Magnetism and spin-fluctuation induced superconductivity in ruthenates.

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Abstract

Layered and pseudocubic Ru-based perovskites have been the subject of considerable recent attention, due to their unusual magnetic properties and the discovery of superconductivity in one member of the family, Sr$_2$RuO$_4$. From a magnetic point of view, interest derives from the stable ferromagnetism in SrRuO$_3$, gradually disappearing to a non-magnetic phase upon substituting Sr with isovalent Ca, a very unusual kind of behavior for 3d perovskites. On the superconducting side, interest was stimulated by theoretical conjectures and experimental indications that Sr$_2$RuO$_4$ might be a $p$-wave superconductor. We report first-principles LSDA calculations for ferromagnetic SrRuO$_3$, antiferromagnetic Sr$_2$YRuO$_6$, non-magnetic CaRuO$_3$, and superconducting Sr$_2$RuO$_4$. In all cases, magnetic properties are well reproduced by the calculations. Anomalous properties are explained in terms of simple TB models and Stoner theory. An important result is that O bears sizable magnetic moments and plays an important role in the formation of the magnetic states. Based on these calculations, we have built a model for the $q$-dependent Stoner interaction, which we consequently applied to Sr$_2$RuO$_4$ to estimate superconducting and mass-renormalization electron-paramagnon coupling constants. We found that spin-fluctuation induced $p$-wave superconductivity is possible in Sr$_2$RuO$_4$. The estimated critical temperature, specific heat and susceptibility renormalizations are all in good agreement with experiment.

The recent discovery of superconductivity in the layered ruthenate, Sr$_2$RuO$_4$ [1] has generated new interest in Ru-based perovskites. At first glance this material seems analogous to the high-$T_c$ cuprates. For instance, it has a similar crystal structure (it is isostructural with La$_2$CuO$_4$) and is apparently close to a magnetic instability (Sr$_2$Ca$_{1-x}$RuO$_4$ and Sr$_2$RuYO$_6$ are ferro- and antiferromagnetic, respectively). On the other hand, the more we learn about ruthenates, the less similar to cuprates they seem. While initial interest was largely related to the similarity to the high-$T_c$ materials, now it is more that ruthen-

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ates are deemed interesting *per se*, and, at least in their magnetic properties they are more variegated and probably more interesting than cuprates. Furthermore, it appears that superconductivity in Sr$_2$RuO$_4$ can hardly be understood without a good understanding of magnetism in ruthenium perovskites in general. Thus this paper naturally breaks into two parts. First, we discuss magnetism in ruthenates, specifically antiferromagnetic Sr$_2$RuYO$_6$, ferromagnetic SrRuO$_3$, and paramagnetic CaRuO$_3$. We will show that despite the wide range of magnetic properties, they all are governed by a simple Stoner-type mechanism, which manifests itself differently depending on crystal structure. We then shall show how closeness to a ferromagnetic instability can produce a triplet superconductivity in Sr$_2$RuO$_4$ and explain its normal-state transport properties. We shall also discuss what is currently maybe the most intriguing question in the theory of superconductivity in Sr$_2$RuO$_4$, namely why the experiment shows finite electronic density of states at zero energy (in NMR and specific heat experiments) at as low as 0.3$T_c$.

### 0.1 Magnetism

The great majority of magnetic transition metal oxides are based on the 3$d$-series. Density functional theory in its standard local spin density approximation (LSDA) does not work very well for some of these materials; it often fails to yield the correct magnetic ground state, in many cases it underestimates the magnetic moments, in some others it does not reproduce correct insulating behavior. In such cases it is customary to speak about “strong correlation behavior”. The LSDA is essentially a mean field theory where electron-electron interactions are treated in an averaged way, and the nature of a magnetic instability is related to the standard Stoner model, where the paramagnetic susceptibility, renormalized in the RPA-like manner, may diverge at some wave vector. On the other hand, in the strong correlation picture the zero order approximation is the large-$U$ Hubbard Hamiltonian with an inherent antiferromagnetic instability to it via the superexchange mechanism. The first thing to decide is which of the two basic approaches serves better as the starting approximation.

An important mechanism for magnetic instabilities in a one-electron framework is the “Stoner model”. This is a purely itinerant magnetism approach. In the LSDA the total energy is written as $E = T_s + E_H + E_{e-i} + E_{xc}$, where $T_s$ is the single-particle kinetic energy, $E_H$, $E_{e-i}$, and $E_{xc}$ are the Hartree, the electron-ion, and the exchange-correlation energies, respectively. A ferromagnetic instability is, in this model, an instability with respect to a perturbation consisting of splitting the band by an exchange field, readjusting the Fermi level, and recalculating of $E_{xc}$ taking into account the created magnetic polarization. It is easy to see that the energy between ferromagnetic and the
paramagnetic states in the lowest order in magnetization $M$ is

$$\Delta E = \frac{M^2}{4N(0)} - \frac{M^2}{4} \frac{\delta^2 E_{xc}}{\delta m^2}. \quad (1)$$

The last variation, $I = \delta^2 E_{xc}/\delta m^2$, is called the Stoner parameter. It defines the renormalization of the paramagnetic susceptibility due to spin fluctuations, $\chi = \chi_0/(1 - I\chi_0)$. Note that when the exchange splitting is imposed upon a compound with more than one component, the total magnetization is expressed as $M = \sum_i M_i$, where $M_i$ is the magnetic moment of the $i$-th component and is proportional to its partial DOS at the Fermi level, $M_i/M = N_i(0)/N(0)$. This lets one relate the average Stoner factor for a compound, $I$, with the Stoner factors of the constituent atoms: $4\Delta E_{xc} = -\sum_i M_i^2 I_i = -M \sum_i (N_i/N)^2 I_i$, hence $I = -\sum_i (N_i/N)^2 I_i$. Of course, actual LSDA calculations take into account distortions of the bands as a function of magnetization, as well as the higher order in $M$ terms, neglected in the Stoner model.

Looking at such ruthenates as Sr$_2$RuYO$_6$, SrRuO$_3$, and CaRuO$_3$ from the Stoner point of view, one observes that oxygen $p$-character is present at the Fermi level to a substantially greater extent than in the cuprates or most $3d$ oxides. Calculating the average $I$ for these compounds one finds that the oxygen contribution, $[N_O(0)/N(0)]^2 I_O$ is substantial; if it is neglected, the Stoner criterion $IN(0) \geq 1$ is not satisfied for any of them. If it is included, Sr$_2$RuYO$_6$ and SrRuO$_3$ appear to be unstable against ferromagnetic transitions, while CaRuO$_3$, because of a slightly different DOS, is barely stable. Detailed analysis of the magnetism in these compounds has been published elsewhere [2]. The key ingredient is the strong Ru-O hybridization, which puts O character at $E_F$ and assures the validity of the Stoner model.

One can generalize Stoner approach to antiferromagnetic instabilities. The main difference from the ferromagnetic case is that the DOS in the Stoner formula has to be replaced by the one-electron susceptibility, $N(0) = \chi(0) \rightarrow \chi(Q)$, where $Q$ is the antiferromagnetic vector. What turns out to be important is that if the AFM ordering in question is such that some atoms do not bear a magnetic moment by symmetry, they should be excluded from the calculation of the average Stoner factor. This is the case in SrRuO$_3$, and CaRuO$_3$ where oxygen, bridging two nearest neighbor Ru, cannot acquire a magnetic moment if the two Ru atoms are aligned antiferromagnetically. Correspondingly, the average $I$ for antiferromagnetically ordered (Sr,Ca)RuO$_3$ would be considerably smaller than for ferromagnetic analogues. In Sr$_2$RuYO$_6$ there are no bridging oxygens and the ground state is antiferromagnetic, with the oxygens bearing a large fraction of the total magnetization. This is reproduced by detailed self consistent LSDA calculations.
0.2 Superconductivity

LSDA calculations for Ru-based perovskites generally either predict a magnetic ground state or a paramagnetic state very close to an instability. The quasi-2D Sr$_2$RuO$_4$ is not an exception — LSDA calculations give a Stoner renormalization $(1 - NI)^{-1} = 9$ (experiment gives similar numbers). Thus, one expects strong spin fluctuations to be present in this compound. The situation is similar to Pd metal, where $NI$ is also close to 1. It is very hard to expect that a conventional superconducting state would survive in the presence of such spin fluctuations. In fact, Pd has a sizable electron-phonon interaction and would have been a superconductor apart from spin fluctuations, and in fact becomes such in amorphous state where spin fluctuations are suppressed[3]. On the other hand, it is known (see, e.g., Ref.[4]) that spin fluctuations provide effective repulsion for the singlet ($s, d$) pairing, but attraction for triplet ($p$) pairing. Thus it is tempting to ascribe superconductivity in Sr$_2$RuO$_4$ to the spin-fluctuation induced $p$-wave pairing[5,6]. LSDA calculations can be used as a tool to get a feeling about the size of the attraction provided by exchange of spin fluctuations and whether it is sufficient to explain the superconducting and normal state properties of this material.

The valence bands of Sr$_2$RuO$_4$ are formed by the three $t_{2g}$ Ru orbitals, $xy, yz,$ and $zx.$ These are hybridized with the in-plane oxygen and, to a considerably lesser extent, with the apical oxygen[7,8] $p$-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 Ru $t_{2g}$ levels, and assisting in the $d - d$ hopping. With nearest neighbors only, this gives one nearly circular cylindrical electronic sheet ($\gamma$) 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 ($\alpha$) and an electron one ($\beta$). De Haas-van Alphen experiments confirm this fermiology[9]. In fact, the LDA $\alpha$, $\beta$, and $\gamma$ 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 $\alpha$, $\beta$, and $\gamma$ 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 may be due to some underestimation in LDA calculations of the tiny $xz - yz$ hybridization. Both calculation and experiment give nearly two dimensional Fermi surface: the relative $c$-axis variation of the extremal cross-section areas of the sheets $\beta$ and $\gamma$ is 6% and 1.5%, respectively (for these two sheets the extremal cross-sections are in the planes $k_z = 0$ and $k_z = \pi/c$). For the sheet $\alpha$ the relative change is 2% (for this sheet the extremal cross-sections are in the planes $k_z = 0$ and $k_z = \pi/2c$). Experiment gives the numbers about twice smaller for all three sheets[10]; the difference is larger than the computational error, and presumably has its origin in the effects beyond the density functional theory. We repeated the calculations
using two non-LDA techniques, generalized gradient approximation[11] and weighted density approximation[12], but the numbers hardly changed. In the following all calculational results are from the LDA linearized augmented plane wave calculations[7].

We assume that the exchange of the spin fluctuations is responsible for superconductivity (and for the mass renormalization, to be discussed later). Such an interaction in metals was studied with respect to possible superconductivity in Pd in the late 1970-ties (see, e.g.,[13,14]), and later in connection with heavy fermions. Assuming the Migdal theorem (a common approximation, although not well justified for spin fluctuations), the parallel-spin interaction, relevant for triplet pairing is given by the sum of the bubble diagrams with odd numbers of loops,

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

Here $\chi_0$ is the one-electron susceptibility, given as

$$\chi_0(q) = \sum_{k\alpha,\beta} \frac{f_{k\alpha} - f_{k+q,\beta}}{\epsilon_{k\alpha} - \epsilon_{k+q,\beta}} \langle k\alpha|\exp(iqr)|k+q,\beta\rangle^2,$$  \hfill (3)

with the usual notations. We used the approximation[15] $\chi_0(q) = \chi_0(0) = N(0)$; this is a good approximation for an isotropic two-dimensional Fermi liquid[16]; we are currently investigating the quality of this approximation for Sr$_2$RuO$_4$, which is a two-dimensional, but not isotropic, Fermi liquid (so some modification of $\chi(q)$ due to Fermi surface nesting may be expected). In any case, the $q$-dependence of $I(q)$ is to be taken into account. As discussed in the previous section, for the antiferromagnetic arrangement $I_{AFM} \equiv I(\pi/a, \pi/a) = I_{Ru}(N_{Ru}/N)^2$, while $I_{FM} \equiv I(0) = I_{Ru}(N_{Ru}/N)^2 + 2I_{O}(N_{O}/2N)^2$. Atomic Stoner factors for Ru and O ions are calculated in a standard way and are $I_{Ru} \approx 0.7$ eV, $I_{O} \approx 1.6$ eV. We found $I_{AFM}$ to be smaller than $I_{FM}$ 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 $b^2 = 0.5(a/\pi)^2\Delta I/(I - \Delta I) \approx 0.08(a/\pi)^2$.

Using these numbers, we calculate the effective coupling constant in $p$-channel. Following the suggestion of Agterberg et al[17], we calculate the coupling constants separately for the three bands in question: $xy$ ($\gamma$), $yz$ ($\zeta$), and $zx$ ($\xi$). The corresponding formula is

$$\Lambda_{ij}^p = (N_iN_j/N)\langle V(k - k')|\gamma^i_k \cdot \gamma^j_{k'}|/(v^i_kv^j_{k'})\rangle_{ij},$$  \hfill (4)

where $i$ and $j$ label the three bands, and $v$ is the Fermi velocity. By symmetry,
the coupling matrix is
\[
\begin{pmatrix}
\Lambda^p_{\gamma\gamma} & \Lambda^p_{\gamma\xi} & \Lambda^p_{\gamma\zeta} \\
\Lambda^p_{\gamma\xi} & \Lambda^p_{\xi\xi} & 0 \\
\Lambda^p_{\gamma\zeta} & 0 & \Lambda^p_{\zeta\zeta}
\end{pmatrix} ,
\]
(5)
and we calculate \( \Lambda^p_{\gamma\gamma} = 0.16 \), \( \Lambda^p_{\gamma\xi} = 0.075 \), and \( \Lambda^p_{\gamma\zeta} = 0.025 \). The critical temperature is defined by the maximum eigenvalue of the matrix \((N/N_i)\Lambda^p_{ij}[18]\). The corresponding eigenvector defines the relative magnitude of the order parameter in bands \( \gamma \) and \((\xi, \zeta)\) near \( T_c \). We find the maximum eigenvalue of the corresponding coupling matrix is \( \lambda_p = 0.43 \), and the corresponding superconducting state is \( 0.85\gamma + 0.38\xi + 0.38\zeta \). It is worth noting that using notations of Ref.[17], and taking into account the partial DOS \( N_\gamma : N_\xi : N_\zeta = 0.44 : 0.28 : 0.28 \), the matrix (5) can be translated to the interaction matrix \( U \) as
\[
U = \begin{pmatrix}
u_{\gamma\gamma} & v_{\gamma\alpha} & v_{\gamma\beta} \\
v_{\gamma\alpha} & v_{\alpha\alpha} & v_{\alpha\beta} \\
v_{\gamma\beta} & v_{\alpha\beta} & v_{\beta\beta}
\end{pmatrix} ,
\]
(6)
where \( v_{\gamma\gamma} : v_{\gamma\alpha} : v_{\gamma\beta} : v_{\alpha\alpha} : v_{\alpha\beta} : v_{\beta\beta} = 0.96 : 0.08 : 0.16 : 0.25 : 0.51 : 1 \), to be compared with the value conjectured in Ref.[17], \( 0.09 : 0.09 : 0.09 : 1 : 1 : 1 \). Their hypothesis about the smallness of the nondiagonal elements \( v_{\gamma\alpha} \) and \( v_{\gamma\beta} \) is confirmed by the calculations, but the assumption about the smallness of \( v_{\gamma\gamma} \) is not. In any event, the calculated value of \( \lambda_p = 0.43 \) is sizable, and sufficient to explain the observed superconductivity. We would like to emphasize the role of oxygen in this scenario: if not for the oxygen Stoner factor, the \( q \)-dependence of the effective interaction \( V(q) \) would be so small that the coupling in Eq. (4) would average near zero.

0.3 Renormalization

The mass renormalization is not as easy to define. Besides the parallel-spin interaction (2), 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 [13,19]. In the case of a 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 renormalizations by a
factor of 2 to 3 [13,20]. The present 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 (2) only. The mass renormalization then is computed in the same way as the electron-phonon renormalization, i.e., by taking the average of $V(q)$ of Eq.(2) over the FS. One has to remember, though, that there are other effects beyond the LDA, apart from the one that we calculate, which may further increase the observable mass.

The coupling matrix which defines mass renormalization is written as $\Lambda_{ij}^s = (N_iN_j/N) < V(k-k') >_{ij}$, and the mass renormalization in band $i$ is defined as $\lambda_i^s = \nu_i^{-1} \sum_j \Lambda_{ij}$. The average mass renormalization is $\lambda^s = \sum_{ij} \lambda_{ij}^s$. We calculate $\Lambda_{\gamma\gamma}^s = 0.35$, $\Lambda_{\xi\xi}^s = 0.32$, $\Lambda_{\gamma\xi}^s = 0.16$, $\Lambda_{\xi\xi}^s = 0.03$. This gives $\lambda_{\gamma}^s = (\Lambda_{\gamma\gamma}^s + 2\Lambda_{\gamma\xi}^s)/\nu_{\gamma} = 1.5$, $\lambda_{\xi}^s = (\Lambda_{\xi\xi}^s + \Lambda_{\gamma\xi}^s + \Lambda_{\xi\gamma}^s)/\nu_{\xi} = 1.8$, $\lambda^s = 1.7$, 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, as well as to the omission of the non-Migdal diagrams. In view of the underlying approximations, the agreement is fairly good.

One of the key problems, as discussed in Refs. [21,17], is the residual electronic specific heat[22], which remains at about 50% of its normal value well into the superconducting regime. There are superconducting solutions ("nonunitary states") for triplet pairing that are gapless, that is, have finite density of states at zero energy and zero temperature. However, the pairing energy for such states is lower than for the gapped states considered above. This led Agterberg et al [17] to postulate a pairing matrix that yields a vanishing gap for the $\gamma$ band. This, however, does not square with the quantitative estimate presented here. An earlier assumption[21,6] was that the excess pairing energy that forbids nonunitary combination of the order parameters 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[23]. However, a quantitative estimate according to Ref.[23] shows that the effect is by far too weak. The criterion is $\left[ T_c d \frac{\log N}{d E_F} \right]^2 \frac{1}{1-IN} \log \frac{\omega_{sf}}{T_c} \sim 10^{-5}$, while it should be of the order 1 for the nonunitary state to exist.

Another possibility is related to an observation made a decade ago in connection with the high-$T_c$ superconductivity[24]: A well-known fact is that virtual phonons, even in a strongly coupled system, have no pair-breaking effect, so
that the density of states remains zero below the gap at zero temperature in a clean superconductor. However, this is a consequence of an internal symmetry of the Eliashberg equations, namely that the coupling function $\alpha^2 F(\omega)$, entering the equation on $\Delta$, is the same as $\alpha^2 F(\omega)$, entering the equation on $Z$. In case of $p$-wave pairing, for instance, this is not true any more, and formally there is finite density of states inside the gap at any temperature. Unfortunately, direct calculations\cite{25} show that this effect is quantitatively strong only if a noticeable part of $\alpha^2 F(\omega)$ exists at $\omega < \Delta$, which is not the case in Sr2RuO4.

Maybe the simplest explanation of the “residual DOS mystery” is still the most plausible. Despite the large mean free path, which in the reported 1.35 K samples reaches 1500-2000 Å\cite{26}, this superconductor is still in the dirty limit: the Abrikosov-Gor’kov pair-breaking parameter $\gamma = 1/2\tau \Delta = \pi \xi_0 / 2 l_{m.t.p.} = 0.7$, using the value for the coherence length $\xi_0 = 1000$ Å\cite{27}. Nonmagnetic impurities in a unitary 2D $p$-wave superconductor act as magnetic impurities in an $s$-wave superconductor. The DOS is given by the standard expression

$$N(E)/N_{\text{norm}} = Re \frac{u(E)}{\sqrt{u(E)^2 - 1}}$$

where $u(E)$ satisfies the equation

$$E = u - \gamma x / \sqrt{1 - x^2}$$

The resulting DOS at $T = T_c/3$ is shown on Fig.1 and is seen to be very large below the gap (and does not show any trace of piling of the DOS above the gap).

0.4 Conclusions

To summarize, we have presented first principles calculations indicating that 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 of Sr$_2$RuO$_4$.

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Fig. 1. Relative density of states at $T = 0.3T_c$ in Abrikosov-Gor’kov theory for pair-breaking parameters $\gamma = 0$, 0.07, and 0.7. We estimate that for 1.35 K superconducting samples the pair breaking parameter $\gamma$ is at least 0.7.
