Electronic structure, spin state, and magnetism of the square-lattice Mott insulator \( \text{La}_2\text{Co}_2\text{Se}_2\text{O}_3 \) from first principles

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Electronic and magnetic structures of the newly synthesized cobalt oxyselenide \( \text{La}_2\text{Co}_2\text{Se}_2\text{O}_3 \) (structurally similar to the superconducting iron pnictides) are studied through density functional calculations. The obtained results show that this material is a Mott insulator, and that it has a very stable Co\(^{2+}\) high-spin ground state with a \( t_{2g}\)-like orbital ordering, which is substantiated by the calculated crystal-field excitation energies. The square lattice of the Co\(^{2+}\) spins is found to have a strong antiferro (a weak ferro) magnetic coupling for the second nearest neighbors (2nn) via O (Se\(_2\)) and an intermediate antiferro one for the 1nn, with the strength ratio about 10:1:3. The present results account for the available experimental data of magnetism, and the prediction of a planar frustrated (2×2) antiferromagnetic structure would motivate a new experiment.

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Very recently transition-metal oxycalogenides receive revived interest\cite{1,2} due to their similar structural identity to the superconducting iron pnictides\cite{3} in terms of a common square lattice of the transition-metal species [with a local octahedral (tetrahedral) coordination in the former (latter)]. In contrast to bad metal properties of the parent iron pnictides, a Mott insulating behavior has been found in the iron or cobalt oxycalogenides\cite{4,5}. As the strength of electron correlations in the pnictides is currently under a hot debate, and as the superconductivity and magnetism therein have a close relationship, it is worth a lot to study promptly the correlated-electron structure and magnetic properties of those Mott insulating oxycalogenides, which would help to understand the pnictides upon their approaching the limit of a Mott localization. The structure and magnetic properties of (Ba,Sr)\(_2\)Fe\(_2\)(Se,S)\(_2\)OF\(_2\) have recently been studied by Kabbour et al.\cite{6} The observed long-range antiferromagnetic (AF) ordering below 83.6-106.2 K was proposed to be a rare example of a frustrated AF checkerboard spin lattice. More recently, Zhu et al. studied a Mott localization in La\(_2\)Fe\(_2\)(Se,S)\(_2\)O\(_3\) and found that those materials have moderate charge gaps\cite{7}. Their results support the notion that the iron pnictides and chalcogenides possess intermediately strong electron correlations and are not too far away from Mott localizations.

In this Rapid Communication, we study the cobalt oxyselenide La\(_2\)Co\(_2\)Se\(_2\)O\(_3\), which was newly synthesized by Wang et al and found by them to be insulating and to have an AF transition at \( T_{AF} \approx 220 \) K.\cite{8} Those authors suggested an unusual low-spin (LS, \( S=1/2 \)) state of the Co\(^{2+}\) ions and a corresponding orbital order for understanding of the insulating behavior and AF in the checkerboard spin-lattice. The Co\(^{2+}\) LS state is quite surprising, in view of the common high-spin (HS, \( S=3/2 \)) state. Having a close look at the calculated results of Wang et al. (Fig. 6 in Ref. [9]) using the local-spin-density approximation plus Hubbard \( U \) (LSDA+\( U \)) method, one may wonder why three singly occupied orthogonal orbitals have two up-spins and one down-spin, which obviously violates the Hund’s first rule. This infers that their LSDA+\( U \) calculation with an orbital-polarized potential ran into an exotic solution which should not be the ground state. Secondly, if the Co\(^{2+}\) is in the LS state as Wang et al concluded using measurements of magnetic susceptibility and specific heat\cite{8} (which will be commented on below), the magnetic coupling between the \( S=1/2 \) ions, with a most probable frustration, would not be expected to yield the quite high \( T_{AF} \approx 220 \) K. Thus the electronic structure and magnetism of this interesting new material were poorly understood. For this reason, we carry out a rather complete set of density functional calculations to study the electronic and magnetic structures of La\(_2\)Co\(_2\)Se\(_2\)O\(_3\), which are closely related to the Co\(^{2+}\) spin and orbital states. In strong contrast to the previous finding\cite{8} all the present calculations using LSDA, LSDA-Fock-0.25, and LSDA+\( U \) functionals consistently conclude the HS ground state, which is also substantiated by the calculated crystal-field level splittings. The orbital multiplet effect and a \( t_{2g}\)-like orbital ordering are discussed. Moreover, the exchange constants of the Co\(^{2+}\) square lattice are calculated and a planar frustrated (2×2) AF structure is proposed. The present work sheds new light on this interesting material, and a comparison is also made with the above iron oxycalogenides.

La\(_2\)Co\(_2\)Se\(_2\)O\(_3\) has the Co\(_2\)Se\(_2\)O layers which are separated by the La\(_2\)O\(_2\) layers, see Fig. 1(a). Each Co\(_2\)Se\(_2\)O layer consists of the CoSe\(_2\)O\(_2\) octahedra having the Co-O (Co-Se) bondlength of 2.035 (2.688) Å.\cite{10} Those octahedra are face-shared for the first-nearest-neighboring Co sites and edge- (corner-) shared via Se\(_2\) (O) for the second-nearest Co neighbors. In our calculations, we used for each CoSe\(_2\)O\(_2\) octahedron such corresponding local \( xyz \) coordinates that for the body-centered Co site as an example, the \( z \) axis is along the Co-O bond and the \( x \) along the crystallographic \( c \) axis. As a result of the \( D_{2h} \) point-group symmetry seen by the Co\(^{2+}\) ions, the lower-lying \( t_{2g}\)-like orbitals \( (x^2-y^2, yz, \text{ and } xz) \) and the higher \( e_g \) \( (xy \text{ and } 3z^2-r^2) \) all split\cite{11} see Fig. 1(b) and the detailed results below. Our calculations were carried out using the...
FIG. 1: (Color online) (a) Crystal structure of La$_2$Co$_2$Se$_2$O$_3$ having the Co$_2$Se$_2$O layers. For each constituent CoSe$_4$O$_2$ octahedron the corresponding local coordinates are used, e.g., the $xyz$ for the body-centered Co site and the $y$ and $z$ interchanged for the $c$-axis edge Co$^{2+}$. (b) Orbitally resolved Co 3d DOS for the nonmagnetic state by LDA. The lower-lying $t_{2g}$-like orbitals ($x^2-y^2$, $yz$, and $xz$) and the higher $e_g$ ($xy$ and $3z^2-r^2$) all split. (c) DOS of the HS FM half-metallic state by LSDA. The solid (dashed) curves refer to the majority (minority) spin. Fermi level is set at zero energy.

full-potential augmented plane waves plus local orbital method. The muffin-tin sphere radii are chosen to be 2.8, 2.2, 2.0 and 1.5 Bohr for La, Co, Se, and O atoms, respectively. The cut-off energy of 16 Ryd is used for plane wave expansion, and $15 \times 15 \times 3$ k mesh for integrations over the Brillouin zone, both of which ensure a high accuracy of our results.

We start with the standard LSDA calculations. The results show that independent of the initialized spin moment, a ferromagnetic (FM) state always converges to the same HS solution, see its density of states (DOS) in Fig. 1(c). It is half metallic, with the fully occupied (and thus insulating) spin-majority channel and partially occupied (metallic) Co 3d bands. This solution is calculated to be more stable than the nonmagnetic state by 593 meV/f.u. We also did for the assumed LS state a fixed-spin-moment calculation (otherwise it converges to the above HS ground state) and find that the LS-fixed state is less stable than the HS state by 435 meV/f.u., see Table I. Moreover, our calculations show that the HS FM state is more stable than the HS checkerboard-AF state by 26 meV/f.u. This is most probably due to a maximal kinetic energy gain in the FM half-metallic state. Note, however, that this FM half metallic ground state disagrees with the experimental insulating and AF state.

| Table I: Relative total energies in unit of meV/f.u. (and the Co spin moment in unit of $\mu_B$) of La$_2$Co$_2$Se$_2$O$_3$ having the HS or LS Co$^{2+}$ ions in the checkerboard AF or FM state. The three functionals all show the HS ground state. The symbol "→" stands for "converges to". |
|-------------------------------|----------------|------------------|
|                               | LSDA           | LSDA-Fock-0.25   | LSDA+U(4 eV)     |
| HS-AF                         | 26 (+1.97)     | 0 (+2.63)        | 0 (+2.55)        |
| HS-FM                         | (2.38)         | 258 (2.65)       | 55 (2.58)        |
| LS-AF                         | →HS-AF         | 1503 (+0.91)     | →HS-AF           |
| LS-FM                         | 435 (0.93)     | 1527 (0.92)      | →HS-FM           |

By a comparison with LaFeAsO (La$_2$Fe$_2$Se$_2$O$_3$) in which the Fe 3d bandwidth is 4.4 (3.2) eV the entire Co 3d bandwidth in La$_2$Co$_2$Se$_2$O$_3$ is only 2.8 eV, see Fig. 1(b). This signals a stronger correlation effect in La$_2$Co$_2$Se$_2$O$_3$ due to the band narrowing. Indeed a presence of the local magnetic moment suggests a Mott localization behavior of La$_2$Co$_2$Se$_2$O$_3$. Therefore, it is not surprising that the standard LSDA calculations (albeit quite informative) cannot provide a correct description of the electronic and magnetic structure of this Mott insulator.

In order to study the electron correlation effect, we carried out hybrid functional calculations using the LSDA-Fock-0.25 which mixes 25% Fock exact exchange into the LSDA exchange functional and is applied to the Co 3d electrons. This was demonstrated to be an alternative way (to the LSDA+U, see below) for studying correlated electron systems. Our hybrid functional calculations show again that the Co$^{2+}$ HS is the ground state, being much more stable than the LS state by about 1.5 eV/f.u., see Table I. The corresponding much smaller value of about 0.4 eV/f.u. given by the LSDA may well be due to the artificial (half-) metallic band structure which significantly suppresses the energy splitting of the spin and orbital multiplets of the Co$^{2+}$ ions. Fig. 2 shows the orbitally resolved DOS for the HS (left panel) and LS (right panel) solutions in the checkerboard AF state. The HS Mott insulating solution has one $t_{2g}$ hole on the minority-spin $xz$ orbital and two $e_g$ ($xy$ and $3z^2-r^2$) holes, thus forming a $t_{2g}$ orbital ordering. This is the ground-state solution of the orbital multiplets for the HS Co$^{2+}$ ions, as confirmed by the following LSDA+U calculations. In this HS insulating state, the AF exchange and superexchange are expected to be dominant, and indeed our calculations show that the HS checkerboard AF state is more stable than the FM state by 258 meV/f.u., see Table I. In contrast, the very unstable LS state has the $t_{2g}^0 e_g^0$ configuration with the $e_g^0$ being an $xy$ electron, fully according with the crystal-field level sequence calculated below. The LS AF state is (a little) more stable than the LS FM state, but the energy difference of 24 meV/f.u. is less than one tenth of that for the HS state. Although exchange constants may well be overestimated by a hybrid functional those two values confirm, as expected, that the LS state would yield much weaker magnetic couplings than the HS state.
As the LSDA+$U$ method has been widely used to study the electronic and magnetic properties of the correlated electron systems, here we further performed a set of LSDA+$U$ calculations using the double-counting correction in an atomic limit and the effective $U=4$ eV. We have initialized the corresponding density matrix (and orbital-dependent potential) and then done self-consistently a full electronic relaxation. This procedure turns out to be suitable for study of the spin and orbital physics. The obtained electronic structure, the HS ground state, the orbital multiplet splitting, the exchange constants and the ground-state magnetic structure are discussed as follows.

For both the FM and checkerboard AF configurations, the LS state turns out to be unstable and converges to the HS ground state. For the HS ground state, we find that the orbital multiplet splitting, the exchange energies (i.e., exchange energies) onto a Heisenberg model. The resultant values are $-9.97$ meV ($J_1$, AF, counted once per pair), $-3.06$ meV ($J_2$), and $0.98$ meV ($J_3$, FM) for the second-nearest-neighbor (2nn) Co pair via O, the first-nearest-neighbor (1nn) pair, and the 2nn pair via Se, respectively, as shown in Table I. As the J1 is more than three times as big as the J2 (well meeting the requirement $|J_1| > |J_2|$) and the J3 is positive, the ground state AF structure $E_{exx} = (J_1 - J_3)S^2$ per Co$^{2+}$ with $S = 3/2$ is what we show in Fig. 3. It is more stable (albeit the frustrated J2 couplings) than the checkerboard AF state $E_{exx} = (-J_1 + 2J_2 - J_3)S^2$ per Co$^{2+}$ by 31 meV/Co, and than the stripe AF state $E_{exx} = (J_1 + J_3)S^2$ by 4 meV/Co. We also calculated those $J$ values using a smaller $U (=3$ or 2 eV) when the system approaches an itinerant limit, and find that while the FM J3 becomes a bit smaller, both the AF J1 and J2 get larger with a nearly constant J1/J2 ratio of about 3. Thus, the HS planar (2×2) AF structure as shown in Fig. 3 remains to be the ground state as the system is a Mott insulator with the effective $U \geq 2$ eV. This prediction calls for an experimental study.

Here we compare our LSDA+$U$ results with those calculated previously for the isostructural Ba$_2$Fe$_2$Se$_2$OF$_2$ and La$_2$Fe$_2$Se$_2$O$_{1.5}$ All the three materials are calculated to be a Mott insulator with a band gap opening estimated: the $x^2-y^2$, yz, xz, xy, and $3z^2-r^2$ order as 0, 397, 457, 750, and 1187 meV. By a comparison with the LS state ($t^6_g(x^2-y^2)$), the HS ground state ends with an $xz - 3z^2-r^2$ transition which gains, by a simple estimate, two times Hund exchange (in total about 2 eV) with a much lower cost of the crystal-field energy of 730 meV. This is the reason that the HS is the very stable ground state of this Mott insulator, having a localized spin moment larger than 2.5 $\mu_B$ as seen in Table I.
by Hubbard $U$, and in the Mott insulating phase each of the three exchange constants has the same sign (AF or FM) in the three materials. Both the Fe$^{2+}$ ($S_{Fe}=2$) and Co$^{2+}$ ($S_{Co}=3/2$) ions are found to be in the HS state. Considering the strongest AF coupling for the Co or Fe pair via O, $J_1 S_{Co}^2$ in La$_2$Co$_2$Se$_2$O$_3$ is about 1.5 times as big as $J_2 S_{Fe}^2$ in Ba$_2$Fe$_2$Se$_2$OF$_2$ (Ref. 2) and $J'_2 S_{Fe}^2$ in La$_2$Fe$_2$Se$_2$O$_3$ (Ref. 3) (using those $J$ values at the $U=3$ eV for a direct comparison). Moreover, the magnetic frustration appears weaker in La$_2$Co$_2$Se$_2$O$_3$ due to the smaller ratio $J_2/J_1 < 1/3$ (the corresponding ratio $>0.5$ in Ba$_2$Fe$_2$Se$_2$OF$_2$ and La$_2$Fe$_2$Se$_2$O$_3$) Both factors account for the observations that the $T_{AF} \sim 220$ K in La$_2$Co$_2$Se$_2$O$_3$ (Ref. 4) is about two times as high as that of around 100 K in both Ba$_2$Fe$_2$Se$_2$OF$_2$ and La$_2$Fe$_2$Se$_2$O$_3$ Note that if the Co$^{2+}$ was in the LS state, the $T_{AF}$ would decrease probably by one order of magnitude as discussed above by the hybrid functional calculations. This would obviously disagree with the experiments. Therefore the LS-state model is discarded by the present work.

Now we briefly comment on the recent experiments carried out by Wang et al. for La$_2$Co$_2$Se$_2$O$_3$. They used a Curie-Weiss law to fit the magnetic susceptibility in the present work. Therefore the LS-state model is discarded by the hybrid functional calculations. While the LSDA predicts this material to be a possible ferrimagnetic half metal, both the LSDA-Fock-0.25 hybrid functional and LSDA+$U$ calculations show a Mott insulating and antiferromagnetic ground state in agreement with experiments, and a $t_{2g}$ orbital ordering as well. The exchange constants of the frustrated antiferromagnetism are calculated. In contrast to the newly suggested unusual low-spin state of the Co$^{2+}$ ions, all the present calculations conclude the very stable high-spin ground state, which is substantiated by the calculated crystal-field level splittings. A comparison with the iron oxyxalcogenides is made, and the experiments are explained.

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