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Electronic structure, spin state, and magnetism of the square-lattice Mott insulator $La_2Co_2Se_2O_3$ from first principles

Hua Wu
II. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany

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Electronic and magnetic structures of the recently synthesized cobalt oxyselenide $La_2Co_2Se_2O_3$ (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 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 antiferromagnetic (a weak ferromagnetic) coupling for the second-nearest neighbors via O (Se_2) and an intermediate antiferromagnetic one for the first-nearest neighbors with the strength ratio about 10:1:3. The present results account for the available experimental data and the prediction of a planar frustrated (2×2) antiferromagnetic structure would motivate a new experiment.

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Very recently transition-metal oxychalcogenides receive revived interest[1–5] due to their structural similarity to the superconducting iron pnictides[6] 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 oxychalcogenides.[2,4,5] 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 oxychalcogenides, which would help to understand the pnictides upon their approaching the limit of a Mott localization. The structure and magnetic properties of $(Ba,Sr)_2Fe_2(Se,S)_2OF_2$ have recently been studied by Kabbour *et al.*[2] 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.*[5] studied a Mott localization in $La_2Fe_2(Se,S)_2O_3$ and found that those materials have moderate charge gaps. 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 $La_2Co_2Se_2O_3$, which was recently synthesized by Wang *et al.*[4] and found by them to be insulating and to have an AF transition at $T_{AF}\sim220$ K. 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. 4) 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. Second, if the Co^{2+} is in the LS state as Wang *et al.* concluded using measurements of magnetic susceptibility and specific heat[4] (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 $T_{AF}\sim220$ K. Thus the electronic structure and magnetism of this interesting 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 $La_2Co_2Se_2O_3$, which are closely related to the Co^{2+} spin and orbital states. In strong contrast to the previous finding,[4] 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 light on this interesting material and a comparison is also made with the above iron oxychalcogenides.

$La_2Co_2Se_2O_3$ has the Co_2Se_2O layers which are separated by the La_2O_2 layers, see Fig. 1(a). Each Co_2Se_2O layer consists of the $CoSe_4O_2$ octahedra having the Co-O (Co-Se) bond length of 2.035(2.688) Å.[4] 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 $CoSe_4O_2$ 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, and xz) and the higher e_g (xy and $3z^2-r^2$) all split,[7] see Fig. 1(b) and the detailed results below. Our calculations were carried out using the full-potential augmented plane waves plus local-orbital method.[8] 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 Ry is used for plane-wave expansion, and $15\times15\times3$ **k** mesh for integrations over the Brillouin-zone, both of which ensure a high accuracy of our results.

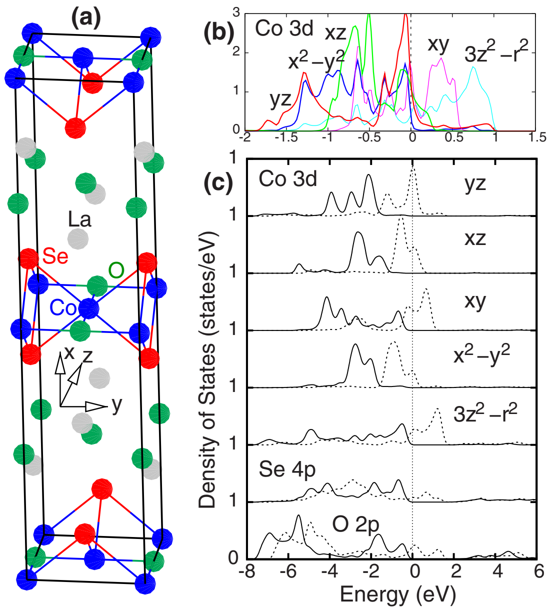

FIG. 1. (Color online) (a) Crystal structure of $La_2Co_2Se_2O_3$ having the Co_2Se_2O layers. For each constituent $CoSe_4O_2$ octahedron the corresponding local coordinates are used, e.g., the xyz for the body-centered Co site and the y and z interchanged for the c-axis edge Co^{2+}. (b) Orbitally 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.

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. By a comparison with LaFeAsO ($La_2Fe_2Se_2O_3$) in which the Fe 3d bandwidth is 4.4 (3.2) eV,[5] the entire Co 3d bandwidth in $La_2Co_2Se_2O_3$ is only 2.8 eV, see Fig. 1(b). This signals a stronger correlation effect in $La_2Co_2Se_2O_3$ due to the band narrowing.[5] Indeed a presence of the local magnetic moment suggests a Mott localization behavior of $La_2Co_2Se_2O_3$.[4] 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.

TABLE I. Relative total energies in unit of meV/f.u. (and the Co spin moment in unit of μ_B) of $La_2Co_2Se_2O_3$ 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	0 (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

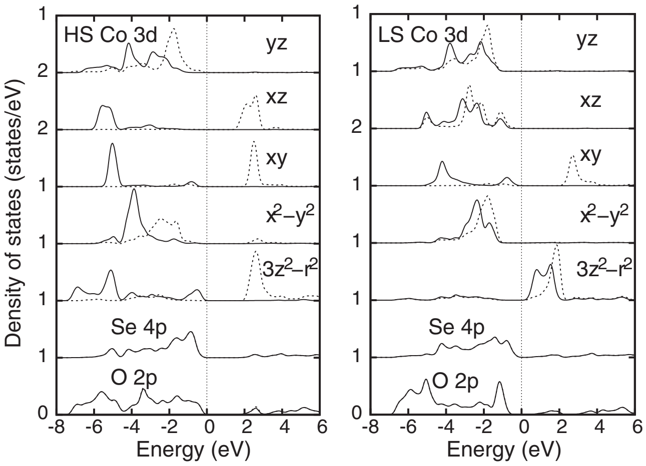

FIG. 2. DOS of the HS (left panel) and LS (right panel) solutions in the checkerboard AF state by the LSDA-Fock-0.25 hybrid functional. The Co^{2+} ions in the HS ground state have an xz-type (t_{2g} hole) orbital ordering. The much less stable LS state has the $t_{2g}^6+e_g^1(:xy)$ configuration. See Fig. 1 for other notations.

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.[9,10] 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.[11]] Figure 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 $t_{2g}^6e_g^1$ configuration with the e_g^1 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,[12] 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[13] 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.[14] 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.[11] 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 tested all the ten different orbital configurations of the two minority-spin electrons (the majority-spin channel is closed in the Co^{2+} HS ground state). We find that the five lowest-energy configurations states, the $(x^2-y^2)(yz)$, $(x^2-y^2)(xz)$, $(yz)(xz)$, $(yz)(xy)$, and $(x^2-y^2)(3z^2-r^2)$, order as 0, 60, 457, 750, and 790 meV/Co (see Fig. 1 for orbital indices). Thus, the ground state of the orbital multiplets is $t^3_{2g\uparrow}e^2_{g\uparrow}(x^2-y^2)^1_\downarrow(yz)^1_\downarrow$, confirming the above hybrid functional results. The corresponding DOS results (not shown here) are very similar to the latter. As each Co^{2+} ion has a t_{2g} hole on the xz orbital in its local coordinates and the local coordinates are rotated around the crystallographic c axis by $\pi/2$, to say, from the body-centered Co^{2+} site to the c-axis edge one [see Fig. 1(a)], each Co_2Se_2O layer has an antiferro xz-type hole-orbital ordering. Moreover, from those above energy differences and by neglecting the difference of the interorbital Coulomb interactions, the crystal-field level splittings (or to say, crystal-field excitation energies) are 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 $[t^6_{2g}(xy)^1]$, the HS ground-state ends with an $xz\rightarrow 3z^2-r^2$ 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 μ_B as seen in Table I.[15]

Now we estimate the three exchange constants of the HS Co^{2+} ions in the square lattice (Fig. 3), by calculating four different magnetic structures (the same as used in Ref. 2, see Fig. 9 therein) and then mapping the total-energy differences (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-neighboring (2nn) Co pair via O, the first-nearest-neighboring (1nn) pair, and the 2nn pair via Se_2, respectively, as shown in Fig. 3. As the J_1 is more than three times as big as the J_2 (well meeting the requirement $|J_1|>|J_2|$) and the J_3 is positive, the ground-state AF structure $[E_{ex}=(J_1-J_3)S^2$ per Co^{2+} with $S=3/2]$ is what we show in Fig. 3: it is more stable (albeit the frustrated J_2 couplings) than the checkerboard AF state $[E_{ex}=(-J_1+2J_2-J_3)S^2$ per Co] by 31 meV/Co, and than the stripe AF state $[E_{ex}=(J_1+J_3)S^2]$ 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 J_3 becomes a bit smaller, both the AF J_1 and J_2 get larger with a nearly constant J_1/J_2 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.

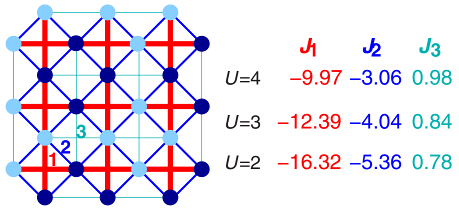

FIG. 3. (Color online) The ground-state (2×2) planar magnetic structure of the HS Co^{2+} square lattice with the 2nn AF exchange J_1 via O (red bold lines), the 1nn AF J_2 (blue solid lines), and the 2nn FM exchange J_3 via Se_2 (cyan thin lines). See also Fig. 1(a). The J_2 couplings are frustrated. Only the spin-up and spin-down Co^{2+} sites are shown for clarity. The listed exchange constants (in unit of meV) are calculated using the LSDA+U with effective $U=4$, 3, or 2 eV.

Here we compare our LSDA+U results with those calculated previously for the isostructural $Ba_2Fe_2Se_2OF_2$ and $La_2Fe_2Se_2O_3$.[2,5] All the three materials are calculated to be a Mott insulator with a band-gap opening 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, $J_1S^2_{Co}$ in $La_2Co_2Se_2O_3$ is about 1.5 times as big as $J_1S^2_{Fe}$ in $Ba_2Fe_2Se_2OF_2$ (Ref. 2) and $J'_2S^2_{Fe}$ in $La_2Fe_2Se_2O_3$ (Ref. 5) (using those J values at the $U=3$ eV for a direct comparison). Moreover, the magnetic frustration appears weaker in $La_2Co_2Se_2O_3$ due to the smaller ratio $J_2/J_1<1/3$ (the corresponding ratio >0.5 in $Ba_2Fe_2Se_2OF_2$ and $La_2Fe_2Se_2O_3$.[2,5]) Both factors account for the observations that the $T_{AF}\sim 220$ K in $La_2Co_2Se_2O_3$ (Ref. 4) is about two times as high as that of around 100 K in both $Ba_2Fe_2Se_2OF_2$ and $La_2Fe_2Se_2O_3$.[2,5] 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.*[4] for $La_2Co_2Se_2O_3$. They used a Curie-Weiss law to fit the magnetic susceptibility in the quite narrow range of $317\text{ K}<T<400$ K, and they also estimated a change in the magnetic entropy below 255 K, both of which led them to a conclusion of the unusual LS state. As this layered material has a two-dimensional spin square lattice with a considerably strong magnetic frustration as found in the above calculations, the observed $T_{AF} \sim 220$ K may well be lower than the dominating AF coupling strength which is suppressed by other frustrated magnetic interactions. This brings about a broad maximum of the susceptibility above the T_{AF} as observed and thus the above fitting using a Curie-Weiss law is less reliable: the strongest AF coupling is not yet well broken, leading to an underestimate of the effective moment. For the same reason, the decreasing magnetic entropy below 255 K represents only a partial but not a full contribution of the spin degree of freedom, leading again to an underestimate of the spin degeneracy. As the HS ground state is very stable as we find above, and it has no room for a transition to a higher spin state with increasing temperature, a magnetic-susceptibility measurement at a higher temperature, e.g., up to about 600 K, would be able to check it.

To conclude, we studied the electronic structure, spin state, and magnetism of the recently synthesized square-lattice cobalt oxyselenide $La_2Co_2Se_2O_3$, using the LSDA, LSDA-Fock-0.25, and LSDA+U calculations. While the LSDA predicts this material to be a possible ferromagnetic 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 recently 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 oxychalcogenides is made and the experiments are explained.

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