^{17}O NMR Evidence for Orbital Dependent Ferromagnetic Correlations in Sr_2RuO_4

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We probed spin correlations in Ru $4d_{xy}$ and $4d_{yz,zx}$ orbitals *separately* in the unconventional metallic state of Sr_2RuO_4 by ^{17}O NMR. We establish that spin correlations are orbital dependent, and only the Ru $4d_{xy}$ spin susceptibility χ_{xy} increases significantly with decreasing temperature prior to the crossover to the canonical Fermi liquid state at $T_{FL} = 25$ K. The temperature dependence of ^{17}O and ^{101}Ru nuclear spin-lattice relaxation rates $^{17,101}1/T_1$ uncovers interplay between the growth of ferromagnetic spin fluctuations and anomalous charge transport properties. [S0031-9007(98)07281-0]

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Sr_2RuO_4 [1] has the identical layered perovskite structure as the prototype high T_c superconductor $(La, Ba)_2CuO_4$. The discovery of superconductivity near 1 K [2] enhanced interest in the physical properties of the RuO_2 square lattice [2–9]. The resistivity ρ_{ab} along the ab plane (RuO_2 plane) and ρ_c along the c axis are highly enhanced due to electron-electron correlations. ρ_c shows a crossover from metallic to semiconducting behavior above $T^* \equiv 80$ K [2]. Both ρ_{ab} and ρ_c are proportional to T^2 below $T_{FL} \equiv 25$ K, indicating that a crossover to a canonical Fermi-liquid state takes place below 25 K prior to the superconducting transition [2]. The nature of the Fermi liquid state and the crossover to it has been a focus of intensive experimental and theoretical [10–14] investigation to clarify the mechanism of superconductivity.

On the other hand, the magnetic properties of RuO_2 planes and their interplay with charge transport properties have been almost entirely unknown. A major source of complications is that there are four electrons in three nearly degenerate Ru t_{2g} orbitals (i.e., $4d_{xy}$, $4d_{yz}$, and $4d_{zx}$). In addition, the crystal field, the spin-orbit interaction, and Hund's coupling compete with each other. The only consensus is that the total spin susceptibility at the low temperature limit is enhanced by a factor of 4 to 8 [2,7,9,10] over the LDA (local density approximation) calculations [11], again pointing towards correlation effects. Since the cubic perovskite $SrRuO_3$ is an itinerant ferromagnet with Curie temperature 150 K and spin $S = 1$ due to the strong Hund's coupling [15], a popular *assumption* is that Sr_2RuO_4 has spin $S = 1$ with predominantly ferromagnetic spin correlations. However, the presence of the van Hove singularity similar to that in high T_c cuprates [16] gives rise to a possibility that antiferromagnetic spin fluctuations are also enhanced for finite wave vector $\mathbf{q}$ near (π, π) [17]. In fact, if the Sr^{2+} ions are replaced with Ca^{2+} ions, Ca_2RuO_4 forms an insulating antiferromagnet [18], suggesting a subtle competition between ferro- and antiferromagnetic spin correlations.

Based on the scenario of ferromagnetic correlations with $S = 1$, Rice and Sigrist proposed that the modest ferromagnetic enhancement in the Fermi liquid state of Sr_2RuO_4 favors a p-wave superconductivity similar to that realized in liquid ^{3}He [10]. More recently, Agterberg, Rice, and Sigrist [12] emphasized the necessity of distinguishing the properties of the Ru $4d_{xy}$ and $4d_{yz,zx}$ orbitals in order to account for the p-wave-like superconducting properties [5,9,19].

In principle, NMR should be able to cast light from a microscopic viewpoint on the orbital dependent spin correlations and their interplay with anomalous charge transport properties, in addition to the superconducting pairing state probed by Ishida *et al.* in their ^{101}Ru NMR experiments conducted below 4.2 K [9]. Unfortunately, the intensity of ^{101}Ru NMR is miserably weak above 4.2 K, limiting the earlier NMR study to the vicinity of T_c deep inside the canonical Fermi liquid state. Moreover, since Ru NMR probes only an average of the magnetic behavior of four electrons in three t_{2g} orbitals, a different approach is necessary to probe *separately* the magnetic properties of $4d_{xy}$ and $4d_{yz,zx}$ orbitals.

In this Letter, we report the first ^{17}O NMR in ^{17}O isotope-enriched aligned single crystals of Sr_2RuO_4 between 4.2 and 500 K [20]. We also succeeded in detecting ^{101}Ru NMR up to 300 K despite the extremely weak signal intensity above 4.2 K. Our NMR measurements provide the first experimental evidence for *orbital and temperature dependent* spin susceptibility. We demonstrate that only the spin susceptibility χ_{xy} from the electrons in the Ru $4d_{xy}$ orbital shows significant temperature dependence. Moreover, we present the first experimental evidence that the spin correlations are predominantly *ferromagnetic* in origin, and low frequency ferromagnetic spin fluctuations grow with decreasing temperature down to T_{FL}. Our NMR observation of magnetic crossovers at T_{FL} and T^* calls for further theoretical investigation into the interplay between ferromagnetic spin correlations, anomalous charge transport properties, and the mechanism of superconductivity.

We conducted all the ^{17}O and ^{101}Ru NMR between 7.4 and 9 T for aligned single crystals grown by the floating zone technique. We enriched the crystals with ^{17}O isotope by annealing in $^{17}O_2$ gas at 900 °C. We observed two sets of quadrupole-split ^{17}O NMR signals. We identified the

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signals with the nuclear quadrupole interaction tensor axially symmetric around the c axis as the apical O(2) site. Our results of the ^{101}Ru Knight shift ^{101}K and the nuclear spin-lattice relaxation rate $^{101}1/T_1$ at 4.2 K agreed with those reported by Ishida *et al.* [9].

In Fig. 1(b), we present the temperature dependence of the ^{17}O NMR Knight shifts $^{17}K(1,2)$ for the planar O(1) and apical O(2) site. In general, Knight shifts have spin and orbital contributions, $K_{\rm spin}$ and $K_{\rm orb}$ [21,22]. $K_{\rm spin}$ is proportional to uniform spin susceptibility $\chi_{\rm spin}$, while $K_{\rm orb}$ originates from orbital currents and is temperature

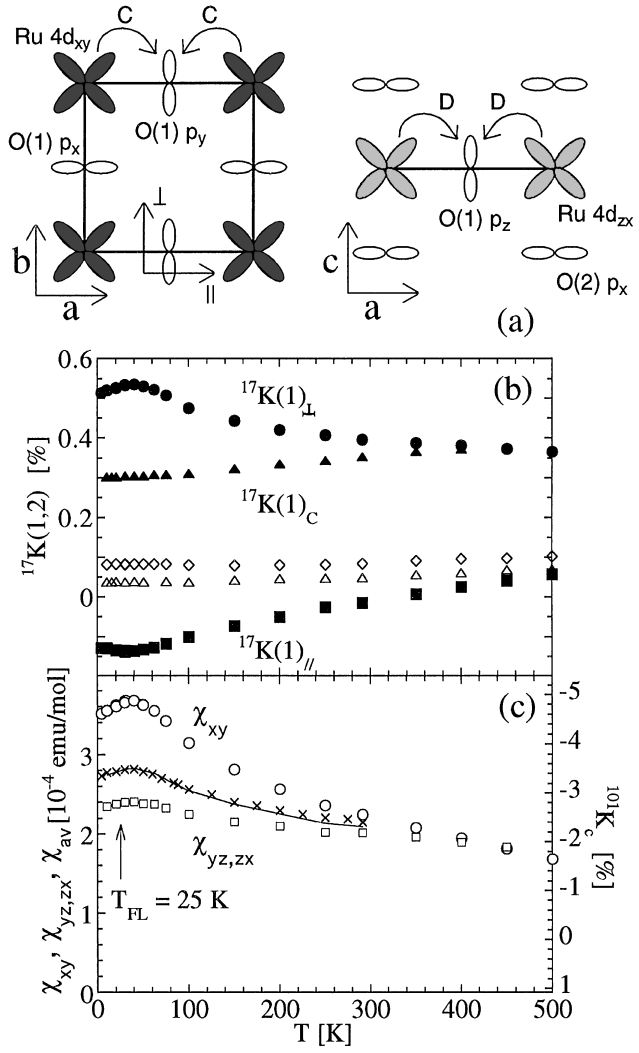

FIG. 1. (a) Top view (left panel) and side view (right panel) of the local geometry of the RuO_2 plane (Ru $4d$ and O $2p\pi$ orbitals). (b) ^{17}O NMR shift $^{17}K(1,2)$ at the planar O(1) and apical O(2) sites. $^{17}K(1)_c$ [▲], $^{17}K(1)_{\parallel}$ [■], $^{17}K(1)_{\perp}$ [●], $^{17}K(2)_c$ [△], and $^{17}K(2)_{ab}$ [◇]. (c) The uniform spin susceptibility χ_{xy} of $4d_{xy}$ orbital [○] and $\chi_{yz,zx}$ of $4d_{yz,zx}$ orbital [□], deduced from $^{17}K(1)$ based on Eqs. (1a)–(1c) with $C = D = 34$ kOe/μ_B. Also plotted are the average $\chi_{av} \equiv (\chi_{xy} + 2\chi_{yz,zx})/3$ [solid line], and ^{101}Ru Knight shift $^{101}K_c$ [×]. Notice that we invert the scale of $^{101}K_c$ to account for the negative hyperfine coupling, and offset the origin by 1.08% [9] to account for $^{101}K_{\rm orb}$.

independent. In what follows, we ignore the small contribution of $^{17}K_{\rm orb}$ (typically $^{17}K_{\rm orb} \lesssim 0.03\%$ [23]). If we plot $^{17}K(1)$ measured for one direction versus another as implicit functions of temperature, we do not obtain linear relations (not shown). We also found that $^{17}K(1)$ and Ru Knight shift along the c axis, $^{101}K_c$, do not show a linear relation either. Without any further analysis, these findings imply the existence of more than one separate component of spin susceptibility.

Recalling that there are four $4d$ electrons in three orbitals, we need to separate the temperature dependence of χ_{xy} and $\chi_{yz,zx}$ of the Ru $4d_{xy}$ and $4d_{yz,zx}$ orbitals in the total spin susceptibility, $\chi_{\rm spin} = \chi_{xy} + 2\chi_{yz,zx}$. (Notice that $4d_{yz}$ and $4d_{zx}$ orbitals are equivalent in the tetragonal symmetry.) On general grounds [22] we write ^{17}K as

$$^{17}K(1)_c = \frac{1}{N_A\mu_B}(-C\chi_{xy} + 2D\chi_{zx} + \sigma\chi_{2s}), \quad (1a)$$

$$^{17}K(1)_{\parallel} = \frac{1}{N_A\mu_B}(-C\chi_{xy} - D\chi_{zx} + \sigma\chi_{2s}), \quad (1b)$$

$$^{17}K(1)_{\perp} = \frac{1}{N_A\mu_B}(2C\chi_{xy} - D\chi_{zx} + \sigma\chi_{2s}), \quad (1c)$$

where N_A is Avogadro's number, and the subscripts c, $\parallel$, and $\perp$ indicate the direction of the applied magnetic field $\mathbf{H}$, as defined in Fig. 1(a). Because of the covalency of π bonds, spin polarization in the Ru $4d_{xy}$ and $4d_{zx}$ orbitals is transferred to the O $2p_y$ and $2p_z$ orbital, respectively. We represent the dipole hyperfine fields [21] from these $2p$ orbitals to the ^{17}O nuclear spin as C and D, respectively, as shown in Fig. 1(a). The dipole field takes the maximum value along the lobe of the $2p$ orbital, and $-1/2$ of the maximum value along the two orthogonal directions [21]. We note that other spin transfer processes are prohibited by the orthogonality between Ru $4d$ and O $2p$ orbitals. The third term $\sigma\chi_{2s}$ in Eqs. (1a)–(1c) is added to account for a nearly temperature independent isotropic component of ^{17}K [24]. We tested the validity of Eqs. (1a)–(1c) by taking rotational spectra with $\mathbf{H}$ in the RuO_2 plane, and confirmed the sinusoidal modulation due to the axial symmetry of the dipole fields.

By subtracting Eq. (1b) from Eqs. (1a) and (1c), we can separate $\chi_{xy} = N_A\mu_B[^{17}K(1)_{\perp} - {}^{17}K(1)_{\parallel}]/3C$ and $\chi_{yz,zx} = N_A\mu_B[^{17}K(1)_c - {}^{17}K(1)_{\parallel}]/3D$. We plot the results in Fig. 1(c) by setting the magnitude of the vertical axis as described in the next paragraph. Surprisingly, uniform spin susceptibility χ_{xy} increases monotonically with decreasing temperature down to ~40 K, turns over, and then tends to level below $T_{\rm FL}$ in the canonical Fermi liquid state, indicating a clear connection to the crossover in charge transport measurements. On the other hand, the temperature dependence of $\chi_{yz,zx}$ is much weaker. Physically, orbital dependent behavior of Ru $4d$ spin susceptibility indicates that the Hund's coupling is not strong enough to bind all four electron spins, and the spin degrees of

freedom in the $4d_{xy}$ and $4d_{yz,zx}$ orbitals behave more or less independently at least down to $T_{\rm FL}$.

Next, we will discuss the quantitative aspect of χ_{xy} and $\chi_{yz,zx}$. Since we have found that $\chi_{yz,zx}$ shows little temperature dependence, we can match the observed increase of the bulk susceptibility data $\chi_{\rm bulk}$ [7,18,25] below 300 K to the increase of χ_{xy} in Fig. 1(c). Thus we obtain $\chi_{xy} \sim 3.6 \times 10^{-4}$ emu/mol at 4.2 K, and $C \approx 34$ kOe/μ_B. By subtracting χ_{xy}, the orbital contribution $\chi_{\rm orb} \sim 1.5 \times 10^{-4}$ [9], and the core diamagnetic contribution $\chi_{\rm dia} \sim -0.96 \times 10^{-4}$ emu/mol from the observed bulk susceptibility, $\chi_{\rm bulk} \sim 9 \times 10^{-4}$ emu/mol [7], we obtain $\chi_{yz} = \chi_{zx} \sim 2.4 \times 10^{-4}$ emu/mol at 4.2 K, which also implies $D \approx 34$ kOe/μ_B. Our results indicate that χ_{xy} accounts for ~40% of the total spin susceptibility in the canonical Fermi liquid state below $T_{\rm FL}$, and χ_{yz} and χ_{zx} contribute ~30% each. We note that relatively large uncertainties in bulk susceptibility data [7,18,25] leave corresponding uncertainties (~30%) in our estimate of the *magnitude* of C, D, χ_{xy}, and $\chi_{yz,zx}$, but none of the fundamental conclusions of this Letter depend on the numerical details discussed in this paragraph.

To test the preceding analysis, in Fig. 1(c) we compare the average spin susceptibility of all three t_{2g} orbitals, $\chi_{av} = (\chi_{xy} + 2\chi_{yz,zx})/3$, and the ^{101}Ru Knight shift $^{101}K_c$. Since the filling of $4d_{xy}$, $4d_{yz}$, and $4d_{zx}$ orbitals is nearly even, i.e., 1.28, 1.36, and 1.36 electrons, respectively [3,11], χ_{av} represents the average spin susceptibility of four electrons in three t_{2g} orbitals. On the other hand, $^{101}K_c$ also probes an average of the spin susceptibility of four electrons through the isotropic hyperfine fields arising from the inner core polarization by all three t_{2g} orbitals [22]. Accordingly, we expect that $^{101}K_c \propto \chi_{av}$. The agreement with this proportionality in Fig. 1(c) confirms the consistency of our analysis.

Finally, we turn our attention to the spin dynamics. In general, the nuclear spin-lattice relaxation rate $1/T_1$ satisfies the following formula [22]:

$$\frac{1}{T_1 T} = \frac{\gamma_n^2}{\mu_B \hbar} \sum_{j,\mathbf{q}} [|A_j(\mathbf{q})_a|^2 + |A_j(\mathbf{q})_b|^2] \frac{\chi_j''(\mathbf{q}, \omega_n)}{\omega_n}, \quad (2)$$

where the subscript j represents the jth orbital, and $\chi_j''(\mathbf{q}, \omega_n)$ is the imaginary part of the dynamical electron spin susceptibility at wave vector $\mathbf{q}$ and NMR frequency ω_n. The quantization axis of $1/T_1$ measurements is the c axis. The hyperfine form factor $|A_j(\mathbf{q})_{a,b}|^2$ is $\mathbf{q}$ independent for $^{101}1/T_1$ at the Ru site [26], and is proportional to $\cos^2(q_{x,y}/2)$ with a proportionality constant that is a function of C and D for $^{17}1/T_1(1)$ at the O(1) site [22]. This means that in principle $^{101}1/T_1T$ can sense both ferromagnetic and antiferromagnetic spin fluctuations. On the other hand, the form factor for the planar O(1) site is zero at the staggered wave vector $\mathbf{q} = (\pi, \pi)$ due to geometrical cancellation of the antiferromagnetic component of transferred hyperfine fields. Accordingly, antiferromagnetic spin fluctuations do not contribute to $^{17}1/T_1(1)T$ [23]. Therefore, one can test whether the spin correlations are ferromagnetic or antiferromagnetic in origin by comparing $^{17}1/T_1(1)T$ and $^{101}1/T_1T$.

In Figs. 2(a) and 2(b), we compare the temperature dependence of $1/T_1$ and $1/T_1T$, respectively. Evidently, O(1) and Ru sites show identical temperature dependence. To the best of our knowledge, this is the first experimental demonstration that the spin correlations in the RuO_2 plane are predominantly *ferromagnetic* in origin. Furthermore, we found that both $^{17}1/T_1(1)T$ and $^{101}1/T_1T$ increase monotonically down to $T_{\rm FL}$, and almost saturate in the canonical Fermi liquid state [27]. Besides the crossover at $T_{\rm FL}$, both $^{17}1/T_1(1)$ and $^{101}1/T_1$ show a kink at T^*, as indicated in Fig. 2(a). This means that the growth of ferromagnetic spin fluctuations as measured by $1/T_1T$ begins to saturate at T^*, where the c-axis resistivity ρ_c crosses over from semiconducting to metallic behavior upon cooling [2,8]. In passing, the smaller values of $^{17}K(2)$ and $^{17}1/T_1(2)$ imply weaker spin polarization at the apical O(2) site transferred from the RuO_2 planes, reflecting the quasi-two-dimensional nature of the electronic states.

Combining the results in Figs. 1 and 2, we can draw the following physical picture for the magnetic properties of Sr_2RuO_4. Unlike the case of the cubic analog $SrRuO_3$ ($S = 1$), Hund's coupling between the four electrons in the Ru t_{2g} orbitals does not align all four electron spins to form a simple $S = 1$ state in Sr_2RuO_4. The spin degrees

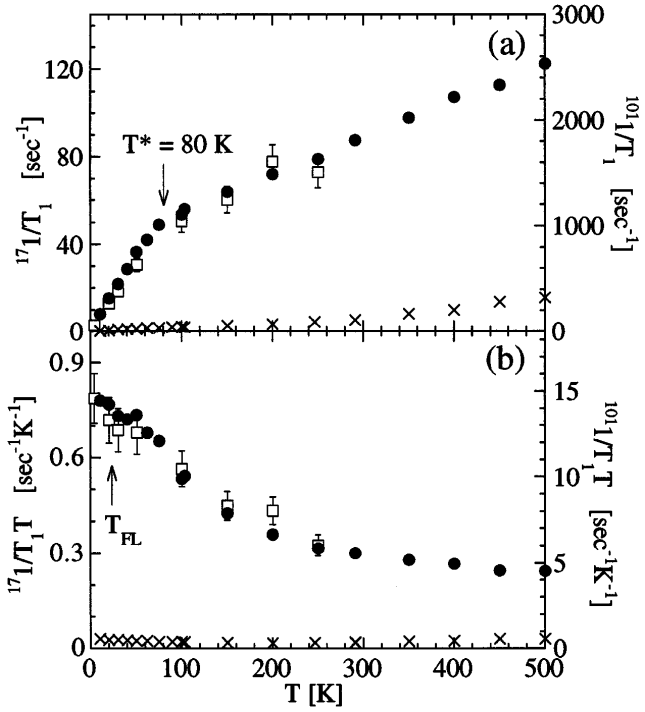

FIG. 2. (a) Nuclear spin-lattice relaxation rate $^{17}1/T_1(1)$ of the planar O(1) site [●], $^{17}1/T_1(2)$ at the apical O(2) site [×], and $^{101}1/T_1$ at the Ru site [□]. (b) $^{17}1/T_1(1)T$ [●], $^{17}1/T_1(2)T$ [×], and $^{101}1/T_1T$ [□].

of freedom in the Ru $4d_{xy}$ orbital and the $4d_{yz,zx}$ orbitals behave more or less independently at least down to T_{FL}. The enhancement of ferromagnetic spin correlations begins to saturate below T^*, when the charge transport along the c axis gains coherence. The entire electronic system crosses over into a modestly mass-enhanced canonical Fermi liquid state below T_{FL} only after the ferromagnetic enhancement observed for χ_{xy} and $1/T_1T$ saturates. Our observation of magnetic crossovers at T_{FL} and T^* is evidence that the anomalous charge transport properties of the RuO_2 planes [2,4,6,8] are coupled to the growth of ferromagnetic spin fluctuations. Within the scenario of p-wave superconductivity induced by ferromagnetic spin fluctuations, stronger temperature dependence observed for χ_{xy} than $\chi_{yz,zx}$ seems to favor the opening of the primary superconducting energy gap in the $4d_{xy}$ orbital [28]. Much weaker but qualitatively similar temperature dependence of $\chi_{yz,zx}$ suggests a weak but finite coupling between $4d_{xy}$ and $4d_{yz,zx}$ orbitals, as required by some theoretical models [12].

To conclude, we succeeded in detecting ^{17}O and ^{101}Ru NMR signals in a broad temperature range of the anomalous metallic state of Sr_2RuO_4. We established that spin correlations are predominantly ferromagnetic in origin, and orbital dependent. We also presented evidence that the growth of low frequency ferromagnetic spin fluctuations has close connections to the anomalous charge transport properties of RuO_2 planes. Whether various theoretical models can reproduce our new results remains to be seen.

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[24] Even though the dipole hyperfine field is traceless, we found an unusually large isotropic component of the ^{17}O Knight shift, $^{17}K(1)_{\mathrm{iso}} = [^{17}K(1)_c + {}^{17}K(1)_{\parallel} + {}^{17}K(1)_{\perp}]/3 \sim 0.23\%$ for the O(1) site, and $^{17}K(2)_{\mathrm{iso}} = [^{17}K(2)_c + 2\,{}^{17}K(2)_{ab}]/3 \sim 0.07\%$ for the O(2) site. Both $^{17}K(1,2)_{\mathrm{iso}}$ increase slightly above 200 K. We cannot attribute $^{17}K(1,2)_{\mathrm{iso}}$ to the transferred spin polarization in the O(1,2) $2s$ orbitals from the nearest neighbor Ru $4d$ orbitals, because they are orthogonal. In Eqs. (1a)–(1c), we included the isotropic $2s$ hyperfine coupling σ {$\sim$4000 kOe/μ_B [A. K. Koh and D. J. Miller, At. Data Nucl. Data Tables **33**, 239 (1985)]} and the corresponding spin susceptibility χ_{2s}. We note that both $\chi_{2s}(\sim 3 \times 10^{-6}$ emu/mol) and the corresponding density of states ($\sim$0.004 states/Ry) are $\sim$2–4 orders of magnitude smaller than the contribution of the Ru $4d$ and O(1) $2p$ orbitals, and therefore the $2s$ electrons are not playing significant roles in electronic properties. However, the similarity of the temperature dependence between $^{17}K(1,2)_{\mathrm{iso}}$ and $^{17}K(2)_{ab,c}$ might be an indication that the $2p_{x,y}$ orbitals at the apical O(2) site form a relatively extended network, since the $2p_{x,y}$ orbitals at the O(2) site are not orthogonal to the $2s$ orbitals at the nearest neighbor O(1,2) sites.
[25] F. C. Chou (unpublished).
[26] The orthogonality between the Ru t_{2g} orbitals and the Ru $5s$ orbital at the nearest neighbor sites prohibits the so-called supertransfer hyperfine processes.
[27] The multiband nature of Sr_2RuO_4 makes it difficult to test whether the Korringa behavior for a canonical Fermi liquid ($1/T_1T \sim K^2$ for each separate spin contribution [21]) breaks down above T_{FL}. Judging from the unconventional behavior of resistivity $\rho_{ab,c}$ above T_{FL}, there is no reason *a priori* to expect that the Korringa relation should hold above T_{FL}. We also note that our estimate of the orbital contribution [22] to $^{101}1/T_1T$ using the LDA results [11], $\sim$1 sec^{-1} K^{-1}, is more than an order of magnitude smaller than the observed rate.
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