On the Electronic Structure Required for the Uniaxial Magnetic Properties of the Magnetic Metal $SrCo_6O_{11}$

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The ternary cobalt oxide $SrCo_6O_{11}$ is a magnetic metal with uniaxial (i.e., Ising-like) magnetic properties.[1,2] It is isostructural with NaV_6O_{11}[3,4] and has three different cobalt sites, Co(1), Co(2), and Co(3). The edge-sharing $Co(1)O_6$ octahedra form $Co(1)_3O_8$ Kagomé layers, whereas the face-sharing $Co(2)O_6$ octahedra form $Co(2)_2O_9$ dimers. The $Co(2)_2O_9$ dimers and $Co(3)O_5$ trigonal bipyramids share corners to form trigonal layers, which share corners with the $Co(1)_3O_8$ layers such that the two types of layers alternate along the *c*-direction (Figure 1). $SrCo_6O_{11}$ exhibits highly anisotropic magnetic properties.[1,2] The magnetization *M* as a function of the magnetic field *H* shows a stepwise increase when *H* is parallel to the *c*-direction;[1] given that M_s is the saturation moment, the *M* vs *H* curve presents a plateau at $M = M_s/3$ as *H* increases up to $H \approx 2.5$ T, and then a plateau at $M = M_s$ as *H* increases beyond ~2.5 T. When *H* is perpendicular to the *c*-direction, the magnetization is quite small and linear with *H*. By analogy with the uniaxial magnetic oxide $Ca_3Co_2O_6$,[5,6] Ishiwata et al. interpreted these results by assuming that the $Co(3)O_5$ trigonal bipyramids possess Ising-like spins, and the $M_s/3$ plateau arises from the triangular sublattices made up of $Co(3)O_5$ trigonal bipyramids. The recent ^{59}Co NMR study[2] of $SrCo_6O_{11}$ reported that the Co(1) and Co(2) sites are nonmagnetic and that the Co(3) sites are responsible for the magnetic moment of $SrCo_6O_{11}$. The saturation moment M_s of $SrCo_6O_{11}$ was initially reported to be 2.7 μ_B per formula unit (FU)[1] and later revised to 4 μ_B/FU.[2,7] In this communication, we examine the origin of the uniaxial magnetic properties of $SrCo_6O_{11}$ on the basis of first-principles density functional theory (DFT) electronic structure calculations for $SrCo_6O_{11}$ to find that the uniaxial magnetic properties of $SrCo_6O_{11}$ are explained if its total moment per FU is close to 6 μ_B instead of 4 μ_B.

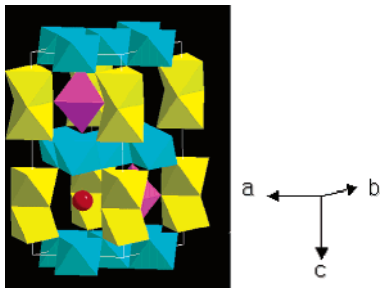

Figure 1. Polyhedral perspective view of $SrCo_6O_{11}$. The cyan, yellow, and pink polyhedra represent the $Co(1)O_6$ octahedra, $Co(2)O_6$ octahedra, and $Co(3)O_5$ trigonal bipyramids, respectively. The red sphere represents a Sr atom.

We first consider the uniaxial magnetic properties of $SrCo_6O_{11}$ from the viewpoint of the local electronic structures of the Co(1), Co(2) and Co(3) sites. The bond valence sum calculations for $SrCo_6O_{11}$[1] showed that the oxidation states of Co(1), Co(2), and Co(3) are +3.6, +3.4, and +2.8, respectively. Thus, the cobalt oxidation state is close to +3 for Co(3), which means the d-electron count d^6. Low-spin Co^{4+} (d^5) and high-spin Co^{2+} (d^7) ions at octahedral sites give rise to anisotropic magnetic properties[8,9] but cannot cause uniaxial magnetic properties.[8] To a first approximation, the octahedral sites Co(1) and Co(2) of $SrCo_6O_{11}$ are nonmagnetic sites.[2] Therefore, the Co(1) and Co(2) sites cannot be responsible for the uniaxial magnetic properties of $SrCo_6O_{11}$. Analyses of crystal field and spin−orbit coupling (SOC) effects for transition metal ions at linear two-coordinate, trigonal prism, and square pyramidal sites show[8,9] that a high-spin d^6 ion has uniaxial magnetic properties if it has a doubly degenerate d-block level and if this level is unevenly filled (i.e., filled by three electrons). The d-block levels of an isolated $Co(3)O_5$ trigonal bipyramid show the sequence $(xz/yz) < (xy/(x^2 - y^2)) < z^2$.[10] Thus, a high-spin Co^{3+} (d^6) ion at the Co(3) site has the electron configuration $(xz/yz)^3(xy/(x^2 - y^2))^2(z^2)^1$ with an unevenly filled degenerate level (see Figure S1 of the Supporting Information), for which $S = 2$ and $L = 1$ (from the viewpoint of crystal field theory). Given the SOC interaction $\lambda\hat{L}\cdot\hat{S}$ (with negative λ for a more than half-filled d-shell), therefore, the orbital and spin moments should be parallel in the ground state of the spin−orbit coupled states so that the ground-state Kramers doublet is described by $J_z = \pm 3$ and hence $\Delta J_z = 6$. An external magnetic field *H* splits this ground doublet when *H* is parallel to the 3-fold rotational axis of the $Co(3)O_5$ trigonal

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Table 1. Total Moment of $SrCo_6O_{11}$ (per FU) and Net Spin Moments of the Co Atoms (per Atom) Obtained from the GGA and GGA+U Calculations

method	total[a]	Co(1)	Co(2)	Co(3)
GGA	4.64	0.38	0.39	1.79
GGA	6.00	0.51	0.39	2.37
GGA+U	4.01	0.34	0.08	1.33

[a] There are one Co(3), two Co(2), and three Co(1) atoms per FU. The total moment per FU has contributions from the muffin-tin spheres representing the six Co and 11 O atoms as well as from the intersphere region.

bipyramid (i.e., //*c*-direction), but does not when *H* is perpendicular to the *c*-direction (i.e., ⊥*c*-direction) because $\Delta J_z > 1$.[8] Namely, a high-spin Co^{3+} (d^6) ion at the Co(3) site with unevenly filled degenerate level provides uniaxial magnetic properties. In contrast, the low-spin d^6 electron configuration $(xz/yz)^4(xy/(x^2 - y^2))^2$ of the Co(3) site with no unevenly filled degenerate level (see Figure S1 of the Supporting Information), for which $S = 1$ and $L = 0$, cannot cause uniaxial magnetic properties because $L = 0$.

To describe the uniaxial magnetic properties of $SrCo_6O_{11}$ on the basis of first-principles DFT electronic structure calculations, we carried out calculations for the ferromagnetic state of $SrCo_6O_{11}$ by employing the full-potential linearized augmented plane wave + local orbitals method[11,12] implemented in the WIEN2k code[13] with the generalized gradient approximation (GGA)[14] for the exchange-correlation functional. We also performed SOC calculations[15] as well as GGA+U[16] calculations with $U = 0.4$ Ry for all Co atoms. The muffin-tin radii (R_{MT}) of 2.47 au for Sr, 1.81 au for Co, and 1.61 au for O were used. The irreducible wedge of the Brillouin zone was sampled with a 44 k-points mesh, and the plane-wave cutoff was set at $R_{MT}K_{max} = 7$. All our calculations show that $SrCo_6O_{11}$ is a metal, e.g., see the density of states (DOS) plots obtained from the GGA calculations with total spin moment 4.64 μ_B/FU and the GGA+U calculations with total spin moment 4.01 μ_B/FU (see Figures S2 and S3 of the Supporting Information). In addition, all our calculations show that the net spin moment on Co(3) is much greater than that on Co(1) or Co(2) (Table 1). These results are in good agreement with the experiment. The small net-spin moments calculated at the Co(1) and Co(2) sites should arise from the fact that their d-block bands are partially empty and become spin-polarized by the large spin moments of the Co(3) atoms. In the following, our discussion will be focused on the origin of the uniaxial magnetic properties of $SrCo_6O_{11}$ and its consequence.

With no constraint on the total spin moment per FU, GGA calculations lead to 4.64 μ_B/FU, but the corresponding partial

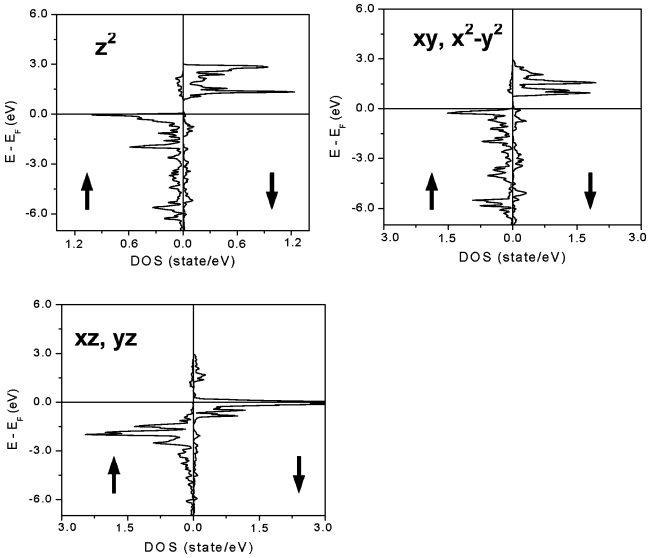

Figure 2. Partial DOS (per atom) plots of the d-orbital contributions of the Co(3) atom obtained from the GGA calculations with a total moment of 6 μ_B per FU.

DOS plots for the d-orbitals of the Co(3) site reveal that the local electronic structure of the Co(3) site is close neither to the high-spin d^6 configuration $(xz/yz)^3(xy/(x^2 - y^2))^2(z^2)^1$ nor to the low-spin d^6 configuration $(xz/yz)^4(xy/(x^2 - y^2))$.[2] It is close to the high-spin d^7 configuration $(xz/yz)^4(xy/(x^2 - y^2))^2(z^2)^1$ (see Figure S4 of the Supporting Information). As found for the low-spin d^6 configuration $(xz/yz)^4(xy/(x^2 - y^2))$,[2] the high-spin d^7 configuration $(xz/yz)^4(xy/(x^2 - y^2))^2(z^2)^1$ cannot lead to nonzero SOC interactions because $L = 0$. As a consequence, the state with total moment of 4.64 μ_B/FU obtained from GGA calculations cannot explain the uniaxial magnetic properties of $SrCo_6O_{11}$. To see if this result is due to the neglect of electron correlation in the GGA calculations, we carried out GGA+U calculations with no constraint on the total spin moment per FU. These GGA+U calculations lead to 4.01 μ_B/FU, and the corresponding partial DOS plots for the d-orbitals of the Co(3) site show that the local electronic structure of the Co(3) site is given by the low-spin d^6 configuration $(xz/yz)^4(xy/(x^2 - y^2))^2$ (see Figure S5 of the Supporting Information). In essence, the GGA and GGA+U calculations respectively predict the total moment slightly larger than and equal to 4 μ_B/FU reported for $SrCo_6O_{11}$.[2,7] However, these calculations cannot explain the observed uniaxial magnetic properties. This failure led us to speculate if the reported crystal structure of $SrCo_6O_{11}$ is accurate enough for the electronic structure description and hence prompted us to optimize the oxygen atom positions of $SrCo_6O_{11}$ (with the unit-cell parameters frozen at the experimental values) by performing GGA and GGA+U calculations. However, the resulting optimized crystal structures are very similar to the experimental one, and hence provide the same results as found from the experimental crystal structure.

Our search for the high-spin d^6 configuration $(xz/yz)^3(xy/(x^2 - y^2))^2(z^2)^1$ for the Co(3) site shows that this local electronic structure is obtained if GGA calculations are carried out with fixed total moment of 6 μ_B/FU. The corresponding partial DOS plots for the d-orbitals of the Co(3) site, presented in Figure 2, reveal that the up-spin (*xz*/

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Table 2. Total Moment of $SrCo_6O_{11}$ (per FU), Net Spin, and Orbital Moments of the Co Atoms (per atom) Obtained from the GGA+SOC and GGA+U+SOC[a]

method	spin	total	Co(1)	Co(2)	Co(3)
GGA+SOC	//c	3.98	0.37 (0.01)	0.17 (0.02)	1.70 (0.00)
	$\perp c$	3.23	0.32 (0.03)	0.07 (0.00)	1.51 (0.06)
GGA+SOC	//c	5.80	0.48 (0.03)	0.38 (0.05)	2.32 (0.14)
	$\perp c$	5.80	0.49 (0.05)	0.38 (0.03)	2.32 (0.08)
GGA+U+SOC	//c	3.75	0.33 (0.01)	0.10 (0.01)	1.54 (−0.01)
	$\perp c$	3.18	0.31 (0.09)	0.06 (0.01)	1.51 (−0.03)

[a] The orbital moments on Co(1), Co(2), and Co(3) atoms obtained from the calculations with SOC are given in parentheses. The SOC calculations with ⊥c spin orientation give rise to two slightly different Co(1) sites. The net spin and orbital moments listed are their average values.

yz), (xy/($x^2 - y^2$)) and z^2 bands are completely filled, the down-spin (xy/($x^2 - y^2$)) and z^2 bands are completely empty, and the down-spin (xz/yz) bands are partially empty, as expected for the local electronic structure close to the high-spin d^6 configuration. (The state with total moment 6 μ_B/FU is calculated to be slightly less stable than that with total moment 4.64 μ_B/FU, i.e., by 18 meV/FU.) Consequently, it appears possible to predict the uniaxial magnetic properties of $SrCo_6O_{11}$ if the total spin moment is 6 μ_B/FU, but impossible if it is 4 μ_B/FU. To verify this point, we carried out GGA+SOC and GGA+U+SOC calculations, with the spin moments oriented parallel and perpendicular to the c-direction (hereafter the //c- and $\perp c$-directions, respectively), by employing the converged densities from the corresponding GGA and GGA+U calculations, respectively. Results of our SOC calculations are summarized in Table 2. Note that SOC calculations are performed without constraint on the total moment per FU during self-consistent-field (SCF) cycles. For the total moment per FU, therefore, the SCF-converged GGA+SOC and GGA+U+SOC calculations can predict values different from those of the corresponding GGA and GGA+U calculations, respectively. Likewise, for the moments of the spin−orbit-coupled states with //c and $\perp c$ spin orientations, GGA+SOC or GGA+U+SOC calculations can predict different values. This is why the GGA+SOC and GGA+U+SOC calculations, which started with the total moments of 4.64 and 4.01 μ_B/FU, respectively, give substantially different total moments for the //c and $\perp c$ spin orientations (Table 2). In contrast, the GGA+SOC calculations started with total moment 6 μ_B/FU show that both the //c and the $\perp c$ spin−orbit-coupled states have an identical total moment not far from 6 μ_B/FU (i.e., 5.80 μ_B/FU).

Because the d-shells of the Co(1), Co(2), and Co(3) sites are more than half filled, the orbital moments of these sites calculated from SOC calculations should be positive (i.e., parallel to the spin moment), and the Co(3) site should have the largest orbital moment because, to a first approximation, only the Co(3) site has a nonzero orbital angular momentum ($L \neq 0$), as already discussed. Table 2 shows that these two requirements are met only by the GGA+SOC calculations that started with total moment 6 μ_B/FU. Furthermore, the spin−orbit-coupled state with //c spin orientation is calculated to be more stable than that with $\perp c$ spin orientation (by 63 meV/FU). The latter shows that the magnetic easy axis of $SrCo_6O_{11}$ is along the c-direction, as expected from the observed uniaxial magnetic properties.[1,2] Finally, one may speculate if the electronic state of $SrCo_6O_{11}$ with total moment close to 4 μ_B/FU can explain the uniaxial magnetic properties in the absence of SCF iterations. To check this point, we performed GGA+SOC and GGA+U+SOC calculations with only one SCF cycle using the converged densities of the corresponding GGA and GGA+U calculations. These calculations fail to describe the uniaxial magnetic properties of $SrCo_6O_{11}$ (Table S1 of the Supporting Information).

In summary, the uniaxial magnetic properties of $SrCo_6O_{11}$ require that the Co(3) site have the local electronic structure close to the high-spin d^6 configuration (xz/yz)^3(xy/($x^2 - y^2$))^2(z^2).[1] The latter is possible if the total moment of $SrCo_6O_{11}$ is close to 6 μ_B/FU, but impossible if it is close to 4 μ_B/FU as experimentally reported.[2,7] To resolve this discrepancy between theory and experiment, further studies are necessary.

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Supporting Information Available: Figures S1−S5 and Table S1 (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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