$ cluster using the $d_0$ *ansatz*. The right-hand panel of Fig. 4 reveals that the total energy decreases for both directions of $H_{ex}$, but now with the important distinction that the energy for $H_{ex}$ along $x$ is always lower than for $H_{ex}$ along $z$. This implies that the easy-magnetization axis should be perpendicular to the $z$ axis, which is not consistent with the experimental facts. Also this contradiction thus effectively falsifies the $d_0$ *ansatz*.[17,19]

To conclude, using soft x-ray absorption spectroscopy and the magnetic circular dichroism therein at the Co-$L_{2,3}$ edges we have experimentally determined that both Co ions in $Ca_3Co_2O_6$ are 3+, with the $Co_{trig}$ ion in the high-spin state and the $Co_{oct}$ in the nonmagnetic state. The $Co_{trig}$ ion carries an anomalously large orbital moment of $1.7\mu_B$ which we have been able to relate to the double occupation of the $d_2$ orbital. In addition, the detailed analysis of the spectral line shapes together with that of the magnetocrystalline anisotropy firmly establishes that the $d_2$ orbital lies lowest in energy[18] and not the $d_0$.[17,19] This in turn also demonstrates that a proper incorporation of the spin-orbit interaction is required for the *ab initio* calculation of the delicate electronic structure of this material.

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