Journal of Superconductivity: Incorporating Novel Magnetism, Vol. 13, No. 5, 2000

Superconductivity and Magnetism in $RuSr_2GdCu_2O_8$

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The ruthenocuprate $RuSr_2GdCu_2O_8$ orders magnetically at 135 K and then becomes superconducting at 45 K. These transitions have been observed by several groups, but the intrinsically complex nature of the compound, as well as the unexpected coexistence of magnetism with high-temperature superconductivity, makes it uncertain what the magnetic, electronic, and structural character of its ground state is. We find that density functional-based evaluations give a magnetic and structural character that is consistent with the latest data: the RuO_6 octahedra rotate (by 7° around the $\hat{c}$ axis) causing a $\sqrt{2} \times \sqrt{2}$ doubling of the cell, and an antiferromagnetic structure that has this same cell doubling is favored over a ferromagnetic alignment of Ru spins. The minority Ru d_{xy} states are partially occupied, leaving a metallic RuO_2 layer that dopes the CuO_2 bilayer and may lead to canting of the Ru spins.

KEY WORDS: Magnetism; $RuSr_2GdCu_2O_8$; superconductivity; coexistence; ruthenocuprate; generalized gradient approximation.

1. INTRODUCTION

The competition between ferromagnetism (FM) and *singlet* superconductivity (SC) was addressed originally by Ginzburg [1], who showed that a FM SC would produce an *inverse* Meissner tendency: it would set up surface currents to shield the *external region* from the frozen-in magnetic field $B_{int} = 4\pi M$. The result is that coexistence was not possible except in samples not much larger that the field penetration depth. These arguments do not apply directly to type II superconductors, and Krey showed how to circumvent this restriction [2] by the formation of spiral magnetic order or by the formation of a spontaneous vortex phase where the order parameters are inhomogeneous.

Tallon *et al.* [3,4] have injected new excitement into this question of coexistence of SC and FM by reporting the superconducting ferromagnet $RuSr_2GdCu_2O_8$. This system was first reported by Bauernfiend *et al.* [5] as superconducting but not magnetic, and other reports [6, 7] indicate that its properties are dependent on the method of preparation. This material is first magnetic ($T_M \sim 135$ K, due to ordering of Ru ions) and then becomes SC only well within the FM phase ($T_S \approx 45$ K). These data seem to be reproducible, specific heat data indicate a bulk SC transition, and muon spin rotation experiments indicate that the magnetism is homogeneous and is unaffected by the onset of superconductivity [3,4]. This SC FM is quite different from previous materials [8] where SC and FM order have similar critical temperatures, compete strongly and adjust to accommodate each other, and coexist only in very limited regions where magnetic order is small [9].

We have addressed elsewhere some questions raised by this system [10]. In a layered type II superconductor—in this case, the CuO_2 bilayer—the most urgent question is the extent of the exchange splitting in the CuO_2 bilayer induced by the magnetic RuO_2 layer. The magnetization measured in applied fields of 1 T is at least 1 μ_B per formula unit (i.e., per Ru ion), and indeed our calculations (described below) assuming FM ordering lead to a moment of roughly this size. In spite of the exchange splitting of ~1 eV on the Ru ion, the Cu ion that is less than 5 Å distant feels an exchange splitting of the order of 20 meV, a factor of 50 less. This ineffective electronic coupling is due to the facts that (1) the moment lies in the t_{2g}

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0896-1107/00/1000-0687$18.00/0

orbitals of the Ru ion, and (2) these states do not couple directly through the apical O 2*p* orbitals of the active $d_{x^2-y^2}$ orbital of the Cu ion. The coupling must involve other O ions and/or the Cu *s* orbital, and these intermediate states lead to nonzero, but quite small, exchange coupling. Thus coexistence of FM with SC in this type of compound can be understood on this ground. As we discuss in the next section, antiferromagnetism (AFM) is now an issue in this compound.

2. CRYSTAL STRUCTURE AND COMPUTATIONAL METHODS

This hybrid ruthenocuprate Ru1212, isostructural with insulating triple perovskite $NbSr_2GdCu_2O_8$, [11] (which is formally Cu^{2+} and Nb^{5+}), is comprised of double CuO_2 layers separated by a Gd layer, sandwiched in turn by SrO layers, as shown in Fig. 1. The unit cell is completed by a RuO_2 layer, making it structurally similar to $YBa_2Cu_3O_7$ except that the CuO chain layer is replaced by a RuO_2 square planar layer, with resulting tetragonal symmetry. The structure of $RuSr_2GdCu_2O_8$ determined by synchrotron X-ray diffraction on polycrystal samples was reported by McLaughlin *et al.* [12], and their refinement was based on the symmetric P4/mmm structure of $NbSr_2GdCu_2O_8$. Displacements of O ions from their ideal lattice sites was treated in a split atom model.

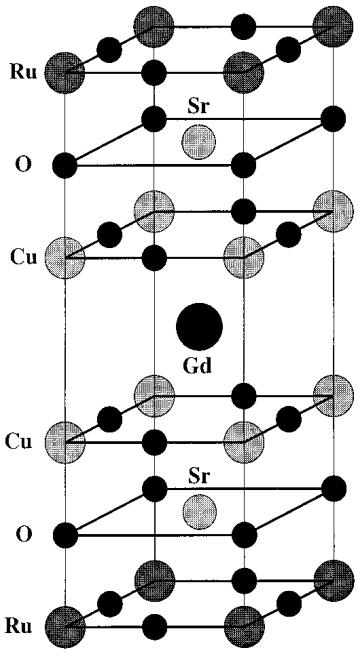

Fig. 1. The crystal structure of $RuSr_2GdCu_2O_8$, with small distortions of the RuO_6 octahedron and the CuO_5 pyramids neglected. Magnetism occurs in the RuO_2 layer; superconductivity, in the Cu–O bilayer.

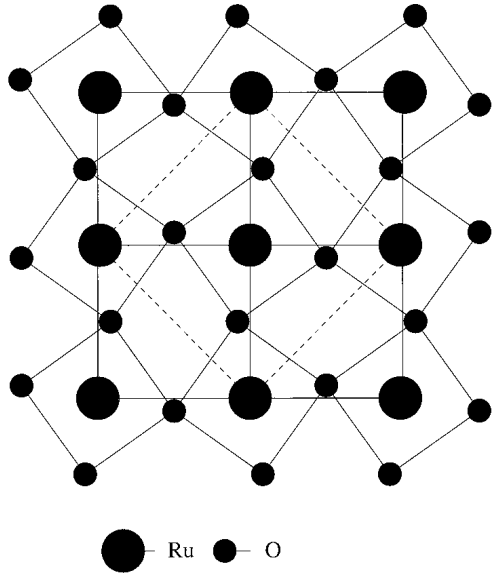

Fig. 2. Schematic diagram of the rotation in the RuO_2 plane that causes a $\sqrt{2} \times \sqrt{2}$ doubling of the unit cell, which is shown by the dashed lines. The rotation of the RuO_2 square is approximately 7°.

Chmaissem *et al.* [13] reported a neutron powder diffraction study in which the sample was presumed to be composed of twinned polycrystals with the P4/mbm space group. In the P4/mbm structure, the cell is a $\sqrt{2} \times \sqrt{2}$ doubled cell due to the rotation of RuO_6 octahedra around the $\hat{c}$ axis as illustrated schematically in Fig. 2. Lynn *et al.* [14] have, in addition, observed a superlattice peak at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ that appears at the magnetic transition temperature and whose strength follows the temperature dependence expected of magnetization. This superstructure is naturally anticipated to reflect antiferromagnetic order, and their observations are consistent with AFM ordering of Ru moments at 135 K. This ordering does not increase the unit cell within the layers but doubles the cell along the $\hat{c}$ axis. This $\hat{c}$ axis doubling should have little effect on the electronic structure and magnetic moments, so we consider the two structures, P4/mmm and P4/mbm.

Our calculations were carried out using the linearized augmented plane wave method [16,17] and the structure reported by Chmaissem *et al.* for the distorted P4/mbm crystal. The Gd ion is magnetic (it

orders antiferromagnetically at 2.6 K). In our calculations we have used aligned Gd spins. The magnetic moment of the $4f^7$ Gd ion is decoupled from the electronic and magnetic behavior of the itinerant states.

Differences in our results are found (see below) depending on whether we use for the exchange-correlation energy functional the simple local density approximation (LDA) or the generalized gradient approximation (GGA) [15] that uses the local gradient of the density as well as the local density. Since the GGA incorporates additional information not included in LDA, and does so in a controlled way, we are more confident in the GGA results.

3. DISCUSSION

The calculated energies follow. The LDA energy gain due to distortion is 0.24 eV/f.u. for FM spin alignment and 0.18 eV/f.u. for AFM alignment. Thus the distortion is favored regardless of the type of spin order and probably is not directly related to magnetism. The magnetic energy difference, FM relative to AFM, is +90 meV/f.u. (LDA) for the P4/mmm structure and 32 ± 1 meV/f.u. (both LDA and GGA) for the distorted P4/mbm structure. Thus AFM spin alignment is favored over FM in both structures, regardless of whether LDA or GGA is used. The convergence of these energy differences has been considered by looking at 7 k-point and 18 k-point meshes in the irreducible Brillouin zone of the doubled cell, using the tetrahedron method for integration. While the numbers are probably not converged to the number of significant figures given (1 meV/f.u.), we are confident of the sign and magnitude of these energy differences.

The Ru magnetization lies within the t_{2g} orbitals, and the value of the moment differs for our GGA and LDA calculations. For GGA (respectively, LDA), we obtain the following for the spin moments within our atomic spheres: Ru, FM 1.57 (1.27) and AFM 1.53 (1.40); apical O, FM 0.18 (0.19) and AFM 0.16 (0.16); and O in Ru layer, FM 0.16 (0.11) and AFM 0.00 (0.00) by symmetry. The moments on the Cu and the O within the Cu bilayer are smaller and more delicate to obtain accurately, and will be reported later.

We regard then the distorted AFM crystal/magnetic structure as the basis for further analysis of the properties of $RuSr_2GdCu_2O_8$. The RuO_2 layer is predicted to be metallic, which is related to a variety of important questions: What is the valence of Ru, and thus Cu, presuming that if Ru were Ru^{5+} (as in the Nb counterpart), the compound would be insulating? What is the character of the carriers in the Ru layer? What is the induced magnetic moment in the CuO_2 (bi)layer? and How does it affect (compete with?) superconductivity? To the latter question there is one general comment: unlike the coexistence of FM and SC, where the inequivalence of ↑ and ↓ spin bands directly inhibits spin pairing, AFM pairing leaves the two spin directions degenerate and thus competes with SC in less direct ways. The classic competition in an itinerant AFM is that the onset of AFM order destroys some but usually not all of the Fermi surface. We will report elsewhere on this effect, which will be very important for the understanding of the value of the observed SC transition temperature (45 K).

As might have been anticipated, AFM ordering reduces the Ru d bandwidths because hopping to nearest Ru neighbors is hampered by the ~1-eV exchange splitting. For the d_{xz}, d_{yz} bands that are 0.7 eV (majority) and 1.0 eV (minority) wide for FM alignment, the bandwidth drops to 0.3–0.4 eV. These states are fully polarized. For the Ru d_{xy} band, the majority states also are occupied. However, the dispersion of the minority band results in occupation of a pocket of ~0.2 minority d_{xy} electrons, in a Fermi surface center at the Γ point. Hence the charge carriers in $RuSr_2GdCu_2O_8$ reside in Cu $d_{x^2-y^2}$ states in the Cu–O bilayer and in Ru d_{xy} states in the Ru–O layer. These orbitals are both "perpendicular" to the $\hat{c}$ axis, and dispersion along k_z is quite small.

4. SUMMARY

Our earlier considerations showed how coexistence of SC with a net FM moment is possible: (i) the average magnetization—whatever its origin, and we now expect that it results from canted antiferromagnetism—is not large (1/30 that of iron, for 1 μ_B/Ru); (ii) the SC and FM subsystems are disjoint, in this case precisely and thinly layered; (iii) both the SC and the FM layers presumably are thin enough to allow coupling perpendicular to the layers, hence three-dimensional ordering; and (iv) the chemical bonding is such that coupling between the FM and the SC layers is weak enough not to suppress superconductivity entirely. Our latest results support the assignment of AFM order in the RuO_2 layer. The layer remains metallic, however, and dopes the Cu–O bilayer, accounting for the observation of superconductivity.

ACKNOWLEDGMENTS

We gratefully acknowledge extended communication with J. Tallon and recent discussions with C. Bernhard and J. W. Lynn. This work was supported by Office of Naval Research Grant N00014-97-1-0956 and National Science Foundation Grant DMR-9802076.

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