Magnetic and electronic structures of superconducting RuSr$_2$GdCu$_2$O$_8$

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The coexistence of ferromagnetism and superconductivity in RuSr$_2$GdCu$_2$O$_8$ was reported both from experiments (by Tallon et. al.) and first-principles calculations (by Pickett et. al.). Here we report that our first-principles full-potential linearized augmented plane wave (FLAPW) calculations, employing the precise crystal structure with structural distortions (i.e., RuO$_6$ rotations) determined by neutron diffraction, demonstrate that antiferromagnetic ordering of the Ru moments is energetically favored over the previously proposed ferromagnetic ordering. Our results are consistent with recently performed magnetic neutron diffraction experiments (Lynn et. al.). Ru $t_{2g}$ states, which are responsible for the magnetism, have only a very small interaction with Cu $e_g$ states, which results in a small exchange splitting of these states. The Fermi surface, characterized by strongly hybridized $d_{pr}$ orbitals, has nesting features similar to those in the two-dimensional high $T_c$ cuprate superconductors.

74.25.Jb, 74.25.Ha, 74.72.Jt 71.15.Mb

I. INTRODUCTION

The reported discovery of the coexistence of ferromagnetism and superconductivity by Tallon et. al. [1] has attracted a great deal of interest, since ferromagnetism breaks the degeneracy of spin-up and spin-down partners of Cooper pairs. [2] The experiments demonstrated that RuSr$_2$GdCu$_2$O$_8$ exhibits ferromagnetic ordering of Ru moments below a Curie temperature, $T_C \approx 133$ K, and becomes superconducting at a lower temperature, $T_c$ up to 40 K. From a theoretical point of view, Pickett et. al. [3] calculated the electronic structure of RuSr$_2$GdCu$_2$O$_8$ and discussed how the superconductivity, which may behave as a Fulde-Ferrell-Larkin-Ovchinniko (FFLO) type superconductor, can coexist with the ferromagnetism. However, the X-ray determined crystal structure used in their calculations was different from that recently determined by neutron diffraction [4] - and so they did not consider the structural distortions (i.e., oxygen rotations) in the RuO$_6$ octahedra.

The crystal structure of RuSr$_2$GdCu$_2$O$_8$ with a P4/mnb tetragonal space group, determined by the neutron experiment, [5] is shown in Fig. 1 (a). This is a structure similar to that of YBa$_2$Cu$_3$O$_7$, where Y, Ba and Cu (chain atom) are replaced by Gd, Sr and Ru, respectively. Ru lies at a six-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$_{apical}$). Since the interatomic distance of Cu-O$_{apical}$ (2.190 Å) is much larger than that of Ru-O$_{apical}$ (1.912 Å), the Cu has a rather weak interaction with O$_{apical}$. Thus, this may yield a two-dimensional (2D) electronic structure of the Cu-O$_{Cu}$ layer. The RuO$_6$ octahedra are rotated by about 140 around the c-axis to fill the space more efficiently, as shown in Fig. 1 (b). These rotations may lead to a significant reduction in the $d$-electron bandwidth due to a deviation of the angle $\angle$Ru-O$_{Ru}$-Ru from 180°, and so the magnetism of Ru may be strongly perturbed by the structural distortion. Hence, it is necessary to again investigate the stability of the magnetic structure in RuSr$_2$GdCu$_2$O$_8$ by first-principles calculations with the precise crystal structure parameters.

With the experimentally determined structure, [6] our highly precise first-principles full-potential linearized augmented plane wave (FLAPW) calculations [7] on three different magnetic orderings demonstrate [8] that antiferromagnetic ordering of the Ru moments is energetically favorable over the previously proposed ferromagnetic ordering. Furthermore, in agreement with our result, recent neutron diffraction experiments by Lynn et. al. [9] observed antiferromagnetic Ru ordering. In the present paper, we report the first-principles results on RuSr$_2$GdCu$_2$O$_8$, and discuss the magnetic and electronic structures and their implications for the coexistence of superconductivity.
II. MODEL AND CALCULATION METHOD

In our FLAPW calculations, we employed the experimentally determined room temperature crystal structure. For the magnetic structures, we assumed three kinds of magnetic orderings for Ru and Gd moments as depicted in Fig. 2: (a) a FM structure with ferromagnetic orderings for both Ru and Gd moments; (b) an AFM-I structure with a C-type antiferromagnetic ordering of Ru moments and a ferromagnetic ordering of Gd moments (more precisely, a ferrimagnetic structure); and (c) an AFM-II structure with C-type antiferromagnetic orderings for both Ru and Gd moments. (Note that the symmetry of both the AFM-I and AFM-II structures makes two inequivalent sublattice sites for Ru, O\textsubscript{apical} and Cu.) While the recent experiment \cite{8} revealed antiferromagnetic alignments for both Ru and Gd moments with G-type orderings, in which nearest neighbors of Ru (Gd) moments along all three crystallographic axes are coupled antiferromagnetically, we employed the C-type antiferromagnetic ordering 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 may be less important than that along the a-axis since the distance between the neighboring Ru (Gd) atoms in the c-axis (11.56 Å) is significantly greater than that in the a-axis (3.84 Å). Thus, the assumption of C-type magnetic structure would not alter the results or the insight obtained.

Calculations were performed based on the local spin density approximation (LSDA) with the Hedin-Lundquist exchange correlation \cite{9}, in which the core states are treated fully relativistically and the valence states are treated semi-relativistically. Although the effects of electronic correlation in a strongly correlated system may be taken into account within a scheme such as LDA+U, Ru\textsubscript{Sr}Gd\textsubscript{Cu}O\textsubscript{8} shows metallic character even in the RuO layer, as will be presented in Sec. IV, which causes that effect to be weak. Hence, while our results are restricted within LDA, they may be sufficient to discuss qualitative conclusions. The LAPW basis functions were used with a cut-off, $|\mathbf{k}+\mathbf{G}| < 3.6$ a. u., corresponding to about 1800 plane waves. Muffin-tin (MT) sphere radii in a. u. were chosen as: 2.4 (Ru), 2.5 (Sr), 2.5 (Gd), 2.2 (Cu) and 1.2 (O). Inside the spheres, the angular momentum expansion was truncated at $l = 8$ for wave functions, charge density and potential. Integrations were performed over a first Brillouin zone using 126 special $\mathbf{k}$-points, corresponding to 16, 16 and 32 $\mathbf{k}$-points in the irreducible Brillouin zone for the FM, AFM-I and AFM-II structures, respectively.

III. RESULTS

A. Magnetic Moments

The calculated magnetic moment of each atom inside the MT sphere for the FM, AFM-I and AFM-II structures is given in Table I. The moment of Gd is close to 7 $\mu_B$ - as expected. In the AFM-I structure, the magnitude of the Ru, O\textsubscript{apical} and Cu magnetic moments with opposite spin directions is slightly different since the ferromagnetically ordered Gd moments break the symmetry of the two sublattice sites. Among all three structures, the Ru magnetic moments are almost of the same magnitude, about 1.55 $\mu_B$. Note that since the magnitude depends on the MT sphere radius, the rather large MT sphere radius (2.4 a.u.) we used gives rather large values. However, the experimental value (1.18 $\mu_B$) of the Ru magnetic moment determined by neutron diffraction \cite{8} is smaller than our results. This may be attributed to possible canted antiferromagnetic ordering of the Ru magnetic moments, for which further investigations are necessary. The induced magnetic moments of O\textsubscript{apical} and O\textsubscript{Ru} are very sensitive to the Ru magnetic structures, while the Cu and O\textsubscript{Cu} moments are negligibly small.

B. Total energy

Total energies for all three FM, AFM-I and AFM-II structures are also given in Table I. From a comparison between the FM and AFM-I structures, we found that an antiferromagnetic ordering of Ru moments is favored over the ferromagnetic ordering. The total energy difference, 22.5 meV/Ru-atom, between both FM and AFM-I corresponds to the Neél temperature ($T_N$) of 73 K, crudely estimated by mean field theory with $S = 3/2$. Although the calculated $T_N$ is lower than the experimentally determined $T_N$, 136 K, \cite{8} our prediction for the magnetic structure is consistent with the experiment by Lynn et. al. \cite{8} Further, we found that an antiferromagnetic ordering of the Gd moments (AFM-II) reduces the total energy, but only by 2.3 meV/Gd-atom, from that of the AFM-I structure, corresponding $T_N \approx 7$ K (assumed $S = 7/2$), which is approximately in agreement with the observed low Neél temperature, 2.5 K, \cite{8} for the Gd moment alignment.
IV. DISCUSSION

A. Density of states

Figure 3 shows the total density of states (DOS) and partial DOS of each atom for the FM, AFM-I and AFM-II structures. The peaks at 2 eV above the Fermi level (E_F) and 3 eV below E_F in the total DOS for all three structures correspond to Gd 4f states which are strongly localized, and their states do not significantly affect the electronic structure around E_F. An exchange splitting in the total DOS in the AFM-I structure is due to the ferromagnetism of Gd, but the difference between majority and minority spin DOS is very small except in the region of the localized Gd 4f states. Note that the total DOS for all three structures shows metallic character.

From the partial DOS in Fig. 3, we can see that the magnetism of Ru is dominated by antibonding t_{2g} states, and the major O_{Ru} and O_{apical} peaks correlate strongly with those of Ru. In contrast, the partial DOS for Cu d and O_{Cu} p states, which are strongly hybridized, are insensitive to the magnetism of Ru. The exchange splitting of the Ru d states for all three structures is about 1 eV, while the induced exchange splitting in the Cu d states is smaller by two orders of magnitude - 0.01 to zero eV. Our results for the exchange splitting and magnetic moments of the Cu d states is smaller, even in the FM case, than those in the undistorted FM case reported by Weht et. al. [10] This may be due to the different structure parameters employed in the two calculations. The fact that the Ru-Cu distance, 4.10 Å, in our calculations is larger than in their case, 3.58 Å, results in a rather weak magnetic interaction and leads to smaller exchange splittings and magnetic moments in the Cu d states. Further, the relative atomic position of O_{apical} between the Ru and Cu may be sensitive to the magnetism. [11] However, the exchange splitting and the magnetic moments in the Cu d are quite small. The small exchange coupling is due to the unique electronic structure of the layered Ru t_{2g} and Cu e_g states separated by p orbitals of O_{apical}, as discussed by Pickett et. al., [12] and is roughly valid regardless of the magnetic ordering of Ru moments: Ru t_{2g} states couple only to the p_x and p_y orbitals of O_{apical}, but do not couple to the Cu-O d_{x^2−y^2} states.

B. Magnetism of Ru

We focus here on the magnetism of Ru. Figure 3 shows the projected DOS in real space for Ru d, O_{Ru} p and O_{apical} p states for the FM, AFM-I and AFM-II structures. The x and z-axes for the Ru (O_{Ru}) DOS are chosen as directions to the neighboring O_{Ru} (Ru) site and c-axis, respectively. Compared to the DOS of the FM structure presented by Weht et. al., [10] which did not include a structural distortion due to RuO_6 rotations, our calculated majority d_{xy} states (cf., Fig. 3 (a)) are more localized below E_F, due to deviation of the angle \angleRu−O_{Ru}-Ru from 180° and the elongation of Ru−O_{Ru} bonds by the RuO_6 rotations. This results in the d_{xy} states being almost fully occupied, and in a depletion of the majority spin hybridization channel at E_F. In the AFM-I and AFM-II structures, the majority d_{xy} and d_{xz(yz)} states on a Ru site can hybridize with the minority spin states on neighboring Ru sites through O_{Ru} p_y and O_{Ru} p_z orbitals, respectively, by the superexchange mechanism. The d_{xz(yz)} states also couple strongly to the O_{apical} p_z(y) orbitals. The charge configuration of Ru seems to be t_{2g}^3 with a high spin state, namely close to Ru^{5+}. Generally, the superexchange interaction between fully occupied t_{2g} states in nearest neighbor magnetic ions tends to be stabilized with an antiferromagnetic ordering of their moments. On the other hand, the double exchange mechanism through itinerant electrons may not be favorable, since the majority t_{2g} states are strongly localized and almost fully occupied - as seen in Fig. 3 (b) and (c). Therefore, the magnetism of Ru in RuSr_2GdCu_2O_8 is determined by the superexchange mechanism.

C. Band structure and Fermi surface

The calculated band structures for RuSr_2GdCu_2O_8 are shown along high symmetry directions in Fig. 3. The majority and minority spin states in AFM-II are degenerate due to the symmetry of the antiferromagnetic Ru and Gd moment alignments, as shown in Fig. 3. In the AFM-I structure, a small difference between majority and minority spin states was observed due to the assumed ferrimagnetic Gd moments, but its difference is negligibly small. The band structure of AFM-I is practically the same as that observed in the AFM-II structure. The bands around E_F for all three structures arise from the Ru-O_{Ru}-O_{apical} bands (solid light circles) and Cu-O_{Cu} bands (solid dark circles). In the AFM-I and AFM-II structures, there are three bands crossing E_F - as indicated in Fig. 3 (c). They arise from a Ru-O_{Ru} band with antibonding d_{xy} − p_y (dπσ) orbitals, and two Cu-O_{Cu} bands composed of antibonding d_{x^2−y^2} − p_x (dπσ) orbitals with even and odd symmetry derived by a mirror operation in the Cu-O_{Cu} bilayer. The two Cu-O_{Cu} bands are almost the same as those in the FM structure. As expected from the structural similarity between
RuSr$_2$GdCu$_2$O$_8$ and YBa$_2$Cu$_3$O$_7$, their band structures arising from Cu-O$_{Cu}$ layers are close to each other, showing a strong two-dimensionality. The energy states are slightly changed upon going from Γ to Z along the z direction. Also, the strong d$_{pσ}$ hybridization leads to a wide bandwidth of 10.1, 9.7 and 9.7 eV for FM, AFM-I and AFM-II, respectively. These values are almost the same as observed in the 2D d$_{pσ}$ bands in YBa$_2$Cu$_3$O$_7$, 9.0 eV. The slightly larger bandwidth may be due to the smaller interatomic distance (1.93 Å) of Cu-O$_{Cu}$ bonds and the smaller puckling angle (5.7°) in the CuO$_2$ plane of RuSr$_2$GdCu$_2$O$_8$, compared with those of YBa$_2$Cu$_3$O$_7$ (1.95 Å and 7.8°).

From a comparison of band structures between the FM and AFM-I structures, we found that the antibonding d$_{pσ}$ bands are not influenced significantly by the magnetism of Ru except around the M point in the zone. Around M, where they possess small components of Cu d$_{3z^2-r^2}$ character, the Cu e$_g$ states couple to the Ru e$_g$ states through the O$_{apical}$ p$_z$ orbitals, but do not couple to Ru t$_{2g}$ states. Therefore, the quite small exchange splitting in the d$_{pσ}$ states may be mediated through a more indirect coupling path with O$_{apical}$-O$_{Ru}$. Note that the Cu t$_{2g}$ states are coupled to the Ru t$_{2g}$ states through the O$_{apical}$ p$_{x,y}$ orbitals, but the Cu t$_{2g}$ states are almost fully occupied, so the hybridization channel at E$_F$ is depleted.

The calculated Fermi surfaces (FS) at k$_z$ = 0 for the AFM-II structure are shown in Fig. 4(a). For convenience, a sketch of the FS is given in Fig. 4(b), which makes for an easier comparison with the high T$_c$ results. Two closed FS centered at the zone corner arising from the Cu-O$_{Cu}$ bands and a closed FS from the Ru-O$_{Ru}$ band, are found. The inner and outer FS (1 and 2 in Fig. 4(b)) correspond to antibonding d$_{pσ}$ states with even and odd symmetry under z reflection, respectively. Note that the FS has no exchange splitting, due to the antiferromagnetic ordering of the Ru and Gd moments, implies that the superconductivity need no longer be of the FFLO type - in contrast to the FM case. A folding in k-space due to the antiferromagnetic ordering of Ru makes intersections between the bands (a, b and c in Fig. 4(b)), showing the band-band interaction. As observed in the undistorted FM, the FS clearly demonstrates similar nesting structures with those in the other high T$_c$ cuprate superconductors; these will give rise to singularities in the generalized susceptibility, and lead to possible anomalous behavior of the electronic properties. Further, the FS (3 in Fig. 4(b)), derived from Ru d$_{xy}$ states, shows a pocket of electrons centered at Γ, which may lead to the superconductivity in the Cu-O$_{Cu}$ layer with hole-doped character, as observed in experiments.

In contrast, the FS in the FM structure is complicated due to the Ru-O$_{Ru}$ bands. The majority spin Ru d$_{xz(yz)}$ bands (4 in Fig. 4(a)) become more dispersive and cross at E$_F$ compared to the AFM-I structure, which makes an additional hole pocket centered at Γ, leading to a less hole-doped character in Cu-O$_{Cu}$ layers. Hence, the FM structure may show low T$_c$ or non-superconductivity.

V. SUMMARY

We have performed first-principles FLAPW calculations to investigate magnetic structures in superconducting RuSr$_2$GdCu$_2$O$_8$. Contrary to the previously ferromagnetic RuSr$_2$GdCu$_2$O$_8$ structure proposed from susceptibility experiments and first-principles calculations, we found that antiferromagnetic ordering of the Ru moments is energetically favored over ferromagnetic ordering. Our results are consistent with those of a recent neutron diffraction experiment, in which the antiferromagnetic ordering of Ru moments was predominantly observed. The magnetism arises from Ru t$_{2g}$ states through the superexchange mechanism. The Ru t$_{2g}$ states have a very small interaction with the Cu e$_g$ states - which results in quite a small exchange splitting in the antibonding d$_{pσ}$ states. The Fermi surfaces derived from the antibonding d$_{pσ}$ states have similar nesting structures with those in the 2D high T$_c$ cuprate superconductors, which may give a basis for superconductivity in this material. Further experimental and theoretical investigations are necessary to confirm this conclusion. In any case, the coexistence of antiferromagnetism and superconductivity in RuSr$_2$GdCu$_2$O$_8$ is clearly allowed.

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TABLE I. Total energy difference, $\Delta E$ (in meV/cell), and calculated magnetic moments, $m$ (in $\mu_B$), in the MT sphere of each atom for the FM, AFM-I and AFM-II structures of RuSr$_2$GdCu$_2$O$_8$. The symmetry of the AFM-I and AFM-II structures makes two inequivalent sublattice sites for Ru, O$_{apical}$ and Cu.

|        | FM  | AFM-I | AFM-II |
|--------|-----|-------|--------|
| $\Delta E$ | 50.5 | 5.5   | 0.0    |
| Ru     | 1.59 | 1.57 (-1.53) | 1.55 (-1.55) |
| $O_{Ru}$ | 0.11 | 0.00 | 0.00 |
| O$_{apical}$ | 0.13 | 0.11 (-0.10) | 0.11 (-0.11) |
| Cu     | 0.004 | 0.007 (0.015) | 0.004 (-0.004) |
| O$_{Cu}$ | 0.004 | 0.006 | 0.000 |

FIG. 1. (a) Crystal structure of RuSr$_2$GdCu$_2$O$_8$ with P4/mmbm space group; (b) Top view of Ru-O$_{Ru}$ layer.

FIG. 2. Magnetic ordering of Ru and Gd magnetic moments for (a) FM, (b) AFM-I and (c) AFM-II structures of RuSr$_2$GdCu$_2$O$_8$, where the Cu, O$_{Ru}$, O$_{Cu}$ and O$_{apical}$ atoms are not given.

FIG. 3. Total density of states (DOS) and partial DOS of Ru $d$, O$_{Ru}$ $p$, O$_{apical}$ $p$, Cu $d$ and O$_{Cu}$ $p$ orbitals for the FM, AFM-I and AFM-II structures of RuSr$_2$GdCu$_2$O$_8$. Solid and dashed lines represent majority and minority spin states, respectively. A vertical dotted line denotes the Fermi level.

FIG. 4. Projected density of states (DOS) in real space for Ru $d$, O$_{Ru}$ $p$ and O$_{apical}$ $p$ orbitals for the FM, AFM-I and AFM-II structures of RuSr$_2$GdCu$_2$O$_8$. The $x$-axis for the Ru $d$ (O$_{Ru}$ $p$) DOS are chosen as directions to neighboring O$_{Ru}$ (Ru) sites.

FIG. 5. Calculated band structure along high symmetry directions for the FM, AFM-I and AFM-II structures of RuSr$_2$GdCu$_2$O$_8$. The bands originating mainly in the Cu-O$_{Cu}$ layers are represented with solid dark circles.

FIG. 6. (a) Calculated Fermi surfaces (FS) of RuSr$_2$GdCu$_2$O$_8$ for the AFM-II structure at $k_z = 0$ and (b) its schematic illustration, which makes for an easier comparison with the high $T_c$ results.
Fig. 1 K. Nakamura, et. al.
Fig. 2  K. Nakamuiira, et. al.
Fig. 3  K. Nakamura et. al.
Fig. 4 K. Nakamura, et. al.
Fig. 5  K. Nakamura, et. al.
Fig. 6 K. Nakamura, et. al.