Correlation induced half-metallicity in a ferromagnetic single-layered compound: Sr_2CoO_4

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The electronic and magnetic properties of Sr_2CoO_4 compound have been studied using *ab initio* electronic-structure calculations. As opposed to a generalized gradient approximation (GGA) calculation, which gives ferromagnetic metallic solution, GGA+U calculations provide two kinds of ferromagnetic solutions: (i) half-metallic and (ii) metallic. The half-metallic solution is a ground state of the system and the metallic one is a metastable state. The strong hybridization between Co 3d and O 2p orbitals decides the electronic and magnetic properties of the compound. The total magnetic moment per formula unit is found to be $\sim 3\mu_B$ (S =3/2). Our calculations give the magnetocrystalline anisotropy energy of ~ 2.7 meV, which provides a good description of experimentally observed large magnetocrystalline anisotropy. The Heisenberg exchange parameters up to fourth nearest neighbors are also calculated. The mean-field theory gives T_C=887 K. The possible physical implications of the ferromagnetic half-metallic ground state are also discussed.

I. INTRODUCTION

The single-layered compounds with a general formula of A_2BO_4 (*A* and *B* stand for rare-earth/alkali metals and transition metals, respectively) have attracted a great deal of attention after the discovery of high-temperature superconductor in $La_{2-x}Sr_xCuO_4$.[1] These compounds show many exotic physical phenomena such as spin/charge stripes formation in nickelates and manganites[1] and spin-triplet superconductivity in ruthenates.[2]

Among the single-layered compounds recently synthesized Sr_2CoO_4 has been reported to show ferromagnetic (FM) and metallic behaviors, which have never been found in any other such materials.[3,4] The magnetization data show T_C around 250 K. The large magnetic anisotropy where magnetic easy axis is the *c* axis is also observed. Moreover, the resistivity data reveal the quasi-two-dimensional electronic nature for the system. Interestingly, there are contradicting reports on the magnetic moments. The Matsuno *et al.*[3] and Wang *et al.*[4] have reported the saturation magnetization of about 1.8 and 1.0μ_B/Co, respectively. The effective magnetic moment of 3.72μ_B has also been found by fitting Curie-Weiss behavior in the paramagnetic phase, which suggests the magnetic moment corresponds to $S \approx 3/2$ spin configuration.[4]

Lee *et al.*[5] tried to understand the above contradictory reports on the saturation magnetization by using local-density approximation (LDA) plus *U* calculations. Their studies suggest that such values of magnetization can be intrinsic to the system as they got similar two values for the total magnetic moment for different ranges of *U*. However, if we read the works of Matsuno *et al.* and Wang *et al.* carefully we can easily make out that the different values of saturation magnetization they got may not be intrinsic to the system. The $M(H)$ data of both the groups look similar. For example, the values of total magnetization at 5 T found by Wang *et al.* and Matsuno *et al.* are about 1.4 and 1.6μ_B/Co, respectively, which are not very different. The different values of saturation magnetization quoted in the last paragraph appear to arise due to two different approaches the authors used in extracting them.

The partial replacement of Sr by rare-earth elements leads to the formation of interesting magnetic phases keeping the crystal structure intact.[6–8] For example, $Sr_{1.5}La_{0.5}CoO_4$ compound retains the FM ground state of Sr_2CoO_4 whereas $SrLaCoO_4$ manifests spin-glass state.[6] Contrary to FM state for $Sr_{1.5}La_{0.5}CoO_4$, the ground state of $Sr_{1.5}Pr_{0.5}CoO_4$ compound is found to be spin glass.[7] Similarly, the formation of spin-glass state is also reported in $Sr_{1.25}Nd_{0.75}CoO_4$ compound.[8] The existence of spin-glass state in the doped compounds appears to be a generic phenomenon. It is well known that the spin-glass state arises due to the presence of competing ferromagnetic and antiferromagnetic interactions. Therefore, it would be interesting to calculate the nature of magnetic interactions between the neighboring Co atoms in the Sr_2CoO_4 compound.

Here, we report the detailed electronic and magnetic states of Sr_2CoO_4 using *ab initio* electronic-structure calculations. The ground-state solution is found to be a ferromagnetic half-metallic state having S=3/2 spin configuration, which is different from that reported by Lee *et al.* The strong hybridization between Co 3d and O 2p orbitals decides the electronic and magnetic properties of the compound. The calculation gives magnetocrystalline anisotropy energy of ~ 2.7 meV. The nature of magnetic interactions between the Co atoms is calculated up to fourth nearest neighbors, which shows mixed ferromagnetic and antiferromagnetic couplings. The estimated ferromagnetic transition temperature within mean-field theory is ~ 887 K.

II. COMPUTATIONAL DETAILS

The nonmagnetic and ferromagnetic electronic-structure calculations of Sr_2CoO_4 compound were carried out using LmtArt 6.61.[9] For calculating charge density, full-potential linearized muffin-tin orbital method working in plane-wave representation was employed. In the calculations, we have used the muffin-tin radii of 2.915, 1.965, 1.608, and 1.778 a.u. for Sr, Co, O1, and O2, respectively. The charge density and effective potential were expanded in spherical harmonics up to l=6 inside the sphere and in a Fourier series in the
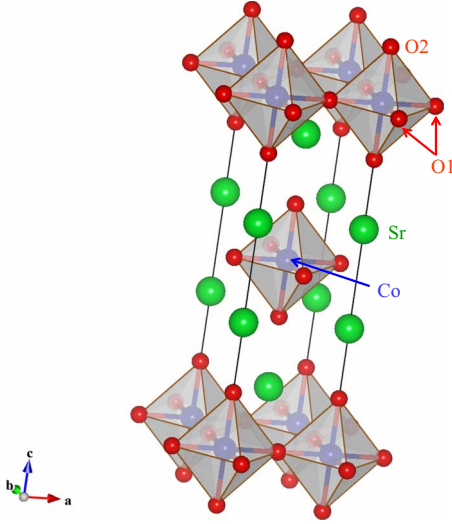
FIG. 1. (Color online) Atomic arrangements in the unit cell. Sr, Co, and O atoms are represented by spheres with decreasing radii.
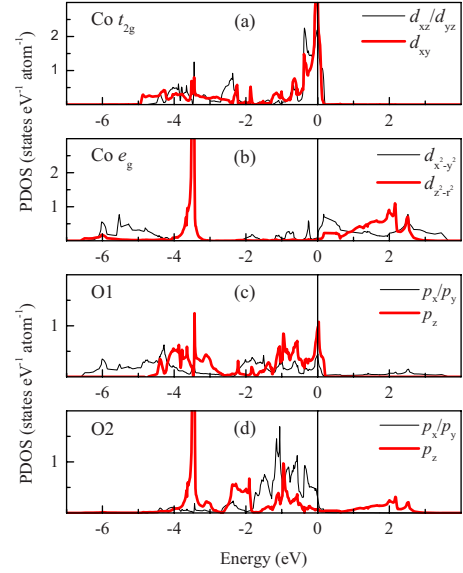

FIG. 2. (Color online) The partial density of different symmetric states obtained from nonmagnetic solution. (a) d_{xz}/d_{yz} (thin lines) and d_{xy} (thick lines) states and (b) $d_{x^2-y^2}$ (thin lines) and $d_{z^2-r^2}$ (thick lines) states. The p_x/p_y (thin lines) and p_z (thick lines) symmetric partial density of states of planar oxygen (O1) and apical oxygen (O2) are shown in (c) and (d), respectively.

interstitial region. The initial basis set included 5s, 4p, and 4d valence, and 4s semicore orbitals of Sr; 4s, 4p, and 3d valence, and 3p semicore orbitals of Co, and 2s and 2p orbitals of O. The exchange-correlation functional of the density-functional theory was taken after Vosko *et al.*[10] and generalized gradient approximation (GGA) calculations were performed following Perdew *et al.*[11]

The effect of on-site Coulomb interaction (U) under GGA+U formulation of the density-functional theory is also considered in the calculations. The detailed description of the GGA+U method implemented in the code can be found in Ref. [12]. The double-counting scheme used in the code is normally called as fully localized limit in the literature. To study the role of orbital degrees of freedom, we have also included spin-orbit coupling (SOC) in the calculations. The self-consistency was achieved by demanding the convergence of the total energy to be smaller than 10^{-5} Ry/cell. (10, 10, 10) divisions of the Brillouin zone along three directions for the tetrahedron integration were used to calculate the density of states (DOS).

III. RESULTS AND DISCUSSIONS

The atomic arrangement in the unit cell is shown in Fig. 1, which displays body-centered-tetragonal lattice. The Co atoms occupy the corners and body-centered positions and each Co atom is surrounded by six O atoms forming a distorted octahedron. In this structure there are two kinds of O represented by O1 and O2. O1 lies in the *ab* plane and O2 along the *c* axis. The bond distance between the corner and body-centered Co atoms is almost 1.8 times larger than that between nearest Co atoms sitting at the corners. This suggests the quasi-two-dimensional nature of the system where its electronic properties are expected to be decided by transport of electrons in the *ab* plane.

In order to know the crystal-field effect and nature of Co-O bonding in Sr_2CoO_4 we have plotted the partial DOS (PDOS) of Co 3d and O 2p obtained from nonmagnetic so-

lution in Fig. 2. In the octahedral symmetry Co 3d states split into t_{2g} and e_g states and the separation between these states is found to be ~1.5 eV. The degeneracies of these states are further lifted in tetragonal symmetry as evident from Figs. 2(a) and 2(b). The triply degenerate t_{2g} states split into doubly degenerate (d_{xz}, d_{yz}) states and nondegenerate d_{xy} state. Similarly, doubly degenerate e_g states split into nondegenerate $d_{x^2-y^2}$ and $d_{z^2-r^2}$ states. The O 2p orbitals also split in doubly degenerate (p_x, p_y) orbitals and nondegenerate p_z orbital as evident from Figs. 2(c) and 2(d).

The t_{2g} and e_g sectors are spread over the energy range of about 5 and 10 eV, respectively. Roughly two times larger extent of the e_g states is due to larger overlap between e_g and p orbitals in comparison to that between t_{2g} and p orbitals. In the present situation one can get maximum overlaps of $d_{x^2-y^2}$ and O1 (p_x, p_y) orbitals; and $d_{z^2-r^2}$ and O2 p_z orbitals which can lead to larger bandwidth of e_g symmetric states. The occupied $d_{z^2-r^2}$ states are mostly found in the narrow region of 1 eV whereas occupied $d_{x^2-y^2}$ states are spread over an energy window of about 4 eV. Total number of d electrons is found to be ~6.5, which is about 1.5 more than the expected nominal value for Co^{4+} ion. The above observations can be considered as a signature of the covalent nature of the Co-O bonds. There are large Co 3d PDOS at the E_F (~8.4 states/eV/atom) in the nonmagnetic solution which may be considered as a signature of ferromagnetic ground state based on the Stoner theory.

In order to know the electronic and magnetic structures of the compound we have carried out FM calculation. The energy of the FM solution is found to be ~336 meV less than that of nonmagnetic solution indicating the ferromagnetic ground state for the system. This result is in accordance with the experimental observation and earlier theoretical
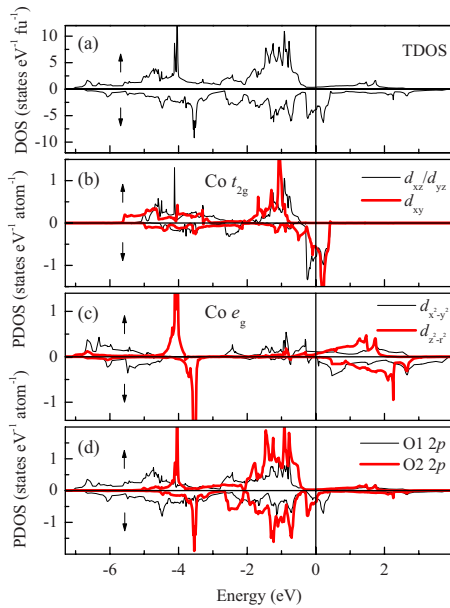
FIG. 3. (Color online) The density of states obtained from ferromagnetic GGA calculation. (a) TDOS, (b) d_{xz}/d_{yz} (thin lines) and d_{xy} (thick lines) states, and (c) $d_{x^2-y^2}$ (thin lines) and $d_{z^2-r^2}$ (thick lines) states. In (d) partial density of p symmetric states for planar oxygen (O1) and apical oxygen (O2) are represented by thin and thick lines, respectively.

calculations.[3,5] The total and partial density of states obtained for the FM configuration are plotted in Fig. 3. There is an asymmetric distribution of states in both the spin channels. The difference between number of electrons in up- and down-spin channels is a measure of net magnetization and found to be ~2. Under the rigid-band picture one can estimate the effective value of the exchange parameter (J) by considering the energy difference between the up and down band edges, which is estimated to be ~0.4 eV. The t_{2g} up-spin bands are fully occupied whereas t_{2g} down-spin and e_g bands are partially occupied.

Similar to the nonmagnetic case, e_g bands are highly extended in comparison to t_{2g} bands. The strength of exchange parameters for t_{2g} and e_g electrons are estimated to be ~0.6 and 0.4 eV, respectively. The larger value of J for t_{2g} electrons can be attributed to more localized t_{2g} states leading to higher Coulomb interaction. Interestingly, O $2p$ PDOS also show spin polarization and the estimated value of J for p electrons is also found to be ~0.4 eV. The values of magnetic moment for Co, O1, and O2 atoms are found to be about 1.52, 0.17, and 0.07μ_B, respectively. The total magnetization per formula unit is ~2μ_B, which is almost same to the earlier reports.[3,5] The appearance of magnetic moments at the O sites may be attributed to the strong hybridization between $d_{x^2-y^2}$ and O1 (p_x, p_y) orbitals; and $d_{z^2-r^2}$ and O2 p_z orbitals. The values of magnetic moment for O1 and O2 atoms also appear to support this conjecture as the magnetic moment of O1 is roughly two times larger than that of O2.

In order to know the role of orbital degrees of freedom on the magnetic properties of the system we have included SOC in the calculations by considering magnetization directions along (001) and (100) axes. Our calculations indicate that the

c axis is an easy axis as the total energy of the system for (001) direction is found to be ~2.7 meV/Co less than that for (100) direction. This result is in line with the experimentally observed magnetic easy axis.[3] This value of magneto-crystalline anisotropy energy (MAE) is ~2.1 meV/Co more than that obtained by Lee *et al.*[5] Based on the magnetization data of Ref. 3, Lee *et al.* have given a rough estimate of ~1.5 meV/Co for the MAE. This value is about three times larger than that of the Lee *et al.* and about half of our value. The inclusion of SOC keeps the spin magnetic moments almost intact and induces 0.1μ_B orbital magnetic moment at the Co site.

The above GGA calculations provide the good representation of experimentally observed electronic and magnetic properties of the system including magnetocrystalline anisotropy. However, the on-site Coulomb interaction parameter U has been found to be important in understanding the detailed electronic and magnetic properties of the 3d transition-metals' oxides.[12] Therefore, it would be interesting to see the effect of U on electronic and magnetic states of the compound under GGA+U. In this approximation U and J are used as parameters.

The values of U and J required to reproduce the electronic structure of a compound are sensitive to the approximations used in the calculations.[13,14] Moreover, it is well known that the GGA+U calculations often converge to the local minima depending on the starting electronic configurations used.[15–17] In the light of these facts we have varied U from 3 to 5 eV and fixed the value of J to 0.4 eV as estimated for the e_g electrons. To know the exact ground state we have also used different starting configurations for the Co 3d electrons. This range of U is found to provide the good representation of the experimentally observed electronic and magnetic properties of different Co-based systems.[13,18–21]

Based on symmetry consideration we used ten different starting electronic configurations for the Co atom in the calculations. For these configurations only two kind of FM solutions S1 and S2 are found to exist. The S1 and S2 give half-metallic and metallic states, respectively. The difference in the electronic structure of Co in both the solutions can be found from Fig. 4, where we have plotted the Co 3d PDOS calculated for U=4 eV. The half-metallicity with a gap of about 1 eV in the down-spin channel is evident for the S1. The S2 shows metallic state with a large t_{2g} symmetric states around the E_F in the down-spin channel. In the up-spin channel both the solutions provide similar PDOS of e_g character in the vicinity of E_F. The comparison of Co 3d PDOS obtained from the S2 and FM GGA solutions indicates that S2 is originating from the FM GGA solution. The S1 solution is quite different and it has origin to the orbital polarization.

The PDOS closer to E_F along with occupancies of the Co 3d orbitals listed in Table I can be used to characterize both the solutions. Numbers written in normal and italics are corresponding to the S1 and S2, respectively. The $t_{2g}^\uparrow$ states are fully occupied in both the solutions. The main difference between the two solutions arises from the $t_{2g}^\downarrow$ sector. In the S1 and S2, $d_{xy}^\downarrow$ state can be considered as fully occupied and unoccupied, respectively. The contribution of $d_{xz}^\downarrow/d_{yz}^\downarrow$ state below the E_F is small (~0.17 electron) and can be considered as fully unoccupied in the S1, which gives rise to the
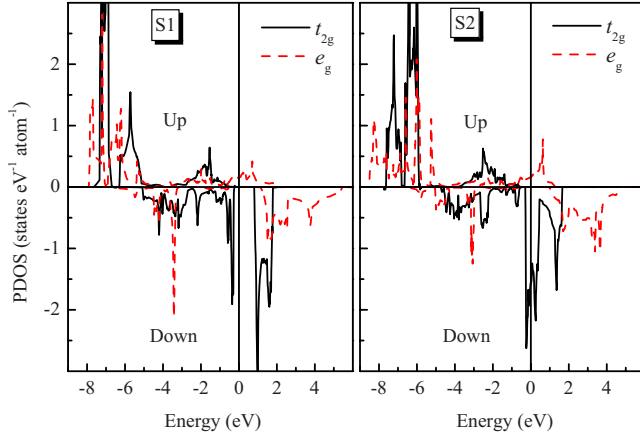
FIG. 4. (Color online) The partial density of Co $3d$ symmetric states obtained from ferromagnetic GGA+U (U=4 eV and J=0.4 eV) calculations corresponding to two conversed solutions represented by S1 and S2. t_{2g} and e_g orbitals are denoted by solid and dashed lines, respectively.

FIG. 5. (Color online) The density of states corresponds to the ferromagnetic half-metallic solution obtained from GGA+U (U=4 eV and J=0.4 eV) calculation. (a) TDOS, (b) d_{xz}/d_{yz} (thin lines) and d_{xy} (thick lines) states, and (c) $d_{x^2-y^2}$ (thin lines) and $d_{z^2-r^2}$ (thick lines) states. In (d) partial density of p symmetric states for planar oxygen (O1) and apical oxygen (O2) are represented by thin and thick lines, respectively.

half-metallic state. However, $d_{xz}^{\downarrow}/d_{yz}^{\downarrow}$ state is roughly half filled ($\sim$0.6) in the S2 and mainly responsible for the metallic state. Thus, we can represent the S1 and S2 by $d_{xy}^{\downarrow 1}$ and $d_{xz}^{\downarrow 1/2}/d_{yz}^{\downarrow 1/2}$ electronic configurations, respectively.

Both the solutions give roughly same magnetic moment ($\sim$2.7μ_B) for the Co. The S1 induces magnetic moment of $\sim$0.08μ_B at the O2 site whereas the S2 provides $\sim$0.18μ_B at the O1 site. The total magnetic moment per formula unit for both the solutions is found to be $\sim$3μ_B/f.u. representative of S=3/2 spin state. Interestingly, the energy of the S1 is $\sim$234 meV less than that of the S2 indicating that the S1 corresponds to the true ground state of the system. Present work clearly shows the importance of U in stabilizing a half-metallic state which turns out to be the lowest-energy state of the system. Thus, the ground state of Sr_2CoO_4 is found to be half-metallic with S=3/2 spin configuration.

Our half-metallic ground state is quite different from that obtained in earlier work.[5] The half-metallic solution of Lee *et al.* gives S=1/2 spin configuration. This solution corresponds to almost occupied $d_{xz}^{\downarrow}/d_{yz}^{\downarrow}$ states and half-filled $d_{xy}^{\downarrow}$ state whereas our S1 corresponds to the opposite situation where $d_{xz}^{\downarrow}/d_{yz}^{\downarrow}$ states are almost vacant and $d_{xy}^{\downarrow}$ state is filled. Here it is worth mentioning that we have also included the generalized gradient approximation in the calculations whereas Lee *et al.* have only considered the LDA. This may give an impression that the different formulations of the exchange-correlation functional can be the reason for the difference between our results and that of the Lee *et al.* To
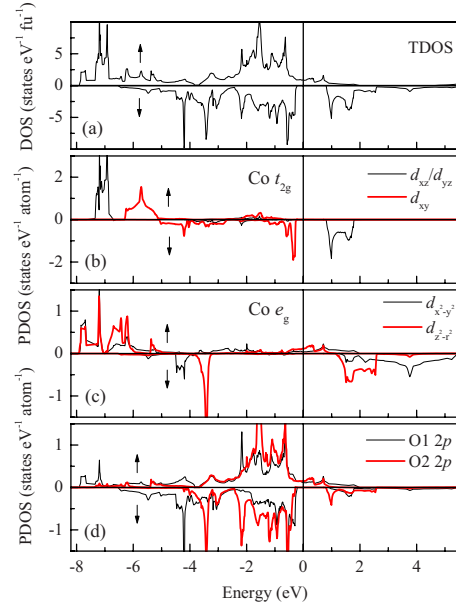
address this issue we have also carried out detailed calculations using spin-polarized LDA+U method. The results obtained from these calculations are found to be almost the same as those obtained by GGA+U. This indicates that the existence of two solutions has nothing to do with the approximations involved in treating different exchange-correlation functional and solely related to the orbital polarization.

The total and partial densities of states correspond to the half-metallic solution are shown in Fig. 5. The large spin polarization is evident from the total density of states (TDOS) plotted in Fig. 5(a). The lowest-occupied band shows the signature of Van Hove singularity arising from the e_g symmetric states as evident from Fig. 5(c). The d_{xy} orbital is fully occupied and a gap of $\sim$1 eV is created between it and the unoccupied d_{xz}/d_{yz} orbitals in the down-spin channel. In the up-spin channel only e_g sector provides the conducting electrons with a dominating contribution from the $d_{z^2-r^2}$ electrons. The $d_{x^2-y^2}$ symmetric PDOS in the vicinity of the E_F is almost flat suggesting that the temperature-dependent behavior of the compound should be decided by

TABLE I. Electronic occupancies of different Co $3d$ orbitals along with the total number of d electrons for both the spin channels obtained from ferromagnetic GGA+U (U=4 eV and J=0.4 eV) calculations corresponding to two self-consistent solutions represented by S1 (normal) and S2 (italics).

	d_{xz}/d_{yz}	d_{xy}	$d_{x^2-y^2}$	$d_{z^2-r^2}$	Total d
Up	0.95,*0.94*	0.94,*0.95*	0.84,*0.90*	0.88,*0.82*	4.56,*4.55*
Down	0.17,*0.61*	0.92,*0.14*	0.22,*0.25*	0.36,*0.25*	1.84,*1.86*
Up-down	0.78,*0.33*	0.02,*0.81*	0.62,*0.65*	0.52,*0.57*	2.72,*2.69*

TABLE II. The Heisenberg exchange parameters (J_{0i}) up to fourth nearest neighbors (coordination shells) obtained by ferromagnetic GGA calculations using FLEUR code. 0 and i stand for central atom and coordination shell index, respectively.

Nearest neighbor	Coordination number	J_{0i} (meV)
First	4	19.06
Second	4	−1.11
Third	8	1.25
Fourth	4	−0.33

$d_{z^2-r^2}$ electrons. Figure 5(b) shows a huge exchange splitting ($\sim$7.5 eV) for the degenerate d_{xz}/d_{yz} orbitals. This result also suggests that the Coulomb correlation in the presence of strong hybridization between Co 3d and O 2p orbitals along with a tetragonal distortion makes full occupation of nondegenerate d_{xy} orbital energetically more favorable. This may be considered as a signature of a ferrodistortive Jahn-Teller ordering.

In order to study the detailed nature of magnetic interactions we have calculated the Heisenberg exchange parameters J_{0i} between the Co atoms using FLEUR code,[22] where 0 and i stand for the central atom and coordination shell index, respectively. The Co atom sitting at the origin is considered as the central atom, Fig. 1. The values of J_{0i} up to fourth nearest neighbors (coordination shells) are shown in Table II. It is evident from the table that the first and third nearest-neighbor interactions are ferromagnetic whereas second and fourth nearest-neighbor interactions are antiferromagnetic in nature. The value of J_{01} is found to be 19.06 meV which is about 15 times larger than the values of neighboring interactions. This suggests that the effective magnetic interaction in Sr_2CoO_4 is ferromagnetic in nature, which is in accordance with the experimentally observed ferromagnetic ground state.[3] Under the mean-field approximation we calculated the Curie temperature (T_C) of $\sim$887 K, which is roughly 3.5 times larger than the experimentally measured value. Such discrepancy between the experimental and calculated T_C is not surprising as the overestimation of T_C under mean-field approximation is well known in the literature.[23–25]

Finally, we discuss the physical implications of our results. The half-metallic ferromagnet has potential application in the spintronics industry.[26] This compound can be considered as a good candidate as it shows T_C closer to the room temperature. The d PDOS at the E_F are quite low (0.19 states/eV/atom) as evident from the S1 of Fig. 4. This suggests that even a moderate hole doping at the Co sites can lead to insulating ground state. The present work predicts the saturation magnetization of $\sim$3μ_B/f.u. The 5K $M(H)$ data of Wang *et al.* do not show any sign of saturation at maximum measured field of 5 T where the value of magnetization is found to be about $1.4\mu_B$/Co.[4] However, their $M(T)$ data suggest to support our calculated $S=3/2$ spin state as they have reported the effective magnetic moment of $\sim$3.72μ_B. Here it is important to note that $M(H)$ data of Matsuno *et al.* show almost saturation of magnetization at 7 T where the value of magnetization is found to be about $1.8\mu_B$/Co.[3] However, this work has been carried out on the thin films, which may suffer from the effects of substrate-induced strain and/or defects present in the films. Moreover, substrate contribution to the magnetization and the weight of the material in the thin-film samples are difficult to measure accurately. All these things may lead to different magnetization value than bulk sample. Interestingly, Matsuno *et al.* have explained their saturation magnetization value by assuming Co^{4+} in intermediate spin state and that would lead to the same magnetic moment we obtained.

IV. CONCLUSIONS

The detailed electronic and magnetic properties of a single-layered compound—Sr_2CoO_4—have been studied using *ab initio* calculations with different formulations of the density-functional theory. The GGA calculation gives a ferromagnetic metallic state with total magnetic moment of $\sim$2μ_B/f.u. The GGA+U calculations provide two ferromagnetic solutions with $S=3/2$ spin configuration: (i) half-metallic and (ii) metallic. The ferromagnetic half-metallic state is the lowest-energy state and representative of the ground state. Our results also suggest that the compound may show metal to insulator transition when a small amount hole is doped at the Co sites. In the present work we have also estimated the crystal-field energy, magnetic moments, Heisenberg exchange parameters, transition temperature, etc., which provide good description of experimentally observed electronic and magnetic properties of the system.

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