Canted ferromagnetism in RuSr$_2$GdCu$_2$O$_8$

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First principles calculations using the full-potential linearized augmented plane wave (FLAPW) method including intra-atomic noncollinear magnetism have been performed to determine the magnetic structures of RuSr$_2$GdCu$_2$O$_8$. The magnetism clearly arises from the RuO$_6$ octahedra where the moments on neighboring Ru sites order antiferromagnetically but cant perpendicular to the AFM axis - and so induce a weak ferromagnetism. The projected Ru moments along the AFM and FM axes result in magnetic moments of 1.16 and 0.99$\mu_B$ respectively. The results are consistent with the possible coexistence of canted ferromagnetism and superconductivity in the RuSr$_2$GdCu$_2$O$_8$ - inferred from experiments.

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The coexistence of magnetism and superconductivity on a microscopic scale has recently been reported in RuSr$_2$RCu$_2$O$_8$ (R=Gd, Eu and Y). These materials have an analogy to the superconductivity in the two-dimensional high $T_c$ cuprate superconductors associated with the Cu $e_g$ states of the CuO$_2$ layers. The superconductivity appears below a superconducting transition temperature, $T_c$ =30-50 K. The magnetism arises from the Ru $t_{2g}$ states of the RuO$_6$ octahedra, which do not produce any significant effects on the superconductivity since the Ru $t_{2g}$ electrons do not couple to the Cu $e_g$ states regardless of the ordering of the magnetic Ru moments.

Although the Ru moments order magnetically below a magnetic transition temperature, $T_m$=130-150 K, the type of ordering still remains controversial. An earlier report of a homogeneous ferromagnetic (FM) ordering of the Ru moments by dc magnetization and muon spin rotation experiments has been brought into a question by neutron diffraction experiments suggesting an antiferromagnetic (AFM) G-type ordering where nearest neighbors of the Ru moments along all three crystallographic axes are coupled antiferromagnetically. First-principles calculations also demonstrated that the AFM ordering is energetically favored over the FM one within the collinear magnetic structures. Nevertheless, recent magnetization and magnetic resonance experiments have provided clear evidence of a weak ferromagnetism. To account for complexity in the magnetism, noncollinear magnetism such as canting of the Ru moments has been proposed to induce a ferromagnetic component.

Here, we determine from first-principles the magnetic structures in RuSr$_2$GdCu$_2$O$_8$ by using the highly precise full-potential linearized augmented plane-wave (FLAPW) method that includes intra-atomic noncollinear magnetism which can describe the canting of the Ru moments. Indeed, we find that the moments on neighboring Ru sites order antiferromagnetically but cant perpendicular to the AFM axis - and so induce a weak ferromagnetism.

In the calculations, we employed a crystal structure with the P4/mnb space group determined by neutron diffraction experiments. This structure is similar to that of YBa$_2$Cu$_3$O$_7$, where Y, Ba and Cu (chain atoms) are replaced by Gd, Sr and Ru, respectively. Ru lies at a six-fold coordinated position in the octahedron composed of six neighboring oxygens (four O$_{Ru}$ and two O$_{apical}$) while Cu lies in a five-coordinated position (four O$_{Cu}$ and one O$_{apical}$). The RuO$_6$ octahedra are rotated by about $14^\circ$ around the c-axis, which leads to a significant modification in the electronic and magnetic structures; hence the magnetism of the Ru is sensitive to the structural distortion.

The FLAPW calculations were performed based on the local spin density approximation, L(S)DA, with the Hedin-Lundqvist exchange-correlation. Although the effects of electronic correlation in a strongly correlated system may be taken into account within a scheme such as LDA+U, RuSr$_2$GdCu$_2$O$_8$ shows metallic character even in the RuO$_2$ layers, which causes that effect to be weak and so may not alter our results. The intra-atomic noncollinear magnetism formalism was incorporated into the FLAPW method with a shape approximation for the magnetization density. In this, the density functional theory is treated with a density matrix with 2×2 components of the charge and magnetization density. Our approach allows the magnetic moment direction as well as the magnitude to vary continuously all over space, i.e., no shape approximation for the magnetization. The plane-wave was augmented with a spin-independent LAPW basis at the muffin-tin boundary. Although this approximation loses freedom compared with having a separate spin-up and spin-down LAPW basis, as is done in calculations for collinear magnetism, we confirmed that the accuracy was not degraded.

The calculations were carried out without spin-orbit coupling (SOC), since the SOC induced energies such as magneto-crystalline anisotropy energy that determines the easy direction, is expected to be much smaller than those of interest here.

The self-consistent calculations were started with an initial magnetization density depicted in Fig. 1(b), which
is a magnetic structure similar to a C-type AFM structure (Fig. 3(a)) but with the Ru moments slightly canted perpendicular to the AFM axis, i.e., to the FM axis direction in the figure. Here, the moment directions throughout the present paper are defined in a spin space since no SOC is taken into account. Although the neutron diffraction experiments revealed an AFM G-type ordering, we employed the C-type one in order to reduce the large computational effort this would entail. (The G-type ordering requires doubling the unit cell of the C-type ordering.) This is justified because the moment alignment along the c-axis is less important than that along the a-axis since the distance between the neighboring Ru atoms along the c-axis (11.56 Å) is significantly greater than that along the a-axis (3.84 Å).

The calculated spin magnetization density in the RuO$_2$ layer for the (110) and (001) planes is shown in Fig. 3 (a) and (b), respectively. The magnetism is clearly visible in the Ru, O$_{apical}$ and O$_{apical}$ ions. The moments on the neighboring Ru sites order antiferromagnetically but their moments cant along the FM axis direction, which induces a ferromagnetic component of the magnetic moments. The canting of the Ru moments appears in the $t_{2g}$ orbitals. The magnetization in O$_{apical}$ is found to correlate with that in the Ru, where the O$_{apical}$ $p_{x(y)}$ moments tilt in the same way as those in the Ru $d_{x^2-y^2}$ orbitals. The O$_{apical}$ moments are also induced but point only along the FM axis direction, which correlates with the Ru $d_{xy}$ states, as seen in Fig. 3 (b). The Ru, O$_{apical}$ and O$_{apical}$ magnetic moments inside the muffin-tin spheres are given in Table 1 where the moments are projected along the AFM and FM axes. It is striking that the projected Ru moments along the AFM and FM axes result in magnetic moments of 1.16 and 0.99 $\mu_B$, respectively, which have similar values to that observed by experiments, 1.18 $\mu_B$ when measured as the AFM structure by neutron diffraction and 1 $\mu_B$ as the FM value by magnetization. However, a direct comparison of the projected FM moment with the experimental one would be difficult, since complicated behaviors, such as a spin-flop transition, accompany the high field experiments. Neutron diffraction demonstrated that the fields exceeding 0.4 T gradually enhance the FM intensity but decrease the AFM intensity; the highest field of 7 T results in a FM moment of 1.4 $\mu_B$ with no significant AFM intensity. In such a high field, the Ru moments tend to align in a collinear FM state, leading to the enhancement of the FM moments, which roughly agrees with the calculated moments (∼1.5 $\mu_B$) in the collinear FM state. Clearly, further investigations including the field dependence are necessary to fully describe the different experimental observations.

By introducing intra-atomic noncollinear magnetism, we found that the calculated total energy is only 10 meV/cell lower than that of the collinear AFM state. Thus, the canting of the Ru moments is energetically favored in the system. However, since the total energy difference is so small compared with $T_m$, there would only be a short-range ferromagnetic ordering. This may be a reason why experiments, such as the neutron diffraction in the low-fields up to 0.4 T, could not clearly detect the ferromagnetic moments within their experimental sensitivity.

In order to discuss the Ru magnetism, we first consider the collinear AFM case and present the density of states (DOS) of the Ru $t_{2g}$ in Fig. 3(a), where the $x$ and $z$-axes are chosen as directions to the neighboring O$_{Ru}$ and O$_{apical}$ sites, respectively. The gray regions indicate the weight of the majority spin states. The magnetism of the Ru is dominated by antibonding $t_{2g}$ states. The majority spin $d_{xy}$ and $d_{x^2-y^2}$ states on the Ru site can hybridize with the minority spin states on the neighboring Ru sites through O$_{Ru}$ $p_{x(y)}$ and $p_z$ orbitals by a superexchange mechanism. The majority spin $d_{xy}$ and $d_{x^2-y^2}$ states are almost fully occupied; therefore, the charge configuration of the Ru is close to $t_{2g}^{1/2}$ ($\text{Ru}^{5+}$) with a high spin state, which prefers an antiferromagnetic alignment of their moments. (Note that itinerant electrons are partially occupied in the minority spin Ru $d_{xy}$ states, which creates an electron pocket at the $\Gamma$ point in the Fermi surface, not shown, and leads to metallic RuO$_2$ layers.)

When the intra-atomic noncollinear magnetism is introduced, however, the admixture of the spin up and down states leads to an additional hybridization between the neighboring Ru ions, and results in the wider bandwidth of the $t_{2g}$ states seen in Fig. 3(b). Although there is an admixture of the spin up and down states by introducing intra-atomic noncollinear magnetism, the spin-projected DOS along the average moment direction is plotted in the figure. The majority spin Ru $d_{x^2-y^2}$ bands become more dispersive and cross the Fermi level ($E_F$) while the minority spin Ru $d_{xy}$ bands are more occupied by itinerant electrons; this causes the system to be more metallic in character and close to a Ru$^{4+}$ state with a low spin state configuration - as expected from experiments. Hence, a double exchange interaction due to the itinerant electrons that induces a weak ferromagnetism is promoted, and the magnitude of the Ru moments is significantly reduced from that expected from Hund’s rule. Of course, the specification of the Ru valence states is, however, not exact due to the metallic character. It should be noted that this noncollinear magnetism arises from the band effects just discussed but does not have its origin in the SOC, such as via Dzyaloshinsky-Moriya interactions.

Finally, we comment the electronic structure of the CuO$_2$ bilayer. Even if the Ru moments cant, the Cu $e_g$ band structure that is responsible to the high $T_C$ superconductivity was found to be almost the same as those predicted by previous calculations of the collinear AFM state. This is because of an unique electronic structure of the layered Ru $t_{2g}$ and Cu $e_g$ states separated by O$_{apical}$ $p$ orbitals. The Ru $t_{2g}$ states couple to the O$_{apical}$ $p_{x(y)}$ orbitals which do not couple to the Cu $e_g$ states. Therefore, as previously demonstrated, the strong hybridized Cu-O $d_{p\sigma}$ orbitals, which show nest-
In summary, the first principles FLAPW calculations including intra-atomic noncollinear magnetism were performed to determine the magnetic structure of RuSr$_2$GdCu$_2$O$_8$. The magnetic moments on the neighboring Ru sites order antiferromagnetically but can be perpendicular to the AFM axis. From the canting of the Ru moments, a double exchange interaction is exerted via itinerant $t_{2g}$ electrons which can travel through the neighboring O $p$ states. The results also suggest the possible coexistence of canted ferromagnetism and superconductivity in RuSr$_2$GdCu$_2$O$_8$.

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18 To confirm the accuracy, we performed FLAPW calculations using the spin-dependent and spin-independent LAPW basis for the collinear AFM C-type structure of RuSr$_2$GdCu$_2$O$_8$ (cf., Fig. 1 (a)) and found that both results are consistent. The calculated Ru and Gd magnetic moments showed the same values 1.57(-1.53) and 6.9 $\mu_B$, respectively, in both cases.

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**Tables**

|      | $m_{\text{AFM}}$ | $m_{\text{FM}}$ | $|m|$ |
|------|-----------------|----------------|------|
| Ru   | ±1.16           | 0.99           | 1.53 |
| O$_{\text{Ru}}$ | 0.00           | 0.08           | 0.08 |

**Figures**

FIG. 1: Schematic magnetic ordering of Ru and Gd moments in (a) collinear AFM and (b) noncollinear AFM structures of RuSr$_2$GdCu$_2$O$_8$, where the Cu, O$_{\text{Ru}}$, O$_{\text{Cu}}$ and O$_{\text{apical}}$ atoms are not given. The ordering of the Ru moments in (b) is similar to a C-type AFM ordering in (a) but the moments cant slightly out of their original direction, i.e., along the FM axis direction. Note that the moment directions are defined in a spin space since SOC is not taken into account.

FIG. 2: Spin magnetization density in the RuO$_2$ layer for the (110) and (001) planes of RuSr$_2$GdCu$_2$O$_8$, where the moment direction and magnitude are represented by arrow and the size, respectively.

FIG. 3: Density of states (DOS) of Ru $t_{2g}$ states for (a) collinear AFM and (b) noncollinear AFM structures. The gray regions indicate the weight of their majority spin states.
| $O_{\text{apical}}$ | ±0.08 | 0.07 | 0.11 |
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Fig. 2  K. Nakamura et. al.
Fig. 3 K. Nakamura et al.