On the origin of the Non-Fermi Liquid Behavior of SrRuO$_3$.

M. S. Laad and E. Müller-Hartmann

Institut für Theoretische Physik, Universität zu Köln, 77 Zülpicher Strasse, 50937 Köln, Germany
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Motivated by the unusual features observed in the transport properties of the ferromagnetic "bad metal" SrRuO$_3$, we construct a model incorporating essential features of the realistic structure of this nearly cubic material. In particular, we show how the $t_{2g}$ orbital orientation in the perfectly cubic structure determines the peculiar structure of the hybridization matrix, and demonstrate how the local non-Fermi liquid features arise when interactions are switched on. We discuss the effects of the slight deviation from the cubic structure qualitatively. The model provides a consistent explanation of the features observed recently in the optical response of SrRuO$_3$.

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Strongly correlated electronic systems continue to present new surprises in condensed matter physics. In particular, d-electron systems exhibit fascinating phenomena, from unconventional high-$T_c$ superconductivity to colossal magnetoresistance [1]. These dramatic behaviors are believed to be associated with the fact that the important electronic states are often intermediate between the itinerant and localized limits, necessitating the development of new ideas [2].

Ruthenates constitute a class of d-band oxides occurring in both layered [3,4] as well as nearly cubic forms. The electronic states responsible for both conduction and magnetism (or superconductivity) are associated with bands which involve Ru-4d orbitals hybridized with the O-2p states. The cubic material SrRuO$_3$ exhibits a transition from a high-$T$ paramagnetic metallic to a ferromagnetic metallic state below $T_c^{FM} = 150K$ [5]. State-of-the-art bandstructure calculations do produce this basic feature [6]. However, photoemission [7] measurements reveal a much reduced spectral density at the Fermi surface, compared to the results from a bandstructure calculation. Moreover, the authors of [7] do not observe a clear separation between the "coherent" and incoherent parts of the spectral function, suggesting that the low-energy spectral weight may have a significant incoherent contribution. The mass enhancement factor deduced from this is in excellent agreement with that extracted from the low-$T$ specific heat, showing the importance of correlation effects. More unusual features are observed in transport studies. At low $T$, a resistivity minimum is observed even as the resistivity itself is very low [8,9,10]. At higher $T > T_c^{FM}$, $\rho_{dc}(T)$ increases linearly with $T$, passing through the Ioffe-Regel limit [8] without saturation. It exhibits a kink at $T_c^{FM}$ and continues to increase up to 1000K. In other words, one is dealing with a situation where $k_{B}T \approx 1$ (already for $T \approx 500K$), suggesting the inapplicability of Boltzmann equation approaches for transport. In fact, this similarity with other "bad metals", as well as with dilute ferromagnetic alloys [8], suggests that a local picture (as opposed to a band description) for transport is required for SrRuO$_3$. Near $T_c^{FM}$, anomalous critical behavior in $\rho_{dc}(T)$ has been found by Klein et al. [10]. That this is not related to magnetic critical behavior is shown by the fact that the magnetization data are well fit with conventional universal critical exponents. This line of thinking is further reinforced by a recent study [10] probing the deviations from Matthiessen's rule (DMR) in SrRuO$_3$ and CaRuO$_3$. The latter is not a ferromagnet down to the lowest temperatures. Interestingly, however, the similarity in the radiation-induced change in the resistivity for both samples indicates that the observed DMR is not caused by magnetic ordering. More recently, Kostic et al. [11] have studied the infrared conductivity of SrRuO$_3$ from $50 cm^{-1}$ to $40000 cm^{-1}$ at temperatures ranging from 40K to 300K. Quite astonishingly, $\sigma(\omega) \propto \omega^{-\alpha}$ with $\alpha = 1/2$ deep into the ferromagnetic phase ($T = 40K$) instead of the $\omega^{-2}$ form characteristic of Fermi liquids. This form is close to the phenomenological fit used for doped cuprates [12]. Motivated by the strong correlation features observed experimentally, Ahn et al. [13] attempted to model the optical spectrum in terms of the response of a one-band Hubbard model in $d = \infty$. However, the low-$T$ response in the $d = \infty$ Hubbard model is that of a correlated Fermi liquid, and Ahn et al. themselves point out the importance of extra scattering mechanisms to understand the non-FL fall-off in $\sigma(\omega)$. In particular, they speculate that factors like the $p-d$ hybridization and its interplay with Mott-Hubbard physics might provide some insight into the physics of ruthenates. Given the similarity in their optical response, one might be tempted to look for a possible explanation in terms of theories proposed to understand the non-FL metallic phase of cuprates. In sharp contrast to the cuprates, however, SrRuO$_3$ is not close to any quantum critical point. There are no antiferromagnetic spin fluctuations, neither does it undergo a Mott transition. Actually, it is not clear whether SrRuO$_3$ is close to a Mott transition. The FM spin fluctuations cannot be the cause of the non-FL features, since these features are observed well below $T_c^{FM}$. The scattering rate extracted from an extended "Drude" fit increases linearly with frequency, and remains high above $T_c^{FM}$.
At high $T > T_{c}^{FM}$, $\sigma(\omega)$ even appears to increase with frequency in the far-infrared, reminiscent of strongly disordered systems. However, the nature of such strong scattering and, in particular, its microscopic origin, is completely unclear, given that this system has negligible extrinsic disorder [8]. One is led, therefore, to search for the origin of the (intrinsic) strong scattering in the peculiarities of the material itself.

A proper understanding of the anomalies should, in the final analysis, be linked to the peculiarities in the local quantum chemistry (or the basic electronic structure) of this material. In this connection, it is interesting to notice that Cox et al. [14] have reported three flat bands crossing the Fermi surface: one $e_{g}$ band between $\Gamma$ and $X$, and two $t_{2g}$ bands between the $X$ and $M$ points in the Brillouin zone. The microscopic origin of these features are, however, completely obscured in the numerics.

The appearance of a ferromagnetic metallic state at low $T$ in SrRuO$_{3}$ is understood as follows. In SrRuO$_{3}$, the crystal field breaks the first Hund’s rule and the four Ru $d$ electrons then partially fill the $t_{2g}$ states, giving rise to a local spin $S = 1$ at each site, consistent with the measured magnetization ($M \simeq 1\mu_{B}$) at low $T$. The $t_{2g}$ configuration implies a three-fold orbital degeneracy since the fourth electron can go into any of the three $t_{2g}$ orbitals. If this was the whole story (i.e., if we ignored the $O - 2p$ bands), one would expect SrRuO$_{3}$ to be a $S = 1$, antiferromagnetic Mott insulator (probably with some kind of orbital ordering). We claim that this orbital degeneracy in the perfectly cubic system is the origin of the strong intrinsic scattering observed experimentally (see below). Bandstructure calculations [14] as well as photoemission measurements, however, point to the important role of self-doping in this material, introducing a small concentration of holes into the $O - 2p$ band via charge transfer processes, which put a small concentration of additional electrons into the $t_{2g}$ orbitals. The Ru $4d_{x^{2}y^{2}-z^{2}}$O $2p$ hybridization then drives the resulting mixed-valent system metallic and ferromagnetic via the double-exchange mechanism.

In this letter, we propose a microscopic model for SrRuO$_{3}$ which ties together (i) the local quantum chemistry, (ii) the relevant interactions, and (iii) the observed non-Fermi liquid anomalies within one approach. In particular, we show how the $t_{2g}$ orbital orientation determines the peculiar structure of the hybridization matrix (see below), and how the NFL behavior arises (within a single-impurity picture) when local coulomb interactions are switched on.

We start by deriving the hybridization (Ru $4d_{x^{2}y^{2}-z^{2}}$O $2p$) matrix for the nearly cubic structure of SrRuO$_{3}$. To begin with, we shall assume a perfect cubic structure, and consider the effects of the slight distortion later in the paper.

Considering the local orbital structure of the Ru $- O$ octahedron, the relevant electronically active states involve the hybridization of the triply degenerate $Ru - 4d_{x^{2}y^{2}-z^{2}}$ and $O - 2p_{x,y,z}$ states. In this situation, the hopping part is written as

$$H_{hop} = -t \sum_{\mathbf{k}\sigma}[d_{y\mathbf{k}\sigma}^{\dagger}P_{\sigma} + c.t. + h.c.]$$

where $P_{\sigma} = (p_{y,1-x/2,\sigma} - p_{y,1-x/2,\sigma} + p_{x,1-y/2,\sigma} - p_{x,1-y/2,\sigma})$ and $p_{\alpha,1/2} \sigma$ means the $p_{\alpha}$ orbital placed at the center of the bond(s) leaving site $i$ in the $\pm \beta$ direction. In eqn. (1), c.t. (cyclic terms) means terms which arise by a cyclic permutation of $x, y, z$. Notice that the $d_{xy}$ orbital does not hybridize with $p_{z,1/2,\sigma}$ and $p_{\alpha,1/2,\sigma}$ ($\alpha = x, y$) because of symmetry reasons. It is precisely this peculiarity resulting from the local quantum chemistry of SrRuO$_{3}$ which, together with the orbital degeneracy mentioned above, is responsible for its anomalous behavior, as we show below.

The hopping part of the hamiltonian eqn. (1) describes a planar hybridization of each of the $t_{2g}$ 4d-orbital of Ru with a hybridizing $O-2p$ (Wannier) orbital in close formal analogy to the $3d_{x^{2}-y^{2}} - 2p_{\sigma}$ hybridization in the CuO$_{2}$ planes in cuprates.

In order to make the peculiarity mentioned above more transparent, we Fourier transform the hopping part (1), giving,

$$H_{hop}(t_{2g}) = -2it \sum_{\mathbf{k}\sigma}[d_{y\mathbf{k}\sigma}^{\dagger}(s_{x}p_{yz}\mathbf{k}\sigma + s_{y}p_{zy}\mathbf{k}\sigma)] + c.t. + h.c.).$$

(2)

using the short notations, $s_{\alpha} = \sin(k_{\alpha}/2)$ ($\alpha = x, y, z$), and defining the hybridizing (Wannier) orbitals, $w_{yz,\mathbf{k}} = -i(s_{y}p_{z}\mathbf{k})/f_{yz}, w_{xy,\mathbf{k}} = -s_{y}p_{xz}\mathbf{k}/f_{xy}$, and $w_{xy,\mathbf{k}} = -i(s_{x}p_{yz}\mathbf{k} + s_{y}p_{xy}\mathbf{k})/f_{xy}$. Writing $f_{\alpha,\beta} = (s_{\alpha} + s_{\beta})^{1/2}$ and going back to the Wannier representation we get, finally,

$$H_{hop}(t_{2g}) = -t \sum_{\mathbf{k}}[T_{\sigma,\mathbf{k}}(m)d_{y\mathbf{k}\sigma}] + c.t. + h.c.).$$

(3)

with $T_{\sigma,\mathbf{k}}(m) = 2(s_{\sigma} + s_{\beta})^{1/2}e^{ik\cdot\mathbf{m}}$. Thus, in the perfect cubic symmetry, the bandstructure is purely two-dimensional in each direction solely as a consequence of the orbital orientation.

We now consider the interaction part of the Hamiltonian. The local, intra-orbital Hubbard interaction is large, as can be seen from the satellite feature in photoemission being situated $\approx 5eV$ below the Fermi energy. We can thus roughly estimate $U_{dd} \approx 5eV$ (the results obtained below are insensitive to its actual value). The Hund’s rule coupling is of the order of magnitude of the exchange splitting ($\approx 0.5eV$). The nearest neighbor Ru $- O$ interaction, $U_{pd}$, can be estimated to be $U_{pd} \approx (e^{2}/ae) \approx 1.5 - 2eV$. Setting $U_{dd} \rightarrow \infty$, we write the interaction term as [15],
\[ H_{\text{int}} = U_{pd} \sum_{\langle lm \rangle \sigma} n_{lda}(n_{l+m,w,\sigma'}^d + n_{l-m,w,\sigma'}^d + n_{l+m,w,\sigma}). \]  

(4)

Thus, the total Hamiltonian reads

\[ H = H_{\text{hop}}(t_{2g}) + H_{\text{int}}. \]  

(5)

The peculiar feature coming from the local quantum chemistry of \( \text{SrRuO}_3 \) is now clear. The \( w_{za} \) do not hybridize with the \( d_{xy} \) orbitals, but interact with a strength \( U_{pd} \). The \( w_{za} \) do not hybridize with the \( d_{yz} \), and the \( w_{ya} \) do not hybridize with the \( d_{z} \). Hence, for example, the term

\[ U_{pd} \sum_{\langle lm \rangle \sigma} n_{ldxy\sigma} n_{l+m,w,\sigma}, \]

provides a nonhybridizing (screening) channel that strongly scatters the \( d \)-band carriers. Within the impurity approximation, local non-Fermi liquid behavior [16] now arises from the competition of this term, which drives the system to a non-FL state characterized by X-ray edge singularities, and the hybridization term.

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the three-fold orbital degeneracy in the $t_{2g}$ sector will be slightly lifted, and that the hybridization matrix will contain a small term corresponding to $d_{xy}-w_z$ hybridization. Indeed, we expect that the strict orthogonality of the $p_{x,y,z}$ orbitals in the perfect cubic structure is violated in the presence of a slight lattice distortion, resulting in a term $t'_{pd} \sum_{\sigma} (d_{xy}^{\alpha} p_{k+1/2, \pm \sigma} + h.c.)$ in eqn.(1). We expect the non-FL behavior (the infrared singularity of the X-ray edge type) to be cut off by a low-energy quasicoherent scale related to $t'_{pd}$. At sufficiently low-$T$, (within the local approach) $t'_{pd}$ will become relevant [20], making the system scale to a low-$T$ FL fixed point. Given the small distortion observed in $SrRuO_3$, we expect this scale to be quite small, consistent with the $T_0 = 40K$ [21] below which a $T^2$ component in the dc resistivity is indeed observed. A quantitative estimate of $T_0$ is, however, out of the scope of the present work.

In conclusion, we have developed a model incorporating the basic local quantum chemical aspects of the structure of the nearly cubic ferromagnetic "bad metal" $SrRuO_3$. We have pointed at the three-fold degeneracy of the $t_{2g}$ configuration, as well as at the peculiar features in the hybridization matrix, whose structure is controlled by the orbital orientation in the $t_{2g}$ sector, and is effectively two-dimensional in the perfectly cubic structure. Finally, we have shown how a non-Fermi liquid metallic state is generated within an impurity picture when interactions are switched on, and argued how a small distortion cuts off the low-energy singularity, generating a low energy coherence scale. The model explains the non-FL features observed in optical spectra in a consistent way.

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REFERENCES
[1] M. Imada, A. Fujimori and Y. Tokura, Rev. Mod. Phys. 70, 1039 (1998).
[2] A. Georges, et al., Rev. Mod. Phys. 68, 13 (1996).
[3] Y. Maeno, Physica C 282-287, 206 (1997).
[4] Tamio Oguchi, Phys. Rev. B 51, 1385 (1995).
[5] C. B. Eom et al., Science 258, 1766 (1992).
[6] P. B. Allen et al., Phys. Rev. B 53, 4393 (1996).
[7] K. Fujioka et al., Phys. Rev. B 56, 11, 6380 (1997).
[8] T. H. Geballe et al., J. Phys. Cond. Matt. 8, 10111 (1996).
[9] G. Cao et al., Phys. Rev. B 56, 321 (1997).
[10] L. Klein et al., Phys. Rev. Lett. 77, 2774 (1996).
[11] P. Kostic et al., Phys. Rev. Lett. 81, 2498 (1998).
[12] P. W. Anderson, Phys. Rev. B 55, 11785 (1997).
[13] J. S. Ahn et al., Phys. Rev. Lett 82, 5321 (1999).
[14] P. A. Cox et al., J. Phys. Cond. Matt. 16, 6221 (1983).
[15] Terms like $U_{pd} \sum_{\sigma} \sum_{i,j} n_{ia \sigma} n_{ip' \sigma}$ will be generated in general. However, these have no qualitative effect on the discussion in the text, since they do not modify the main feature coming from the competition of the hybridization and the presence of the screening channel in our model. [16] See the Reference [2], and references therein relating to the "solution" of the multiband Hubbard model with extra screening channels in $d = \infty$.
[17] G. M. Zhang and L. Yu, Phys. Rev. Lett. 81, 4192 (1998).
[18] K. D. Schotte et al., Phys. Rev. 182, 479 (1968).
[19] P. W. Anderson, Phys. Rev. B 55, 11785 (1997).
[20] The effect of $t'_{pd}$ is to block the singularity caused by strong scattering of the "light" $p$ carriers by the "infinitely heavy" $d$-hole (caused by $U_{pd} \sum_{\sigma} n_{io \sigma} n_{ip' \sigma}$); the problem then becomes equivalent to allowing the infinitely heavy $d$-hole to acquire a heavy, but finite mass, leading to recoil and destruction of the low-energy singular features below a temperature (energy) scale related to $t'_{pd}$. See E. Müller-Hartmann et al., Phys. Rev. B 3, 1102 (1971).
[21] A. P. MacKenzie et al., Phys. Rev. B 58, 13318 (1998).