Competitions in Layered Ruthenates: Ferromagnetism versus Antiferromagnetism and Triplet versus Singlet Pairing

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Involvement of O in magnetism leads to ferromagnetic fluctuations in Sr_2RuO_4, while Ca_2RuO_4 is antiferromagnetic, suggesting a possibility of antiferromagnetic fluctuations in Sr_2RuO_4 as well. Our calculations show that the ferro- and antiferromagnetic fluctuations coexist, leading to an instability in Ca_2RuO_4 and to a competition between p- and d-wave superconductivities in Sr_2RuO_4. The antiferromagnetism is due to the nesting, with $\mathbf{Q} \approx (2\pi/3a, 2\pi/3a, 0)$. The p-wave state is more stable than the d-wave one except in close vicinity of the magnetic instability. The d-wave state has a vanishing gap in one out of three bands; in the p channel it is comparable in all three bands. [S0031-9007(99)09181-4]

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In the last few years an understanding emerged, thanks to the progress in the high-T_c problem, that s-wave and d-wave pairing are not entirely antagonistic. It is possible to obtain either symmetry in the framework of one and the same model, depending on the actual values of parameters. It is, however, commonly believed that the triplet (p) and singlet (s, d) pairings are so different in their nature that more than just changing numerical parameters of a model is needed to switch between these symmetries. Here we show that a realistic model of the superconducting layered ruthenate Sr_2RuO_4 is in fact unstable with respect to both p- and d-wave pairing and it is a close competition between the two that determines the actual ground state.

It was suggested a few years ago that Sr_2RuO_4 may be a p-wave superconductor [1]. The main consideration was that the sister 3D compound, $SrRuO_3$, is a strong ferromagnet (FM), so one could expect substantial ferromagnetic spin fluctuations in Sr_2RuO_4. It was also known that superconductivity in the canonical triplet superconductor, ^{3}He, is due to ferromagnetic spin fluctuations, so it was natural to conjecture that the pairing in Sr_2RuO_4 was also triplet. At that time there was hardly any experimental evidence and no microscopic calculations to support this idea. Since then, convincing experimental evidence has been collected (for a review, see Ref. [2]) that the superconductivity in Sr_2RuO_4 is indeed unconventional (not s wave) and most likely triplet. Microscopic calculations revealed the mechanism for ferromagnetism in $SrRuO_3$ [3,4] and demonstrated that a tendency to ferromagnetism is still present in Sr_2RuO_4, although it is weaker and does not result in an actual magnetic instability [5].

The recent discovery of *anti*ferromagnetism in Ca_2RuO_4 forces us to reconsider this simple picture. This compound differs from Sr_2RuO_4 only in that the RuO_6 octahedra are tilted and rotated [6], as it is common in perovskites (cf. La_2CuO_4). This causes some modification of the hopping amplitudes compared to Sr_2RuO_4, but this modification has a tremendous effect on magnetic properties: The material becomes antiferromagnetic (AFM) with a substantial ($>1\mu_B$/Ru) magnetic moment. This suggests that there should be some latent tendency to antiferromagnetism in Sr_2RuO_4 itself, and casts doubt on the basic assumptions of Refs. [1,5] and others that the spin fluctuations in this material are predominantly of the ferromagnetic type. To answer this question, one cannot rely upon analogies with other materials, but needs quantitative (at least semiquantitative) calculations.

Fortunately, and unlike cuprates and most $3d$ oxides, the conventional local density approximation (LDA) provides a very good description of magnetic properties of the ruthenate-based perovskites. Previously, we have performed calculations [3,4] for various ruthenates for which crystal structure and magnetic properties are known experimentally, and we found excellent agreement with the experiment: $SrRuO_3$ comes out ferromagnetic with the total magnetization $1.59\mu_B$/f.u. (experiment: 1.6), $CaRuO_3$ is a paramagnet on a verge of ferromagnetism, and the double perovskite Sr_2RuYO_6 is antiferromagnetic with $3\mu_B$/f.u., again in accord with the experiment. Finally, in Sr_2RuO_4 the paramagnetic state comes out more stable in the LDA calculations than either the ferromagnetic or the antiferromagnetic one.

The reason for ferromagnetism in $SrRuO_3$ (and near-ferromagnetism in $CaRuO_3$) is now well understood [4]: There is substantial oxygen density of states at the Fermi level in these ruthenates (due to strong p-d hybridization), and the difference between the FM and the AFM state is that in the latter case the oxygen is not spin polarized. The oxygen ion has considerable Stoner energy, which is lost in the AFM case. Furthermore, this additional energy is entirely lost for the $\mathbf{q} = \{\pi, \pi, \pi\}$ AFM ordering, two-thirds of that is lost for $\mathbf{q} = \{\pi, \pi, 0\}$, and one-third for $\mathbf{q} = \{\pi, 0, 0\}$, compared with the FM ordering ($\mathbf{q} = \{0, 0, 0\}$). This allows one to construct a q-dependent Stoner interaction, $I(q) \approx 0.46$ eV$/(1 + 0.08q^2)$, where

q is measured in units of π/a. This interaction strongly favors a FM instability, and whether or not the actual instability occurs depends on the density of states at the Fermi level, according to the Stoner criterion, $I(0)N(0) > 1$. It appears that in $SrRuO_3$ this condition is satisfied, $IN = 1.23$, and the material is a FM. In $CaRuO_3$, the smaller ionic radius of Ca leads to a smaller Ru-Ru distance and thus to larger distortion. A peak in the density of states that exists in $SrRuO_3$ is washed out and the material is on the border line, $IN \approx 1$.

The same mechanism is operative in Sr_2RuO_4: For an individual RuO_2 plane, we obtain a (2D) Stoner factor $I(q) \approx 0.43$ eV$/(1 + 0.08q^2)$, favoring ferromagnetic spin fluctuations in the plane [5]. However, the 2D character of the band structure of Sr_2RuO_4 introduces additional complications. As discussed in Refs. [5,7], of the three Fermi surface sheets one (γ) is quasi-isotropic 2D, and two (α and β) are quasi-1D. The latter can be visualized (cf. Fig. 1 in Ref. [5]) as a system of parallel planes separated by $Q = 2\pi/3a$, running both in the x and y directions. This is true in the nearest-neighbor $dd\pi$ tight-binding model, while in reality due to the next hoppings the planes are warped and reconnected at the crossing lines, to form two pseudosquare prisms, obtained in LDA calculations and observed experimentally. Naturally, such a Fermi surface should give rise to sizable nesting effects at the wave vectors $\mathbf{k} = (Q, k_y)$, $\mathbf{k} = (k_x, Q)$, and especially at $\mathbf{k} = \mathbf{Q} = (Q, Q)$. This would lead to AFM spin fluctuations at these vectors, in addition to the FM fluctuations discussed above. To check, we have integrated the LDA band structure of Sr_2RuO_4 to get the bare RPA susceptibility,

$$\chi_0(\mathbf{q}) = \sum_{\mathbf{k}ij} \frac{M_{\mathbf{k}i,\mathbf{k+q},j}[f(\varepsilon_{\mathbf{k},i}) - f(\varepsilon_{\mathbf{k+q},j})]}{\varepsilon_{\mathbf{k+q},j} - \varepsilon_{\mathbf{k},i}}, \quad (1)$$

where f is the Fermi distribution function, i and j label the three bands. All $|\mathbf{k}i\rangle$ states were classified according to the maximal t_{2g} character, xy, yz, and zx, and the matrix element M is taken to be 1 between two states which have the same maximal character and 0 otherwise. This is, of course, a rather crude approximation, but it should reveal the qualitative behavior of χ_0. The results are shown in Fig. 1. Roughly speaking,

$$\chi_0(\mathbf{q}) = N(0) + \chi_n(\mathbf{q}), \quad (2)$$

where χ_n is the nesting-dependent contribution. The total susceptibility can then be expressed as

$$\chi(\mathbf{q}) = \frac{\chi_0(\mathbf{q})}{1 - I(q)\chi_0(\mathbf{q})} = \frac{\chi_0(\mathbf{q})}{1 - I(q)N(0) - I(q)\chi_n(\mathbf{q})}. \quad (3)$$

This form implies two different kinds of spin fluctuations: FM ones, at $\mathbf{q} = 0$, and AFM ones, at $\mathbf{q} = \mathbf{Q}$. If $I(Q)N(0) + I(Q)\chi_n(\mathbf{Q}) > I(0)N(0)$, the AFM fluctuations are stronger. This seems to be the case in Sr_2RuO_4: Our calculations yield $I(0)N(0) = 0.82$, in good agreement with the experimentally observed susceptibility enhancement, and $I(Q)N(0) + I(Q)\chi_n(\mathbf{Q}) = 1.02$ (which actually corresponds to an instability with respect to tripling of the unit cell both in x and in y). Since no instability is observed in the experiment, nor in the direct calculations, we conclude that the approximate treatment of the matrix elements in Eq. (1) leads to an overestimation of χ_n by at the very least 2%, but the conclusion that AFM fluctuations are stronger or at least comparable with the FM ones likely holds.

The direct way to test this experimentally is via neutron scattering [8]. There is, however, an indirect argument in favor of strong AFM spin fluctuations. Increasing the effective dimensionality by adding additional RuO_2 layers, one can increase $N(0)$ and eventually get a FM instability. Experimentally this happens when the number of layers is three or maybe even two [9]. Another possible (but not guaranteed) effect of adding layers is increased z dispersion and thus deteriorated nesting. On the other hand, reducing the next-nearest-neighbor hopping should improve nesting and make an AFM transition more likely. One expects such a reduction from rotating the RuO_6 octahedra [10], as, for instance, in Ca_2RuO_4. Indeed, experimentally Ca_2RuO_4 is an AFM with a magnetization of 1.2–1.3 $(1.2-1.3)\mu_B$/Ru and $T_N \approx 150$ K. Moreover, this AFM state is remarkably different from typical Mott-Hubbard insulators, driven by strong Coulomb correlations. First, although the conductivity grows with temperature, the functional dependence is consistent with a variable-range hopping and not with activation. Second, there is substantial density of states at the Fermi level, as evidenced by specific heat measurements. These two facts indicate that Ca_2RuO_4 is not a simple insulator, but a metal with disorder localized carriers (which is in turn helped by strong coupling between the spin and charge degrees of freedom [4]). We performed LDA calculations for Ca_2RuO_4 similar to those reported in Refs. [3,4] and found a magnetic moment of $\approx 1.5\mu_B$ (of which $\approx 1\mu_B$ is inside the Ru muffin-tin sphere and the rest mostly residing on the apical oxygens) for Ca_2RuO_4 (in agreement

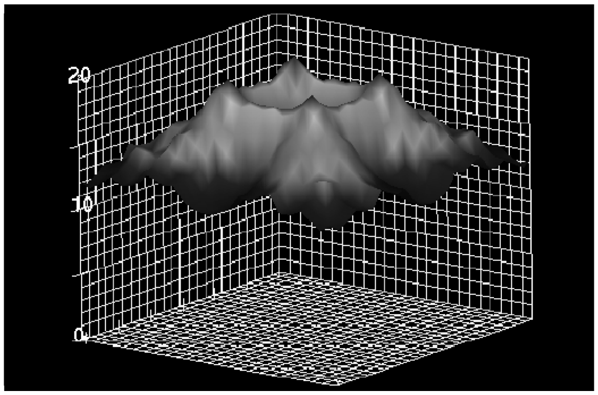

FIG. 1. Calculated bare susceptibility for Sr_2RuO_4.

with the experimental $M = 1.3\mu_B$). In fact, we also find a FM instability, and that the FM and the AFM states Ca_2RuO_4 degenerate within the LDA to within a few meV/atom, indicating a close competition between these two magnetic states [11]. For genuine Mott insulators the LDA either fails to reproduce the magnetic instability, or underestimates the magnetization. The calculated density of states is sizable, $N(E_F) = 1.6$ states/eV spin f.u., but the corresponding effective mass is large (the in-plane average [12] $n/m = 7.5 \times 10^{20}\ \mathrm{cm}^{-3}/m_0$), because Ru is strongly spin polarized and thus Ru-Ru nearest-neighbor hopping is suppressed with AFM order. This also facilitates localization.

We now enumerate the relevant magnetic interactions in the (Sr,Ca) $_2RuO_4$ system. The first two have been discussed above, and they are the Stoner ferromagnetism ($\mathbf{Q} = \mathbf{0}$), nesting-derived antiferromagnetism ($\mathbf{Q} \approx \{2\pi/3, 2\pi/3\}$). As usual, there is also superexchange ($\mathbf{Q} = \{\pi, \pi\}$). One should be reminded at this point that superexchange *per se* is not a strong correlation phenomenon. In a quasi-one-electron approach such as LDA, for sufficiently large exchange splittings, an AFM state is lower in energy than the FM one by roughly Zt^2/Δ, where Z is coordination, t is the hopping, and Δ is the exchange splitting. Since t is usually overestimated in LDA, and Δ is usually smaller than Hubbard U, the effect of superexchange is usually overestimated, not underestimated, in LDA (see Ref. [4] for more).

While superexchange is a universal mechanism and should also be operative in Ca_2RuO_4, it hardly plays a leading role. Otherwise, the LDA calculations that gave the right Ru moment would have overstabilized the AFM state, while in reality the opposite is true (they come out degenerate instead of the AFM being the ground state). The most likely cause for the instability is nesting. Furthermore, superexchange is of less relevance for Sr_2RuO_4 because it manifests itself for finite amplitude spin fluctuations, and not in the low-energy spectrum.

Assuming that the LDA gives a reasonable description of the spectrum of spin fluctuations in Sr_2RuO_4, we can discuss the consequences that the AFM spin fluctuations may have on superconductivity. Recall that in p-wave superconductivity only the small q spin fluctuations are pairing, while in the d-wave case they are mostly pair breaking. For a spectrum with a complicated $\mathbf{q}$ dependence, as the one described by Eq. (3), the most favorable state is defined by an interplay of the Fermi surface geometry and the structure of the effective interaction. In the weak coupling near T_c, the gap equation looks like

$$\Delta_{\mathbf{k}i} = \sum_{\mathbf{k}'j} V_{\mathbf{k}i,\mathbf{k}'j} \Delta_{\mathbf{k}'j}\,, \qquad (4)$$

where for the singlet (d) pairing Δ is the order parameter, and $V_{\mathbf{k}i,\mathbf{k}'j}$ is (negative) pairing interaction, which in the same approximation as the one used in Ref. [5] is given by

$$V(\mathbf{q} = \mathbf{k} - \mathbf{k}') = -\frac{I^2(q)\chi_0(\mathbf{q})}{1 - I^2(q)\chi_0^2(\mathbf{q})}\,. \qquad (5)$$

For the triplet (p) pairing Δ is the amplitude of the order parameter, usually denoted as d, and $V_{\mathbf{k}i,\mathbf{k}'j}$ now includes the sign-changing angular factor:

$$V(\mathbf{q} = \mathbf{k} - \mathbf{k}') = \frac{\mathbf{v_k} \cdot \mathbf{v_{k'}}}{v_\mathbf{k} v_{\mathbf{k}'}} \frac{I^2(q)\chi_0(\mathbf{q})}{1 - I^2(q)\chi_0^2(\mathbf{q})}\,. \qquad (6)$$

The largest eigenvalue of the matrix V in Eq. (4) defines the critical temperature, and the corresponding eigenvector defines the anisotropy of the gap near T_c. Correspondingly, the instability in the singlet channel is defined by the same matrix, but with the opposite sign (the interaction is repulsive in singlet channel), and without the angular factor $\frac{\mathbf{v_k} \cdot \mathbf{v_{k'}}}{v_\mathbf{k} v_{\mathbf{k}'}}$. We have solved these eigenvalue problems numerically using a discrete mesh of $\mathbf{k}$ points at the Fermi line. We used model susceptibility (2), adding an adjustable reduction α for the nesting part, $\chi_0(\mathbf{q}) = N(0) + \alpha\chi_n(\mathbf{q})$, and look for the solutions at different $\alpha < 0.98$ (i.e., below actual AFM instability). Furthermore, to simplify the calculations, we used an analytical form for $\chi_n(\mathbf{q})$ that recovers the main qualitative characteristics of the numerical result of Fig. 1, namely, $\chi_n(\mathbf{q}) = A[\cos(aq_x) + \cos(aq_y)] + B[\cos(2aq_x) + \cos(2aq_y)] + C[\cos(3aq_x) + \cos(3aq_y)] - 2(A + B + C)$, where $A, B, C = -0.103, -0.044, 0.037$ states/eV spin f.u., respectively.

The results are shown in Fig. 2. Amazingly, only in close vicinity to the actual AFM instability ($0.85 < \alpha < 0.98$) the superconducting transition happens in the d-wave channel. For smaller α, the p-wave state is favored. An interesting question is the following: What is the angular and/or interband anisotropy of the gap? We illustrate this anisotropy for the critical value of α (Fig. 3). The p-wave state is relatively isotropic, indicating that at least in the Fermiology there is no reason for substantial interband anisotropy ("orbital-dependent

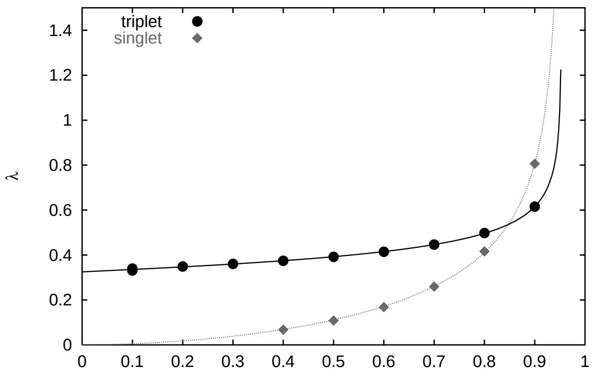

FIG. 2. The maximum eigenvalue for the coupling matrix in the singlet and in the triplet channels, as a function of the relative strength of the AFM component in the bare electronic susceptibility.

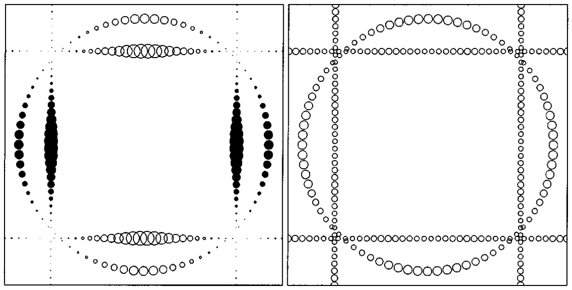

FIG. 3. Relative magnitude of the order parameter in the singlet (left) and the triplet (right) states. Parameter α is the same for both panels (0.83), corresponding to the coupling constant in both channels $\lambda \approx 0.5$.

superconductivity"), suggested in Ref. [1]. The d-wave, to the contrary, is substantially anisotropic beyond the standard anisotropy associated with the nodes along the $\{\pi, \pi\}$ direction; namely, the so-called α pocket of the Fermi surface has a nearly vanishing order parameter, and this is probably why the region of stability of the d-wave solution is so narrow.

Our conclusions are as follows: (i) LDA calculations yield a self-consistent solution with the AFM ordering for Ca_2RuO_4, degenerate with a FM solution. The nonmagnetic state is considerably higher in energy, in agreement with the experiment. The calculated magnetization value of $\approx 1\mu_B$ is in agreement with the experiment as well. (ii) This fact suggests that besides the known tendency to ferromagnetism, there is an intrinsic tendency to antiferromagnetism in Ru based layered perovskites. (iii) Analysis of the Fermi surface geometry of Sr_2RuO_4, as well as direct calculations, indicate a strong nesting at $\mathbf{Q} = \{\pm 2\pi/3, \pm 2\pi/3\}$, as well as a weaker nesting for the wave vectors connecting these four points (Fig. 1). This result also suggests that the AFM ordering in Ca_2RuO_4 is mostly due to nesting, although superexchange may play some role as well. It is, however, unlikely that this compound is a Mott-Hubbard insulator. (iv) The spin fluctuations in Sr_2RuO_4 have both a FM and an AFM component, of comparable magnitude, thus making d-wave superconductivity a strong competitor with the p-wave state. It is possible that the system may be driven to the d-wave superconductivity by an external force, for instance by pressure. (v) A spin fluctuation spectrum combined with the actual Fermiology of Sr_2RuO_4 produced a p-wave state with little angular or interband anisotropy. (iv) The sister compound Ca_2RuO_4 is a low carrier density metal, where carrier are localized due to disorder and electron-magnon scattering, and where antiferromagnetism is primarily due to the nesting effects.

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[8] T. Imai *et al.* [Phys. Rev. Lett. **81**, 3006 (1998)] recently reported NMR relaxation rate measurements which they interpreted as an indication of the absence of substantial AFM spin fluctuations. However, their data relate only with the spin susceptibility at $\mathbf{q} = (\pi, \pi)$, while our calculations predict spin fluctuations at $\mathbf{q} = \mathbf{Q} = \frac{2}{3}(\pi, \pi)$, so there is no contradiction between these data and our results.

[9] In the calculation (to be published elsewhere) the $n = 2$ compound $Sr_3Ru_2O_7$ is not yet ferromagnetic; experimental reports are contradictory, but the $n = 3$ material, $Sr_4Ru_3O_{10}$, is positively FM.

[10] We do not discuss here the smearing of the density of states due to additional Bragg reflections in a distorted structure, an effect that controls the loss of magnetic ordering from $SrRuO_3$ to $CaRuO_3$.

[11] We used crystal and magnetic structure of Ca_2RuO_4 as recently measured by means of neutron scattering [6]. The full-potential linear augmented plane wave method, as described in [4,7] was utilized. The ferromagnetic structure appeared lower than the AFM one by ≈ 0.5 mRy/Ru. While the technical accuracy of the computations is better than that, the LDA itself is not as accurate in magnetic energy differences; including gradient corrections, for instance, usually changes them by a larger margin. It is not excluded that on top of the (π, π) AFM structure reported in Ref. [6] there is an incommensurate superstructure with $\mathbf{Q} \simeq 0.6(\pi/a, \pi/b)$. This would lower the energy slightly and probably render this AFM state more stable than the FM one. A more detailed account of these calculations will be published elsewhere.

[12] The effective mass has substantial (factor of 3) in-plane anisotropy.