Study of Correlation Effects in the High Formal Oxidation State Compound Sr$_2$CoO$_4$

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Two recent reports confirm that the newly synthesized Sr$_2$CoO$_4$ (formal oxidation state Co$^{4+}$) shows a high Curie temperature ($\sim$ 250 K), but they report different moments of 1.8 $\mu_B$ and 1 $\mu_B$ per Co. Using both commonly used functionals in the correlated band approach (LDA+U) as well as the local density approximation (LDA), the combined effects of correlation and hybridization with O 2$p$ states are calculated and analyzed. Sr$_2$CoO$_4$ is already ferromagnetic within LDA ($M=1.95$ $\mu_B$). Increasing $U$ from zero, the two LDA+U schemes affect the moment oppositely out to a critical value $U_c=2.5$ eV, at which point they transform discontinuously from different states to the same large $U$ state. Fixing $U$ at $U_c$, fixed spin moment calculations show similar behavior out to a minimum at 1$\mu_B$ (a half metallic state), beyond which the fully-localized-limit scheme jumps to a state with energy minimum very near 2$\mu_B$ (very close to the LDA moment). Although the energy minima occur very near integer values of the moment/Co ($1\mu_B$, 2$\mu_B$), the strong 3$d$ - 2$p$ mixing and resulting 3$d$ orbital occupations seem to preclude any meaningful $S=\frac{1}{2}$ or $S=1$ assignment to the Co ion.

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I. INTRODUCTION

First row (3$d$) transition metal ions in high oxidation states have been of interest for some time, due to their competing and delicate spin states. There are still several cases where behavior is not understood, indeed sometimes (due to sample questions arising from difficulty in synthesis) the data is not unambiguous. The best known, and most thoroughly studied, example is that of the quasi-two-dimensional (2D) cuprates, which when hole-doped become high temperature superconductors. In their undoped state they are Cu$^{2+}$-based antiferromagnetic insulators. Hole doping drives the Cu oxidation state toward the unstable (practically non-existent) Cu$^{3+}$ state. At a doping level of 0.15-0.20 holes/Cu optimal superconductivity is reached. They can be doped beyond that level, when they become conventional Fermi liquids. Upon hole doping the ‘oxidation state’ designation must be interpreted with care, since it is clear that the holes go onto the oxygen ions to a large degree.

Another high-oxidation-state ion is Co$^{4+}$. This ion has recently gained wide exposure due to the unusual properties of Na$_x$CoO$_2$, including the discovery[1] that this system becomes superconducting (4.5 K) around $x=0.3$ when it is hydrated. This value of $x$ shows that the Co ion is 70% of the way to being Co$^{3+}$, or alternatively, 70% of the ions are Co$^{4+}$ while 30% are Co$^{3+}$. This system is however metallic for all $x$ except for Na ion/orbital/spin/charge ordering[2] precisely at $x=0.5$ (precisely what is responsible is not yet clear). There is magnetism and correlated electron behavior for $x > 0.5$ (the Co$^{3+}$ end) while for $x < 0.5$ the materials appear to be weakly correlated nonmagnetic metals. While there has been much expectation that the (metastable) endpoint member CoO$_2$ (nominally Co$^{4+}$, $d^0$) is a Mott insulator, the evidence is that it remains a nonmagnetic metal.[3] Calculations indicate[4] that, as in the cuprates, upon hole doping from the Co$^{3+}$ end, much of the charge difference occurs on the O ion.

The La$_{2-x}$Sr$_x$CoO$_4$ system (LSCO) with two-dimensional layered K$_2$NiF$_4$ structure has become interesting because of its magnetic and electrical properties. In this system the formal oxidation state Co$^{(2+x)+}$ near the La end is not unusually high, so its behavior might be expected to be readily understandable. With increasing Sr concentration $x$, LSCO shows a structural transition from orthorhombic to tetragonal (i.e., a lattice constant $b \to a$) around $x=0.5$, with enhanced two-dimensional electronic properties.[5] The structural transition may be connected to an antiferromagnetic-ferromagnetic transition (the maximum Curie temperature $T_C=250$ K at $x=0.9$[6]) accompanying a magnetic change that has been interpreted in terms of a Co$^{3+}$ spin-state transition from high spin to intermediate spin configurations around $x=0.7$.[7] There is another suggestion that at $x=1$ the system is a high-spin, low-spin charge-ordered state.[8] However, there is no agreement amongst the measurements on the magnetic behavior[6,9,10,11] or metallic behavior[6,12]. The end member $x=0$ is an antiferromagnetic (AFM) insulator with Neel temperature $T_N=275$ K.[13]

Although earlier studies were confined to the
range below \( x = 1.4 \), recently the end member \( \text{Sr}_2\text{CoO}_4 \), formally \( \text{Co}^{4+} \), was synthesized by Matsuno \textit{et al.} \cite{14, 15} and by Wang \textit{et al.} \cite{14, 15}, and characterized as FM with high Curie temperature \( T_C \approx 250 \, \text{K} \). However, their differing synthetic methods have led to different properties. Matsuno \textit{et al.} synthesized a single-crystalline thin film using pulsed-laser deposition, while Wang \textit{et al.} produced polycrystalline samples under high pressure, high temperature conditions. The former shows metallic \( T \)-dependent resistivity below \( T_C \), although it has definitely higher resistivity of order of \( 10^{-4} - 10^{-3} \, \Omega \, \text{cm} \) at low \( T \) than in a typical metal. The pressure-synthesized samples show nearly temperature independent resistivity (perhaps due to polycrystallinity), but with similar magnitude. The more confusing difference is in the observation of correlation effects on the Co ion.

The related perovskite system \( \text{La}_{1-x}\text{Sr}_x\text{CoO}_3 \) (formally \( \text{Co}^{3+x+} \)) has been studied for some time. \cite{15, 14, 20, 21, 22, 23, 24} Its magnetic properties are also altered by Sr concentration \( x \): nonmagnetic for \( x < 0.05 \), spin glass for \( 0.05 \leq x < 0.2 \), and ferromagnetic above \( x = 0.2 \). For the end member, \( \text{SrCoO}_3 \) (\( \text{Co}^{4+} \)) shows metallic conductivity and has magnetic moments \( 1.25 \) and \( 0.1 \, \mu_B \) respectively. \cite{15} whereas the ground state of \( \text{LaCoO}_3 \) is a nonmagnetic band insulator. Its excitations have been interpreted in terms of a locally orbitally-ordered excited state. \cite{22, 25}

In this paper, we look in some detail at the electronic and magnetic structure of \( \text{Sr}_2\text{CoO}_4 \) both as uncorrelated, using the local density approximation (LDA), and viewing effects of correlation as described by the LDA+Hubbard \( U \) (LDA+U) method. Both commonly used LDA+U functionals are employed, and their results are compared and contrasted. A number of unusual rich magnetic phenomena arise (including a half metallic phase), reflecting the strong hybridization with O 2p states that complicates the accommodation of correlation effects on the Co ion.

II. STRUCTURE AND CALCULATION

\( \text{Sr}_2\text{CoO}_4 \) has the bct \( \text{K}_2\text{NiF}_4 \)-type structure, space group \( \text{F}4/\text{mmm} \) (No. 139), pictured in Fig. \textbf{1}. The Co-planner O (PO) bond length (1.878 \( \text{Å} \)) is shorter by about 6\% than that of Co-apical O (0.1578) and Sr (0.3544) internal parameters optimized by Matsuno \textit{et al.} \cite{14} which are consistent with the experimentally measured values by Wang \textit{et al.} \cite{16}.

Our calculations were carried out within the local density approximation (LDA) and LDA+U approaches with the full-potential nonorthogonal local-orbital (FPLO) method. \cite{28} Both commonly used schemes of the LDA+U method were employed so comparisons of the predictions could be made. Both forms have the same Hubbard-like density-density interaction

\[
E_U = \frac{1}{2} \sum_{m \neq m'} \left[ U_{\sigma \sigma'} m m' n_{m \sigma} n_{m' \sigma'} \right] \tag{1}
\]

where \( \{n_{m \sigma}\} \) is a site occupation set and \( J \) is intra exchange integral. The form displayed here is schematic in the sense that it does not display all of the indices involved in the full coordinate-
system-independent form that is implemented in the code. The two LDA+U approaches differ only in the method of treatment of the “double counting” term, intended to subtract out the shell-averaged interaction that has already been included in LDA. One choice is the so-called “around mean field” (AMF) scheme, which is expected to be more suitable when the on-site Coulomb repulsion $U$ is not so strong. The other choice, called the “fully localized limit” (FLL) (also called “atomic limit”), is more appropriate for large $U$ systems. The methods to treat the double counting problem in the both schemes are given by

$$E_{AMF}^{dc} = \frac{1}{2} \sum_{m \sigma \neq m' \sigma'} [U_{mm'} - \delta_{\sigma,\sigma'}J_{mm'}] \vec{n} \vec{n},$$

$$E_{FLL}^{dc} = \frac{1}{2} \sum_{m \sigma \neq m' \sigma'} [U_{mm'} - \delta_{\sigma,\sigma'}J_{mm'}] \vec{n}_\sigma \vec{n}_{\sigma'},$$

where $\vec{n}$ is the shell-averaged occupation, while $\vec{n}_\sigma$ is its spin-decomposed analog. These double-counting terms can be written in other forms that emphasize other aspects of the interaction. However, this form is illustrative because it emphasizes that the difference lies in the magnitude of the (self-consistent) atomic moment. Clearly it is only the spherically averaged values of $U$ and $J$ that enter the double-counting terms. The difference between the two forms is that the double-counting term, and the resulting potential, includes a spin dependence in the FLL form.

The fully relativistic scheme of FPLO was used when spin-orbit coupling (SOC) in LDA was necessary. The choice of basis orbitals were Sr ($4s4p$)5s5p4d, Co ($3s3p$)4s4p3d, and O 2s2p($3s3p3d$). (The orbitals in parentheses indicate semi-core or polarization orbitals.) The Brillouin zone was sampled by a regular mesh containing up to 641 irreducible $k$ points for LDA and LDA+U, and 1639 irreducible $k$ points for SOC and fixed spin moment (FSM) calculations that require more carefully treatment near the Fermi level ($E_F$).

### III. UNCORRELATED TREATMENT

#### A. Electronic structure

The FM LDA band structures, exhibiting total magnetic moment $M=1.95 \mu_B$ that is only accidentally near an integer value, are shown in Fig. The five Co 3$d$ bands and three 2$p$ bands of each O constitute an entanglement of 17 hybridized bands for each spin, with total $p-d$ bandwidths of 10 eV and 11 eV for the majority and minority bands respectively. The strong hybridization throughout the bands is evident in the corresponding total DOS and accompanying atom-projected DOS, shown in Fig. The crystal field splitting of 2 eV, identified from the density of states, between $t_{2g}$ and $e_g$ manifolds is only a little higher than the exchange splitting 1.3 eV. As noted earlier, these $t_{2g}$ and $e_g$ designations are broken down by the 4/$m$ symmetry of the Co site. The electronic structure shows clear quasi-two-dimensionality, consistent with resistivity measurement by Matsuno et al.

In Fig. the $pd\sigma$ and $pd\sigma^*$ bands (for each of $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ orbitals) are highlighted. The
more dispersive bands (darker, or red) arise from bonding and antibonding interactions between Co $d_{x^2−y^2}$ and PO $p_x$ states. The bonding and antibonding bands have a separation of 10 eV at the X point, this total width arising from a combination of the differences between the $t_{2g}$ and $2p$ site energies, and the hybridization between them. The dispersion of the antibonding (upper) band can be described roughly by effective hopping amplitude $t = 0.40$ eV (majority) and $t = 0.53$ eV (minority). The behavior of the $d_{x^2−y^2}$ band is similar to that observed in the high $T_c$ superconductor La$_2$CuO$_4$, in which this antibonding band plays a central role, but it is mostly unoccupied here. However, with the lower number of 3d electrons the cobaltate electronic structure is influenced more strongly by the $t_{2g}$ manifold, which forms relatively flat bands, the top of which hovers around the Fermi energy. In the minority bands a van Hove singularity lies at $E_F$ at the Z point, perhaps contributing to the positioning of the Fermi level and hence to the total moment.

The less dispersive highlighted bands (green, or lighter), lying in the 0 - 2 eV range, arise from the antibonding interaction of Co $d_{3z^2−r^2}$ and AO $p_z$ states. The bonding band of this pair consists of a remarkably flat band at -4 eV for each spin direction.

### B. Magnetic Tendency

The FM state is favored energetically over the nonmagnetic state by 0.37 eV/Co, similar to the value given by Matsuno et al. The spin magnetic moments are 1.95 total, 1.52 from Co and 0.22 from each PO (in units of $\mu_B$). The large magnetic moment for PO, due to strong hybridization with Co 3d bands, has been observed previously in Li$_2$CuO$_2$ and a few other cuprates. The Mullikan decomposition of O charges as well as the band filling of related bands indicates that AO is consistent with its formal designation $O^{2−}$, whereas PO contributes con-
TABLE I: Co 3d orbital (Mullikan) occupancy in LDA, where $M = 1.95 \, \mu_B$. The difference of occupancies between both spin channels is directly related with contribution of each orbital to spin magnetic moment, which can be seen to be spread over all five 3d orbitals.

|          | $t_{2g}$ | $e_g$ |          |          |
|----------|----------|-------|----------|----------|
| $E_g$    | $xz$     | $yz$  | $B_{2g}$ | $x^2 - y^2$ |
| majority | 1.00     | 1.00  | 1.00     | 0.46     |
| minority | 0.68     | 0.68  | 0.54     | 0.20     |
| difference | 0.32  | 0.32  | 0.46     | 0.20     |

FIG. 6: (Color online) LDA FM Fermi surfaces, for $M = 1.95 \, \mu_B$. Surfaces (a) and (b) are from the majority states, surfaces (c)-(f) from the minority bands. While (a) and (c) contain holes, the others enclose electrons. Each surface has mainly (a) $d_{x^2 - y^2}$ (0.5 holes), (b) $d_{3z^2 - r^2}$ (0.01 electrons), (c) $d_{xz}$ (0.2 holes), (d) $d_{xy}$ (0.4 electrons), (e) $d_{yz}$ (0.4 electrons), and (f) $d_{z^2 - y^2}$ (0.02 electrons) characters. The number in parentheses says carrier number containing each Fermi surface per Co.

FIG. 5: (Color online) Fixed spin moment calculations in LDA and both LDA+U schemes at $U_c = 2.5 \, \text{eV}$. The arrows pinpoint (meta)stable states. The dashed line for LDA FSM indicates fitting line with $E(M) - E(0) \approx \varepsilon_0 - \alpha M^2 + \beta M^4$, where $\varepsilon_0 = 5 \, \text{meV}$, $\alpha = 133 \, \text{meV}/\mu_B^2$, and $\beta = 16 \, \text{meV}/\mu_B^4$. The Stoner-enhanced susceptibility is given by

$$\chi = \chi_0/[1 - N(0)I]$$

where the bare susceptibility $\chi_0 = 2\mu_B^2 N(0)$ and $N(0)$ is the single-spin density of states at the Fermi level. Also in the low-$M$ limit one obtains formally $\alpha = (1/2)\chi^{-1}$, giving the Stoner interaction $I = 1.17(\pm 0.05) \, \text{eV}$. With this value $IN(0) \approx 1.7$, giving a very strong Stoner instability of the nonmagnetic phase that is numerically similar to that of nonmagnetic Fe.

C. Fermiology

The LDA FM Fermi surfaces (FS) pictured in Fig. 6 consist of two sheets from the majority states and four minority sheets, with very simple geometry and strong two-dimensionality. Except for one sheet that has an ellipsoidal shape (majority $d_{3z^2 - r^2}$ character), the FSs have the shape of rectangular cylinders with rounded corners. The X-centered sheets considerably to the conduction bands and cannot be considered fully ionic. According to the Co 3d orbital occupancies given in Table I, however, every 3d orbital contributes to the magnetic moment due to itineracy. The variation from average contribution occurs in two states: $d_{xy}$ has 40% larger, and $d_{3z^2 - r^2}$ orbital 40% smaller, contributions than the average contribution to the moment. The strong itinerant character (all 3d orbitals are neither fully occupied nor fully unoccupied) explains why no Jahn-Teller distortion is observed in Sr$_2$CoO$_4$.

The fixed spin moment method is applied in a following subsection to probe the magnetic behavior. In the LDA fixed spin moment calculations the low moment region is given by $E(M) - E(0) \approx -\alpha M^2 + \beta M^4$ with constants $\alpha = 133 \, \text{meV}/\mu_B^2$, $\beta = 16 \, \text{meV}/\mu_B^4$. The Stoner-enhanced susceptibility is given by

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contain holes, whereas the Γ-centered surfaces contain electrons. The FS arising from majority $d_{x^2-y^2}$ (Fig. 6a) has a clear nesting feature, as does the minority hole sheet in Fig. 6d). The spanning vectors may lead to spin-density-wave or/and charge-density-wave instabilities. Intra-surface scattering may also show some nesting features. For the most part Fermi velocities $v_F$ are in the range of a few $10^7$ cm/sec as usual in a metal, but order of magnitude lower velocities occur along the Γ$_3$ to Z line at $E_F$.

D. Magnetocrystalline anisotropy

We included spin-orbit coupling by using the fully relativistic FPLO method[30] to allow us to study the strong magnetic anisotropy reported[14] by Matsuno et al. The total energies along ⟨100⟩ and ⟨001⟩ directions were calculated to determine the magnetocrystalline anisotropy energy (MAE). The energy difference $E_{(100)} - E_{(001)} = 0.57 \text{ meV/Co}$ is consistent with experimentally observed ⟨001⟩ easy c-axis. The relativistic calculations give an orbital magnetic moment of 0.08 $\mu_B$ for Co, and negligible values for oxygen ions. The spin and orbital magnetic moments depend on the spin direction, differing by about 5%.

The experimental MAE can be estimated from field dependent magnetization along the two directions. The data show half-saturation at 7 T along the ⟨100⟩ direction. Considering the saturated magnetization to be $M_s=1.8 \mu_B$/Co, the MAE from $M_s \cdot B$ is 1.5 meV/Co, a value three times larger than our calculated result. Such underestimation in LDA is common for Co compounds. The reason is still unsettled, but candidate explanations are the poor treatment of orbital polarization[35] or for Hubbard-like correlation[30] in the standard LDA.

Rotating the spin direction induces a change of band structure, as shown Fig. 7. While the band structure for the moment along ⟨100⟩ direction is essentially that of LDA, there are additional splittings at several points for the moment oriented along the easy axis. The most visible splitting occurs in Co $t_{2g}$ manifold, where the spin-orbit splitting spans $E_F$ at the Z point. Applying SOC with spin directed along the easy axis, the bands split into primarily $d_{j=5/2,m_s=-3/2}$ character in the upper band, and $d_{j=3/2,m_s=1/2}$ in the lower band. The splittings are 60 meV and 90 meV at the Z and Γ point respectively.

IV. INCLUSION OF CORRELATION EFFECT

A. Metal to Half-metal Transition

Since the appropriate value of $U$ in this and other cobaltate systems is unclear, we have studied the ground state as $U$ is increased. The moment initially increases slightly in FLL, while it decreases slowly to $1.5 \mu_B$ at $U=2.5$ eV in AMF, as shown in Fig. 8. From their separate states just below and at the critical value $U_c=2.5$ eV, beyond this critical value the moment drops sharply to $1 \mu_B$ in both schemes, and then both schemes produce very similar results in
emphasize Co local magnetic moment decreases to vanishingly small value by \( U \sim 6-7 \) eV. The state remains a HM FM, the moment has been pushed onto the PO ions. Since the moment on Co has vanished, it is not surprising that the two LDA+U schemes give the same result.

The microscopic mechanism behind the magnetic collapse induced by the on-site Coulomb repulsion \( U \) can be unraveled from a study of the charge decompositions in Tables II and III and comparison of band structures. We can compare and contrast the two viewpoints. First we point out that, while the Mullikan charges given in these tables are somewhat basis set dependent so their specific magnitude should not be given undue significance, differences – whether between orbitals or between spin-projections – are more physical. Then, while these orbital occupations provide one characterization, we have also provided in Figs. 2 and 9 by the fatbands technique, the bands that one identifies with the Mullikan charges given in these tables are somewhat. First we point out that, while the Mullikan charges given in these tables are somewhat basis set dependent so their specific magnitude should not be given undue significance, differences – whether between orbitals or between spin-projections – are more physical. Then, while these orbital occupations provide one characterization, we have also provided in Figs. 2 and 9 by the fatbands technique, the bands that one identifies with the Mullikan charges given in these tables are somewhat.

From the tables one can determine that increasing \( U \) does not change the total 3d occupation, but introduces rearrangements in the 3d charge and moment. From the bands, the main difference (between FM LDA and HM FM LDA+U) is that the dispersive majority \( d_{x^2-z^2} \) band has become fully unoccupied, leaving the small gap that results in half metallicity. Returning to the charges and moments, what stands out is that the moment on the \( d_{x^2-z^2} \) orbital has flipped, from +0.35 \( \mu_B \) to -0.43 \( \mu_B \). The \( d_{3z^2-r^2} \) moment has undergone a smaller change in the same manner: 0.20 \( \mu_B \) to -0.09 \( \mu_B \). Thus the net moment on the Co ion, which is \( \sim 0.5 \mu_B \), is the result of \( \sim +1 \mu_B \) in the \( t_{2g} \) orbitals (primarily \( d_{xy} \)).

![FIG. 9: (Color online) LDA+U FM majority (upper) and minority (lower) band structures at \( U_c=2.5 \) eV in the half metallic state with \( M=1 \mu_B \). The majority state shows a gap of 0.25 eV. The thickened (and colored) lines emphasize Co \( d_{3z^2-r^2} \) (green or light) and \( d_{x^2-y^2} \) (red or black) characters. The dashed horizontal line denotes the Fermi energy.](image)

### TABLE II: Co 3d orbital occupancy in half metallic state, having \( M=1 \mu_B \), at \( U=2.5 \) eV. Compared with LDA result shown in Table I there are two remarkable changes in the \( e_g \) state; nearly vanishing contribution of \( d_{3z^2-r^2} \) and negative contribution of \( d_{x^2-y^2} \) (for details, see text). It seems to be close to LS state, but the \( d_{x^2-y^2} \) minority has considerable occupancy due to strong hybridization (itinerary) which makes impossible to be called strictly as LS state. The total occupation is 6.79.

| \( t_{2g} \) | \( e_g \) | \( B_{2g} \) | \( A_g \) |
|---|---|---|---|
| \( xz \) | \( yz \) | \( xy \) | \( 3z^2-r^2 \) | \( x^2-y^2 \) |
| majority | 1.00 | 1.00 | 1.01 | 0.35 | 0.25 |
| minority | 0.81 | 0.81 | 0.44 | 0.44 | 0.68 |
| difference | 0.19 | 0.19 | 0.57 | -0.09 | -0.43 |

Note particularly that this transition starts from distinct states, but occurs at the same value \( U_c \) to the same final state. Both high-moment and low-moment states can be stabilized in the calculations at \( U_c \). Unlike studies in the Na\(_3\)CoO\(_2\) system, no discernible hysteretic region could be found at this first-order transition. This magnetic collapse accompanies a metal to half metal transition, presumably because there is a particular stability of this half metallic (HM) FM state since both LDA+U schemes transition to it. The HM state, with a magnetic moment 1 \( \mu_B \), has been observed also by Wang et al. As \( U \) increases, the Co local magnetic moment decreases to vanishingly small value by \( U \sim 6-7 \) eV. The state remains a HM FM, the moment has been pushed onto the PO ions. Since the moment on Co has vanished, it is not surprising that the two LDA+U schemes give the same result.

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and $\sim -0.5\mu_B$ in the $e_g$ orbitals. This type of cancellation, in more striking form, has been seen previously in LDA+U results for LaNiO$_2$,\textsuperscript{[37]} which has an unusually low formal oxidation state for a nickelate.

B. Fixed Spin Moment Calculation at $U_c$

The results of the previous section show that two magnetic states coexist at $U_c$ in LDA+U, whether one uses the AMF or FLL functional. Such a coexistence has been already observed in LDA+U calculations for the sodium cobaltates, where the change at $U_c$ corresponds to a charge disproportionation transition.\textsuperscript{[37]} Here the change is simply in the state of the (single) Co ion; there is no experimental indication of disproportionation here. Here we analyze the FSM results at $U_c$ for LDA, AMF, and FLL.

The energy versus total magnetic moment behavior, displayed in Fig. 6, shows very interesting differences as well as similarities. Perhaps most interesting is that positions of local minima occur at (or near) integer values $M=0$, 1, and 2 (in units of $\mu_B$), as if there might be underlying states with $S_z=0$, $\frac{1}{2}$, or 1 pervading the behavior. The results of previous sections however established that there is strong $d-p$ hybridization which renders integral moments no more favored than other values. The LDA curve shows simple behavior: a Stoner instability at $M=0$ and a single minimum near (but not precisely at) $M=2$. The LDA+U results show more interesting variation.

For both AMF and FLL the paramagnetic state is metastable, with energy rising up to a moment $M\approx 0.5$, and then decreasing very similarly to the minimum at $M=1$. Beyond that point, AMF levels off to a broad flat region $M=1.3-1.8$ beyond which it increases with $M$. FLL however switches over to a separate phase, with its minimum at $M=2$. The $E(M)$ curve for FLL seems to consist of two separate parabolas (different phases) with minima very near $M=1$ and $M=2$. The $M=1$ result is integral because a half metallic phase is encountered (see Fig. 6) and not due to an $S=1/2$ configuration of the Co ion. Both majority $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ become completely unoccupied, leaving a small gap to the $t_{2g}$ bands.

We must point out that for both AMF and FLL schemes, the minimum at $M=0\mu_B$ does not correspond to a nonmagnetic state. There is a moment on Co with magnitude 0.14 $\mu_B$ that is canceled by magnetization on the PO ion. The driving force for favoring this low, canceling moment phase over a nonmagnetic state is not clear. Possibly an antiferromagnetic result, requiring a doubled unit cell, would be a lower energy $M=0$ solution.

C. Strong Interaction Regime

In Sr$_2$CoO$_4$ correlation effects should not be very strong it seems, since LDA already gives a FM state that seems consistent with one of the experimental reports. However, in a strong correlated regime, but not beyond realistic range of $U$, there is another interesting feature. Figure 10 shows the $U$-dependent orbital-projected local magnetic moment $M_m$, defined by the difference between majority and minority occupancies, of Co $d_{x^2-y^2}$ and $d_{xy}$ states. Upon increasing $U$, the $d_{xy}$ minority state loses electrons, while the $d_{x^2-y^2}$ minority state gains electrons. Beyond $U=U_c=2.5$ eV, $d_{xy}$ and $d_{x^2-y^2}$ have large positive and negative local magnetic moments respectively, leading to an on-site “singlet” type cancellation within this $|m|=2$ channel. This type of cancellation, but within the $e_g$ manifold, has been seen already in our previous results for LaNiO$_2$.\textsuperscript{[37]} In contrast with LaNiO$_2$, which shows the cancellation in the total magnetic moment and Ni$^{1+} \rightarrow$ Ni$^{2+}$ conversion, the moment of the system remains unchanged because of large magnetic moments on planar oxygen ions.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{fig10}
\caption{(Color online) Effect of strength of $U$ on the orbital-projected Co magnetic moment $M_m$, defined by difference between majority and minority occupancies, of Co $d_{x^2-y^2}$ and $d_{xy}$ states in AMF scheme. (Results for the FLL scheme are similar.) In the large $U$ limit an on-site “singlet” type cancellation of moments occurs in this $m=\pm 2$ channel (see Fig. 6 and text).}
\end{figure}
V. SUMMARY

Synthesis of the high formal oxidation state compound Sr₂CoO₄, bulk materials by high-pressure, high-temperature techniques and films by pulsed laser deposition (PLD), have led to a high Curie temperature metallic ferromagnet that introduces new transition metal oxide physics and may be useful in spin electronics devices. We have provided an in-depth study of the electronic and magnetic structure of this compound, looking specifically into the combined effects of correlation on the 3d orbitals and strong hybridization with O 2p states.

Within LDA Sr₂CoO₄ is metallic with a ferromagnetic moment near 2µₓ, close to the saturation magnetization reported for the PLD films. Application of the two commonly used LDA+U functionals reveals several surprises. As U is increased from zero, the two functionals produce changes in the moment of opposite sign up to the critical value Uₓ=2.5 eV. Beyond half metallic ferromagnetic phase with moment 1µₓ. Within this phase, increasing the value of U has the effect of pushing the moment completely off the Co and onto the planar O ions by U∼6-7 eV, while the total moment remains fixed at 1µₓ.

With U fixed at Uₓ=2.5 eV, fixed spin moment calculations were carried out for both LDA+U functionals, and compared with the corresponding LDA result. Both LDA+U schemes behaved similarly out to a minimum at 1µₓ (the half metallic state). Beyond this the two functionals departed in their behavior, with the FLL scheme jumping to a new state with minimum very near 2µₓ, not half metallic and much the same as the LDA minimum (1.95µₓ). In the stronger-interacting regime U≥3 eV (which may not be appropriate for Sr₂CoO₄), the correlation described by the LDA+U approach leads to oppositely directed moments on the dx²−y² and dₓy orbitals, reflecting the strong difference in hybridization of these two orbitals.

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