

## Superconductivity in Ferromagnetic RuSr<sub>2</sub>GdCu<sub>2</sub>O<sub>8</sub>

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Relying on the inhomogeneous (layered) crystal, electronic, and magnetic structure, we show how superconductivity can coexist with the ferromagnetic phase of RuSr<sub>2</sub>GdCu<sub>2</sub>O<sub>8</sub> as observed by Tallon and co-workers. Since the Cu  $d_{x^2-y^2}$  orbitals couple only to apical O  $p_x, p_y$  orbitals (and only weakly), which also couple only weakly to the magnetic Ru  $t_{2g}$  orbitals, there is sufficiently weak exchange splitting, especially of the symmetric CuO<sub>2</sub> bilayer Fermi surface, to allow singlet pairing. The exchange splitting is calculated to be large enough that the superconducting order parameter may be of the Fulde-Ferrell-Larkin-Ovchinnikov type.

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The antagonism between ferromagnetism (FM) and *singlet* superconductivity (SC) was discussed early on by Ginsburg [1]. His simple conclusion, based upon an inverse Meissner effect that would set up surface currents to shield the external region from the frozen-in magnetic field  $B_{\text{int}} = 4\pi M$ , was that coexistence was not viable except in samples not much larger than the field penetration depth. Krey showed how to circumvent this restriction [2] by the formation of spiral magnetic order or, in type-II superconductors, by the formation of a spontaneous vortex phase (SVP). In the SVP the internal magnetic induction is screened locally, vortex-by-vortex, so the problem considered by Ginsburg does not apply. Further work on SVPs has included the suggested realization in ErRh<sub>4</sub>B<sub>4</sub> [3], in Eu<sub>x</sub>Sn<sub>1-x</sub>Mo<sub>6</sub>S<sub>8</sub> [4], in ErNi<sub>2</sub>B<sub>2</sub>C [5], and possibly in  $p$ -wave systems [6].

A serious impediment to SC arising well within the FM phase is the Zeeman splitting of the carrier bands, which makes the majority and minority Fermi surfaces inequivalent, so the states  $|\vec{k} \uparrow\rangle$  and  $|\vec{k} \downarrow\rangle$  do not both lie on the Fermi surface, and total momentum  $\vec{q} \equiv \vec{k} + \vec{k}' = 0$  pairs are not available for pairing. Getting around this difficulty with  $q \neq 0$  pairs in the case of applied fields or dilute magnetic impurities has led to Fulde-Ferrell-Larkin-Ovchinnikov (FFLO) type theories [7], where either the SC or FM order parameter (or both) develops spatial variation to accommodate the other.

Tallon *et al.* [8,9] have injected new excitement into this question of coexistence of SC and FM by reporting the superconducting ferromagnet RuSr<sub>2</sub>GdCu<sub>2</sub>O<sub>8- $\delta$</sub>  (Ru1212). This system was first reported by Bauernfeind *et al.* [10] as superconducting but not magnetic, and other reports [11,12] indicate that properties are dependent on the method of preparation. Unlike almost all previously reported cases of coexisting SC and FM, this material is first magnetic ( $T_M = 132$  K, due to the ordering of Ru ions with an ordered moment of  $1 \mu_B/\text{Ru}$ ) and then becomes SC only well within the FM phase. Superconductivity appears at  $T_S \approx 35\text{--}40$  K, and only at 2.6 K do the

Gd ions order (antiferromagnetically). The data are reproducible, specific heat data indicate a bulk SC transition, and muon spin rotation experiments indicate the magnetism is homogeneous and is unaffected by the onset of superconductivity [8,9]. This SC ferromagnet is quite different from previous materials [13] 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 [14,15].

The observed phenomena present several interrelated questions. The most obvious is, how can SC exist within a FM material? Secondly, how is the FM coupling transmitted between layers without killing superconductivity;  $T_M = 132$  K indicates electronic exchange coupling and not the much weaker dipolar coupling. Finally, how is the SC coupling propagated through the FM layers? These are the questions that we address.

This hybrid ruthenocuprate Ru1212, isostructural with insulating triple perovskite NbSr<sub>2</sub>GdCu<sub>2</sub>O<sub>8</sub> [16], is comprised of double CuO<sub>2</sub> 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<sub>2</sub> layer, making it structurally similar to YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> except that the CuO chain layer is replaced by a RuO<sub>2</sub> square planar layer, with resulting tetragonal symmetry (except for distortions typical of perovskites).

Magnetism is detrimental to superconductivity both through its coupling to spin and to orbital motion, which we consider in turn. Since there is a strong tendency for singlet pairing in materials with CuO<sub>2</sub> layers such as Ru1212 has, and substitution of Zn for Cu leads to a decrease in  $T_S$  similar to that seen in cuprate SCs, we examine specifically the possibility of SC CuO<sub>2</sub> layers [17]. There are three potential limiting mechanisms: (1) Zeeman splitting of pairs due to the dipolar field  $B_{\text{int}}$ , (2) the electronically mediated exchange field  $\Delta_{\text{ex}}$  that also splits majority and minority Fermi surfaces, and (3) charge coupling to the vector potential leading to supercurrents. It is primarily the second item that presents

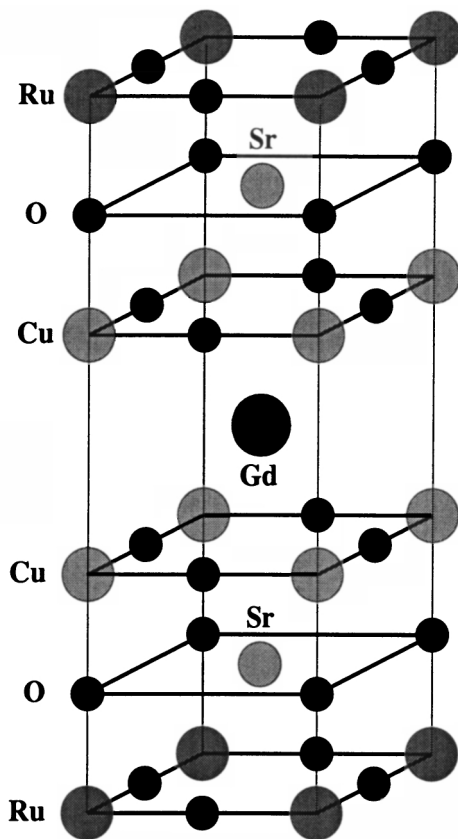


FIG. 1. The crystal structure of  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ , with small distortions of the  $\text{RuO}_6$  octahedron and the  $\text{CuO}_5$  pyramids neglected.

difficulty for singlet SC in this system. We conclude that SC will most likely be accommodated by development of a FFLO-like modulation of the SC order parameter within the  $\text{CuO}_2$  layers, possibly accompanied by “ $\pi$  phase” formation [18].

*Spin-derived pair breaking.*—It is easy to dispense with dipolar spin coupling [(1) above] due to the internal field. The Ru magnetization corresponds to a macroscopic (volume average) field induction  $B_{\text{int}} = 4\pi\langle M \rangle = 700$  G, for which the Zeeman splitting ( $5 \mu\text{eV}$ ) is negligible compared to the pair binding energy  $2\Delta \sim 5k_B T_S \sim 15\text{--}20$  meV as well as to the exchange splitting (discussed below). As mentioned in (2) above, the magnetization  $M$  of the  $\text{RuO}_2$  layer also gives rise to an induced exchange field  $B_{\text{ex}} \equiv 2\mu_B \Delta_{\text{ex}}$  in the  $\text{CuO}_2$  layer that splits each  $\text{CuO}_2$ -derived Fermi surface (FS), with the larger (smaller) FS corresponding to the majority (minority) carriers. Unlike a real field,  $B_{\text{ex}}$  couples only to the spin.

It is necessary first to obtain the magnitude and  $\vec{k}$  dependence of this exchange splitting of the carriers in the  $\text{CuO}_2$  layers. To this end we have applied density functional methods [19]. Our calculations, using both the local density approximation (LDA) and generalized gradient approximation (GGA) [20], resulted in a FM

$\text{Ru-O}$  layer as well as strongly spin polarized Gd (moment of  $7 \mu_B$  [21] as expected). The value of the moment in the Ru layer is sensitive to both the choice of exchange-correlation functional (LDA or GGA) and also to structural distortions, which will be discussed more fully elsewhere. Possible effects of correlation on the Ru moment were checked by applying the LDA + U procedure [22] with a Coulomb repulsion  $U_{\text{Ru}} = 3$  eV. The moment was very similar to the GGA value and in all cases the  $\text{RuO}_2$  layer remained metallic. The calculated moment (using GGA) of  $2.5 \mu_B$  ( $\sim 1 \mu_B$  lies on the six neighboring O ions) for the undistorted structure is larger than the moment of  $1 \mu_B$  reported by Tallon *et al.* The sensitivity of the calculated moment to oxygen positions suggests that using the true (distorted) crystal structure would reduce the discrepancy. We regard our calculated exchange splitting in the  $\text{CuO}_2$  bilayer as an upper bound on the true value, which is sufficient for present purposes.

As expected from previous theory and experiment [23], the  $\text{CuO}_2$  bilayer gives rise to two barrel Fermi surfaces of each spin centered at the zone corner, with the inner (outer) FS corresponding to states (at  $k_z = 0$ ) that are symmetric (antisymmetric) under the mirror operation connecting the two  $\text{CuO}_2$  layers. The symmetric FS, shown in Fig. 2, is regular in shape, has a nearly  $\vec{k}$  independent exchange splitting, and has quasi-one-dimensional nesting features. By direct close inspection of the band structures, we obtain the difference in Fermi wave vectors on this FS (not shown)  $\delta k_F \sim 0.02k_F$ . The antisymmetric FS is less regularly shaped and, due to  $\vec{k}$  dependent hybridization with Ru, has  $\vec{k}$  dependent exchange splitting that makes it less favorable for pairing. Thus we concentrate on the symmetric FS.

### Symmetric Barrel Fermi Surfaces

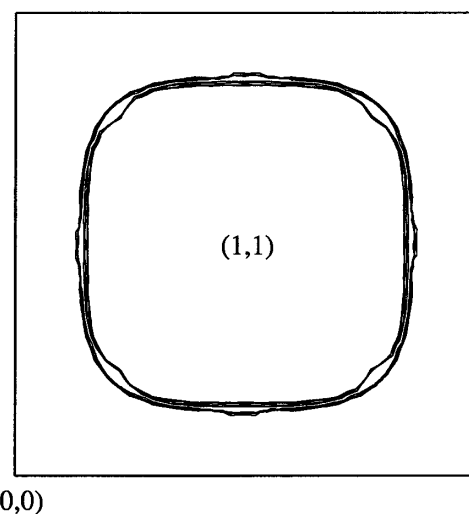


FIG. 2. The symmetric  $\text{CuO}_2$  barrel Fermi surfaces of  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ . Both majority and minority Fermi surfaces are shown, reflecting the small spin splitting. Coordinates shown are in units of  $(\pi/a, \pi/a)$ .

The small exchange splitting (compared to  $\sim 1$  eV in the Ru-O layer)  $\Delta_{\text{ex}} = v_F \delta k_F \approx 25$  meV ( $v_F = 2.5 \times 10^7$  cm/s [24]) is a direct consequence of the electronic, magnetic, and crystal structure. The Ru magnetization lies within the  $t_{2g}$  orbitals, which couple with the apical O  $p_x$  and  $p_y$  orbitals only through a small  $pd\pi$  coupling. These O  $p\pi$  orbitals do not couple either with the Cu  $d_{x^2-y^2}$  orbital, which is the main character of the Cu-O barrel Fermi surfaces, nor do they couple with the Cu  $s$  orbital, which has been found in  $\text{YBa}_2\text{Cu}_3\text{O}_7$  to provide much of the  $\hat{z}$  axis coupling. The exchange coupling that survives must find a secondary route, such as through polarization of the apical O atom that transfers the polarization to the  $p_z$  orbitals and on to the Cu  $s$  orbital, or from the apical O to the O  $p\sigma$  orbitals in the Cu-O layers. This small exchange splitting can be regarded (for effects on the spin) as arising from a vector exchange field  $\vec{B}_{\text{ex}}$ , whose direction is linked to the direction  $\hat{M}$  of  $\vec{M}$ .

*M parallel to the RuO<sub>2</sub> layers.*—In this case the vector potential  $\vec{A}$  can be chosen to be perpendicular to the layers. Then  $\vec{p} \cdot \vec{A}$  orbital pair breaking is confined to the interlayer hopping motion, which we neglect as suggested by Bernhard *et al.* [9]. The semiclassical Green's function treatment of Burkhardt and Rainer (BR) [25] then applies, except that the magnetic field of that work is replaced by the effective exchange field seen by the carriers

$$\vec{B}_{\text{eff}} = \vec{H} + \vec{B}_{\text{int}} + \vec{B}_{\text{ex}} \quad (1)$$

comprised of all contributions to the spin splitting  $\Delta_{Zee} = 2\mu_B |\vec{B}_{\text{eff}}|$  in the CuO<sub>2</sub> layers: an applied field  $H$ , the internal (dipolar) field  $B_{\text{int}}$  (equal to  $4\pi M$  within the RuO<sub>2</sub> layer), and the exchange field  $B_{\text{ex}}$  induced in the CuO<sub>2</sub> layers by the electronic exchange interaction ( $B_{\text{ex}} \equiv \Delta_{\text{ex}}/2\mu_B$ ).  $B_{\text{int}}$  in the Cu-O bilayer is obtained from magnetostatics or, below  $T_S$ , a generalized London equation.

BR have extended the FFLO theory, showing that in-plane “fields”  $\Delta_{Zee} \lesssim 2\Delta$  (the SC gap) can be accommodated by a nonconstant SC order parameter up to a maximum value  $B_{c2}$ . Since the internal field  $B_{\text{int}}$  due to  $1 \mu_B/\text{Ru}$  is only 700 G, for most of the range of accessible fields the exchange field  $B_{\text{ex}}$  will be the limiting field. In an FFLO state the mean pair momentum

$$q = \delta k_F \approx 0.02k_F \sim 0.02\pi/a \quad (2)$$

corresponds to a SC order parameter modulation on the scale of  $\lambda_q = 2\pi/q \sim 400$  Å, which must be no shorter than the SC in-plane coherence length  $\xi_{ab}$ . For conventional cuprates with  $T_S \sim 40$  K, for which  $\xi_{ab} \sim 60$ – $75$  Å, the exchange splitting  $\Delta_{\text{ex}} = 25$  meV (comparable to  $2\Delta$ ) rules out a constant order parameter but allows a nonconstant SC order parameter of a generalized FFLO type in the cuprate layers. BR note that, while

the 2D character enhances tendencies toward a FFLO-type state, the existence of such a state can be sensitive to Fermi surface shape. The quasi-1D sides of the barrel FS (Fig. 2) should strongly favor an FFLO state.

*M perpendicular to the CuO<sub>2</sub> layer.*—For this orientation coupling of orbital motion to the total field  $\vec{H} + \vec{B}_{\text{int}}$  leads to supercurrents and is naturally accommodated in the superconducting CuO<sub>2</sub> bilayer as a SVL. The lattice spacing corresponding to  $M = 700$  G ( $H = 0$ ) is one flux quantum per circle of radius  $\sim 0.7 \mu\text{m}$ , posing no problem for coexistence. At applied fields  $H \gg B_{\text{int}}$ , the effect of the intrinsic magnetization becomes minor. As a result, the Meissner effect measured in fields of a few Tesla may produce normal-looking susceptibility curves, such as found by Tallon *et al.* (albeit on polycrystalline samples). The behavior of the susceptibility for  $H \sim 4\pi\langle M \rangle$  remains to be elucidated.

*Interlayer superconductive coupling.*—Since bulk SC reflects a state that is coherent along the  $c$  axis, pair breaking by the intermediate magnetic RuO<sub>2</sub> layer must not be so strong as to destroy interlayer tunneling of pairs (for which  $\hat{c}$  axis hopping can no longer be neglected). Ru1212 represents the first atomic-scale SC-FM superlattice, and although there exists a literature on *nanoscale* SC-FM superlattices, the theory has not been pushed down to the atomic scale; indeed, no systems except cuprates show superconductivity of a single atomic (bi)layer, which becomes possible only because the  $\hat{c}$ -axis coherence length  $\xi_c$  is only  $\sim 10$  Å (the cell dimension).

The present system is however a natural one to form the  $\pi$ -phase SC order parameter predicted for SC-FM superlattices. The  $\pi$  phase has an order parameter that changes phase by  $\pi$  from SC layer to SC layer, and thus has a node in the FM layer, thereby strongly decreasing the pair breaking effect. Two characteristics of Ru1212 favor the  $\pi$  phase. First, the layer of strong magnetization is extremely thin (the  $\sim 2$  Å of the RuO<sub>2</sub> layer). Second, Prokić *et al.* predict a  $\pi$  phase only above a critical magnetization in the FM layers, and the RuO<sub>2</sub> layer presents a rather high (RuO<sub>2</sub> layer) value of  $4\pi M \sim 4$  kG within this atomic layer. (The 700 G value mentioned above is a cell average.) Since the SC coupling strength in the (CuO<sub>2</sub>)<sub>2</sub> bilayer is not known (and there is not microscopic theory of cuprate SC anyway), a quantitative determination is not possible, but Ru1212 presents a favorable case for  $\pi$ -phase formation.

*FM coupling through the SC layers.*—We comment briefly on the FM order. Since the magnetic ordering temperature depends only logarithmically [26] on the perpendicular coupling  $J_{\perp}$ , the rather high Curie temperature is not inconsistent with the small calculated polarization of the Cu-O bilayer. Although recent theories of FM-SC superlattices [27,28] are not strictly applicable to this atomic scale SC/FM superlattice, the conditions necessary for interlayer FM coupling [28] are present: the SC state must not be destroyed by the proximity to the FM layer (the

induced magnetization is small) and the FM/SC interface roughness must be small (here it is atomically smooth). One likelihood is that the exchange coupling will decrease below  $T_S$  due to the SC gap, which could be observable in the  $q_z$  dependence of the spin waves.

We now summarize. Our considerations show how coexistence of SC with FM is possible: (i) the average magnetization is not large (1/30 that of iron, in the case of Ru1212), (ii) the SC and FM subsystems are disjoint, in this case precisely and thinly layered, (iii) both SC and FM layers 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 SC layers is weak enough (especially on one Fermi surface sheet) not to entirely disallow superconductivity, yet strong enough to require an FFLO phase.  $\text{RuSr}_2\text{GdCu}_2\text{O}_8$  presents a striking illustration of behavior that can arise only in a sufficiently complex crystal structure with several competing interactions.

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