Ferromagnetic Spin Fluctuation Induced Superconductivity in Sr_2RuO_4

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We propose a quantitative model for triplet superconductivity in Sr_2RuO_4 based on first principles calculations for the electronic structure and magnetic susceptibility. The superconductivity is due to ferromagnetic spin fluctuations that are strong at small wave vectors. The calculated effective mass renormalization, renormalized susceptibility, and superconducting critical temperature are all in good agreement with experiment. The order parameter is of comparable magnitude on all three sheets of the Fermi surface. [S0031-9007(97)03720-4]

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The layered ruthenate Sr_2RuO_4 has attracted considerable recent interest. It is structurally similar to the first cuprate superconductor $(La, Sr)_2CuO_4$, is near a magnetic instability [$Sr_xCa_{1-x}RuO_3$ and Sr_2RuYO_6 are ferromagnetic (FM) and antiferromagnetic (AFM), respectively], and was thought to be strongly correlated. However, closer examination reveals more and more differences from the cuprates. It was noted that $SrRuO_3$ is ferromagnetic so it was conjectured that Sr_2RuO_4 must be close to a FM instability as well [1]. This has recently been corroborated by detailed microscopic calculations of magnetic properties of ruthenates [2]. Ferromagnetic fluctuations disfavor both s- and d-wave superconductivity, so it was suggested [1,3] that superconductivity in Sr_2RuO_4 must be triplet (p wave), thus very different from the high T_c cuprates. The idea of the strongly correlated electrons in Sr_2RuO_4 is mostly based on the apparent disagreement of angular resolved photoemission (ARPES) measurements of the Fermi surface [4] with results of local density approximation (LDA) calculations [5,6]. This argument is, however, questionable, because ARPES measurements disagree with de Haas–van Alphen (dHvA) experiments [7]. The notorious failure of the local spin density approximation (LSDA) to describe properly the magnetism of undoped cuprates does not occur in ruthenates [2]. Thus, the case for the strong correlations in ruthenates is questionable.

The following challenges should be met by a quantitative theory of the electronic states and superconductivity in Sr_2RuO_4: (i) Reconciliation of the (well reproducible) ARPES results with the dHvA measurements. This may also relate to whether or not there are strong correlation effects. (ii) The mechanism for superconductivity and how it is related with the large mass renormalization (of a factor of 3–4). In this Letter we address both of these issues.

The valence bands of Sr_2RuO_4 are formed by the three t_{2g} Ru orbitals, xy, yz, and zx. These are hybridized with the in-plane oxygen and, to a lesser extent, with the apical oxygen [5,6] p states. The bare oxygen p levels are well ($\sim$2 eV) removed from E_F, so the effect of the O p orbital is chiefly renormalization of the ionic t_{2g} levels, and assisting in the d-d hopping. The LDA band structure can be reasonably well described in the vicinity of the Fermi level as three mutually nonhybridizing tight-binding bands: $\epsilon_{xy}(\mathbf{k}) = E_0 + 2t_{dd\pi}(\cos ak_x + \cos ak_y) + 4t'_{dd\pi} \cos ak_x \cos ak_y$, and $\epsilon_{\{^x_y\}z}(\mathbf{k}) = E_0 + 2t_{dd\pi}\{^{\cos ak_x}_{\cos ak_y}\} + 8t_\perp \cos \frac{ak_x}{2} \cos \frac{ak_y}{2} \cos \frac{ak_z}{2}$, with the parameter $(E_0 - E_F, t_{dd\pi}, t'_{dd\pi}, t_\perp)$ being $(-0.4, 0.4, -0.12, 0)$ and $(-0.3, 0.25, 0, -0.025)$ eV for the xy and xz, yz bands, respectively, for the bands of Ref. [5]. With nearest neighbors only, this model yields one nearly circular cylindrical electronic sheet (γ) of the Fermi surface (FS) and four crossing planes (quasi-1D FS). The weak xz-yz hybridization reconnects these planes to form two tetragonal prisms, a hole one (α) and an electron one (β), as in Fig. 1. ARPES gives a FS of different topology: the van Hove singularity at $\mathbf{k} = (\pi/a, 0)$, which appears slightly above the Fermi level in the calculations ($\approx$60 meV in the LDA calculations and $\approx$50 meV with the gradient correction [8] included), is seen below it in photoemission experiments. This reconnects the surface γ and makes it holelike instead of electronlike. The total electron count in the ARPES FS is still four, indicating stoichiometry of the samples. Important consequences were ascribed to the fact that the van Hove singularity is situated in the same place as in the cuprates. The main difference between the LDA and the ARPES Fermi surfaces is that the latter corresponds to a larger $E_0(\{^x_y\}z) - E(xy)$ [the $d_{\{^x_y\}z}$ levels are higher because of an additional hybridization with the apical (O2) oxygen $p_{\{^x_y\}}$ orbitals]. Importantly, the calculations imply strong Stoner renormalization. The Stoner factor I, calculated as described in Ref. [2], is 0.43 eV, and $N(0) = 2.06\ \text{eV}^{-1}$ [5]. This yields a Stoner renormalization $1/(1 - IN) = 9$, somewhat larger than deduced from experimental susceptibility [9], $\chi/\chi_{\text{band}} = 7.3$. To fit the experiment, I should be $I_{\text{exp}} = 0.42$ eV. Note that the experiment leaves no room for any renormalization of χ beyond the Stoner one.

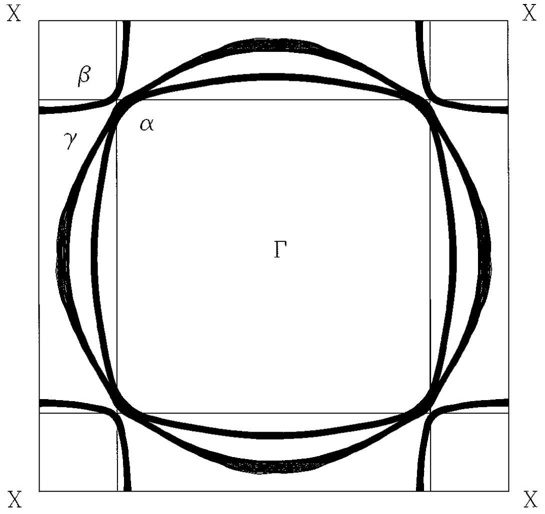

FIG. 1. LAPW Fermi surface. The origin is at Γ. The thickness of the lines is inversely proportional to the Fermi velocity (the inner and the outer contours are $E_F \pm 2$ mRy). The model Fermi surfaces ξ and ζ are shown as straight lines. The model Fermi surface γ is within the 2 mRy window around the actual surface and thus not shown.

However, the topology of the ARPES FS disagrees with that from dHvA experiments. The latter yields three cross sections, which sum up to four electrons/cell with excellent accuracy *only if the surface γ is electronlike.* The LDA calculated α, β, and γ areas deviate from the dHvA experiment by only -2%, -3%, and 5% of the Brillouin zone area, respectively, and an exact match can be achieved by very slight shifts of the bands α, β, and γ by 5, -4, and -3 mRy, respectively. Such agreement is generally considered very good even in simple metals, and the small mismatch (which does not change the FS topology) is likely due to some underestimation in LDA calculations of the tiny xz-yz hybridization. Unlike dHvA, which probes the bulk, ARPES probes essentially first surface the Ru-O layer. The cleavage plane in Sr_2RuO_4 is likely associated with the rocksalt layers, leaving the Ru-O2 bond dangling or otherwise strongly perturbed. As such, this bond is likely to be contracted compared to the bulk, and the electronic structure of the surface RuO_2 layer differs from bulk. The main effect of such a surface relaxation is expected to be a strong modification of the $\mathrm{Ru}(\{{x \atop y}\}z)$-$\mathrm{O2}(\{{x \atop y}\})$ hopping. In a linear approximation, this can be estimated from bulk calculations with the Ru-O2 bond length reduced by a half of the supposed surface contraction of this bond. We performed such calculations for Sr_2RuO_4 with the O2 shifted by 0.1 Å and found that the energy distance between the Fermi level and the van Hove singularity was reduced by 30 meV. Thus, the surface relaxation of the Ru-O2 bond that would bring our linear augmented plane wave (LAPW) calculations in agreement with the ARPES measurements would be less than 0.4 Å (probably, closer to 0.3 Å, due to nonlinearity [10]). Although the actual surface relaxation for Sr_2RuO_4 is not known, the change in the observed electronic structure due to the Ru-O2 bond relaxation is in the right direction and of the right order of magnitude compared to the observed ARPES FS. We conclude that the LDA and dHvA yield the bulk electronic structure of Sr_2RuO_4. The differences in ARPES presumably reflect the surface structure.

This said, we recall that the mass renormalization $(1 + \lambda)$ found in dHvA experiments [7] and from the specific heat [11] is unusually large: for the xy (γ) sheet it is 4, and 3.3 for the two other sheets. Materials with an electron-phonon coupling constant of the order of 2.5 are known, but if it were so large in Sr_2RuO_4, with its high phonon frequencies, the superconducting T_c would be much higher than 1.5 K. This paradox is naturally resolved in the framework of the conjecture [1,3] that Sr_2RuO_4 has strong electron-paramagnon coupling, and may even be a p-wave superconductor, which is also in accord with recent experiments showing anomalously strong dependence of T_c on residual resistivity [12]. In such a case, two different coupling constants appear: λ_0^m which controls the mass renormalization is the average of the electron-paramagnon interaction over the FS, while λ_1^m which determines the p-wave transition temperature is the $l = 1$ angular component of this interaction. Importantly, this holds for any boson-mediated interaction, including electron-phonon, so that $\lambda_0 = \lambda_0^m + \lambda_0^p$, $\lambda_1 = \lambda_1^m + \lambda_1^p$. For s pairing although the mass renormalization is controlled by $\lambda_0^m + \lambda_0^p$, the superconducting coupling constant is $\lambda_0^p - \lambda_0^m$.

The situation with Sr_2RuO_4 is further complicated by the fact that there are three different sheets of the FS and the order parameters on all sheets should be determined simultaneously. Without a quantitative numerical estimate it is impossible to assess whether or not the triplet pairing hypothesis of Refs. [1,3] can be reconciled with the body of experimental facts. Fortunately, the LSDA calculations provide the necessary information for a quantitative analysis.

The most important (and most uncertain) part of such an analysis is the interaction responsible for pairing and for the mass renormalization. This was not specified in the previous works, but we conjecture that it is the exchange of paramagnons. Such an interaction in metals was studied with respect to possible superconductivity in Pd in the late 1970's (see, e.g., [13,14]), and later in connection with heavy fermions. The parallel-spin interaction, relevant for triplet pairing is given in the RPA by the sum of the diagrams with odd numbers of loops,

$$V(\mathbf{q} = \mathbf{k} - \mathbf{k}') = \frac{I^2(q)\chi_0(q)}{1 - I^2(q)\chi_0^2(q)}. \qquad (1)$$

The mass renormalization is not as easy to define. Besides the parallel-spin interaction (1), there is the antiparallel-spin interaction, given in the same approximation by the sum of the chain diagrams with even numbers of loops, plus ladder diagrams [13,15]. In case of contact interaction, the total interaction is three times stronger than the interaction in the parallel-spin channel only. It was pointed out [14], though, that there is no good physical reason to single out any particular class of diagrams. It was found that including all three classes above leads to systematic overestimation of mass renormalization by a factor of 2–3 [13,16]. Our case is further complicated because unlike the electron-phonon interaction, the electron-electron (and, correspondingly, the electron-paramagnon) interaction is already included in some average way in the LSDA band structure. Thus, the electron-paramagnon mass renormalization is to some extent included in the LDA mass as well.

Despite all these difficulties, one can get an idea about the size of the electron-paramagnon mass renormalization by making calculations with the parallel-spin interaction (1) only; one may consider that as a lower bound for the total spin-fluctuation induced renormalization. The mass renormalization then is computed in the same way as the electron-phonon renormalization, i.e., by taking the average of $V(\mathbf{q})$ of Eq. (1) over the FS. One has to remember, though, that there are other effects beyond LDA, apart from the one that we calculate, which may further increase the observable mass.

The triplet pairing constant is calculated by averaging $V(\mathbf{q})$ with the functions reflecting the $\mathbf{k}$ dependence of the direction of the (vector) order parameter, in the simplest case with $\mathbf{k}\cdot\mathbf{k}'/kk'$. A common approximation, which we use here (although it may not be as good in Sr_2RuO_4 as in Pd) is to take $\chi_0(q) = \chi_0(0) = N$. The q dependence of I cannot, however, be neglected and has to be specified. Essentially, it tells us how much the FM state is favored over AFM states [17]. As discussed in Ref. [2], what favors ferromagnetism over antiferromagnetism in ruthenates is the oxygen contribution to the Stoner factor. This is determined from the band structure calculations as follows: Atomic Stoner factors for Ru and O ions are calculated in a standard way and are $I_{\mathrm{Ru}} \approx 0.7$ eV, $I_{\mathrm{O}} \approx 1.6$ eV. The total Stoner factor for the compound is $I = I_{\mathrm{Ru}}\nu_{\mathrm{Ru}}^2 + 2I_{\mathrm{O}}\nu_{\mathrm{O}}^2$, where ν_{Ru} and ν_{O} are partial densities of states at E_F of Ru and in-plane oxygen; the contribution of the apical oxygen is negligible. For AFM ordering, the second term in the expression for I falls out, because oxygen is nonmagnetic by symmetry. We found the AFM Stoner factor I for Sr_2RuO_4 to be smaller than FM one by 14% (oxygen contribution $\Delta I = 0.06$ eV). A q dependence that reflects this effect is $I(q) = I/(1 + b^2q^2)$, where $b^2 = 0.5(a/\pi)^2\Delta I/(I - \Delta I) \approx 0.08(a/\pi)^2$. In the following we use this $I(q)$ together with Eq. (1).

Let us now make a link to the real FS. In Refs. [1,18] the maximum full cylindrical symmetry was assumed for all three FS's. This approximation completely neglects the quasi-1D character of the xz and yz bands and cannot be used for quantitative purposes. Instead, we retain the cylindrical approximation for the xy FS γ and use the 1D approximation for the xz and yz FS's. Then we have three 2D Fermi lines: γ, a circle with the radius $g \approx 0.9\pi/a$, ξ, two lines parallel to x at $\approx\pm 2g/3$ from the $\mathbf{\Gamma}$ point, and ζ, the two corresponding lines parallel to y (Fig. 1). Using the standard multiband technique [19] we now introduce the coupling matrix $\Lambda_{ij}^s = N^{-1}\sum_{\mathbf{k}\mathbf{k}'}\cdot\delta(\epsilon_{\mathbf{k}i})\delta(\epsilon_{\mathbf{k}'j})V(\mathbf{k}-\mathbf{k}') = N\nu_i\nu_j\langle V(\mathbf{k}-\mathbf{k}')\rangle_{ij}$, where (i,j) can be γ, ξ, or ζ, and $\nu_i = N_i/N$ (from our band structure $v_{F\gamma} \approx v_{F\xi,,\zeta}$, and $\nu_\gamma = 0.44$, $\nu_{\xi,,\zeta} = 0.28$). Then the mass renormalization in band i is defined as $\lambda_i^s = \nu_i^{-1}\sum_j \Lambda_{ij}$. The average mass renormalization is $\lambda^s = \sum_{ij}\Lambda_{ij}^s$.

Using this model, we arrive at $\Lambda_{\gamma\gamma}^s = 0.35$, $\Lambda_{\xi\xi}^s = 0.32$, $\Lambda_{\gamma\xi}^s = 0.16$, $\Lambda_{\xi\zeta}^s = 0.03$. This gives $\lambda_\gamma^s = (\Lambda_{\gamma\gamma}^s + 2\Lambda_{\gamma\xi}^s)/\nu_\gamma = 1.5$, $\lambda_\xi^s = (\Lambda_{\xi\xi}^s + \Lambda_{\gamma\xi}^s + \Lambda_{\xi\zeta}^s)/\nu_\xi = 1.8$, $\lambda^s = 1.7$, to be compared with experimental dHvA values of 3, 2.3, and 3, respectively. The difference may be due to an electron-phonon coupling of the order of 1 and/or antiparallel spin fluctuations, neglected in our calculations.

Let us now return to the question of the p-wave superconductivity. The theory for a cylindrical FS is presented exceedingly well by Sigrist *et al.* [1,18,20] and need not be repeated here. The only difference for a FS of arbitrary shape is that instead of the $\mathbf{k}$-vector components, we have to use Allen's FS harmonics [19]. So, there are four possible unitary planar states, all degenerate if spin orbit is neglected. Let us consider, for instance, the A_{1u} state:

$$\mathbf{d}_{\mathbf{k}} = d\,\frac{\mathbf{v}_{\mathbf{k}}}{v_{\mathbf{k}}}, \tag{2}$$

where $\mathbf{v}_{\mathbf{k}}$ is the Fermi velocity. This state has, generally speaking, a finite superconducting gap, and thus zero density of states at the Fermi energy below T_c, in contrast with the experiment [11]. The same holds for three other states, degenerate with the one of Eq. (2). Nonunitary linear combinations of the states which are gapless are also possible. These have, however, generally speaking, lower pairing energy and should not occur.

We now calculate the transition temperature within our spin-fluctuation model. Similar to Agterberg *et al.* [18], we consider the superconducting state with the order parameter d which is constant for each of the three FS sheets, but differing between the sheets. We have to calculate the matrix $\Lambda_{ij}^p = N\nu_i\nu_j\langle V(\mathbf{k}-\mathbf{k}')(\mathbf{d}_{\mathbf{k}}^i\cdot\mathbf{d}_{\mathbf{k}'}^j)/(d_{\mathbf{k}}^i d_{\mathbf{k}'}^j)\rangle_{ij}$, where i and j label the three bands, and find the maximum eigenvalue of the matrix $\nu_i^{-1}\Lambda_{ij}^p$ [19]. The corresponding eigenvector defines the coefficient a and thus the relative magnitude of the order parameter in bands γ and (ξ,ζ). By symmetry, the pairing matrix looks like

$$\begin{pmatrix} \Lambda_{\gamma\gamma}^p & \Lambda_{\gamma\xi}^p & \Lambda_{\gamma\xi}^p \\ \Lambda_{\gamma\xi}^p & \Lambda_{\xi\xi}^p & 0 \\ \Lambda_{\gamma\xi}^p & 0 & \Lambda_{\xi\xi}^p \end{pmatrix}.$$

(If we had used instead of ξ,ζ nomenclature the α,β one, as in Ref. [18], this symmetry would not hold.) Numerical calculations give $\Lambda_{\gamma\gamma}^p = 0.16$, $\Lambda_{\xi\xi}^p = 0.075$, and

$\Lambda^p_{\gamma\xi} = 0.025$. The maximum eigenvalue of the corresponding coupling matrix is 0.43, and the corresponding superconducting state is $0.85\gamma + 0.38\xi + 0.38\zeta$.

Let us now estimate the transition temperature. Using the characteristic paramagnon energy $\omega_{sf} \sim (N^{-1} - I)/4 \approx 160$ K from our calculations, as the cutoff frequency, and the Allen-Dynes formula for strong coupling (although $\lambda = 0.43$ is relatively weak, the relevant number is the renormalization parameter $\lambda^s \approx 1.7$), we obtain

$$T_c \approx \frac{(N^{-1} - I)/4}{1.2k_B} \exp[-(1 + \lambda^s)/\lambda^p_{\text{eff}}] = 0.25\ \text{K}. \tag{3}$$

Again, as in the case of mass renormalization, there is some room for the electron-phonon coupling as well.

One of the key problems, as discussed in Refs. [18,20], is the residual electronic specific heat [11], which remains at about 50% of its normal value in the superconducting regime. This led Agterberg *et al.* [18] to postulate a pairing matrix which yields a vanishing gap for the γ band. This, however, does not square with the quantitative estimate presented in this Letter. An earlier assumption [3,20] was that the excess pairing energy that forbids nonunitary combination of the order parameters (2) may be overcome by additional magnetic (Stoner) energy in a nonunitary state. The requirements are strong Stoner renormalization (supported by the calculations) and strong particle hole asymmetry [21]. However, a quantitative estimate according to Ref. [21] shows that the effect is by far too weak. The criterion is $[\frac{T_c d \ln N}{dE_F}]^2 \frac{1}{1-IN} \ln \frac{\omega_{sf}}{T_c} \sim 10^{-5}$, while it should be of the order 1 for the nonunitary state to stabilize. So, the problem of the residual electronic specific heat remains open, although it cannot be excluded that it results from sample inhomogeneity and is extrinsic to superconductivity.

To summarize, we have presented first principles calculations which indicate that (i) conventional LDA calculations give a correct description of the bulk electronic structure of $\mathrm{Sr_2RuO_4}$, as well as of its renormalization due to the Stoner exchange interaction; (ii) the difference between the bulk and the surface electronic structure (as measured by ARPES) can be explained by the surface effect; (iii) interactions due to exchange of FM spin fluctuations, as calculated from the LDA band structure, are sufficiently strong to explain both the mass renormalization and superconducting critical temperature. We emphasize the main approximations used: (a) neglect of the **q** dependence of χ_0, (b) neglect of strong coupling effects beyond the Allen-Dynes formula [note that a strong coupling effect will lead to a final density of states $N(0)$ at all $T \neq 0$ and thus to nonexponential T dependencies of specific heat and like quantities], and (c) neglect of correlation effects in the mass renormalization beyond the parallel-spin paramagnon induced interaction. In principle, it is clear how to improve the first two items, while the last issue lacks full theory and cannot be easily dealt with.

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