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Ground state in $Sr_3Ru_2O_7$: Fermi liquid close to a ferromagnetic instability

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We show that single-crystalline $Sr_3Ru_2O_7$ grown by a floating-zone technique is an isotropic paramagnet and a quasi-two-dimensional metal, as spin-triplet superconducting Sr_2RuO_4 is. The ground state is a Fermi liquid with very low residual resistivity ($\approx 3\ \mu\Omega$ cm for in-plane currents) and a nearly ferromagnetic metal with the largest Wilson ratio $R_W \geqslant 10$ among paramagnets so far. This contrasts with the ferromagnetic order at $T_c = 104$ K reported on single crystals grown by a flux method [Cao *et al.*, Phys. Rev. B **55**, R672 (1997)]. However, we have found a dramatic changeover from paramagnetism to ferromagnetism under applied pressure. This suggests the existence of a substantial ferromagnetic instability in the Fermi-liquid state.

The discovery of superconductivity in the single-layered perovskite Sr_2RuO_4 (Ref. 1) has motivated the search for new superconductors and anomalous metallic materials in Ruddlesden-Popper (R-P) type ruthenates $(Sr,Ca)_{n+1}Ru_nO_{3n+1}$. The recent determination of the spin-triplet pairing in its superconducting state suggests that ferromagnetic (FM) correlations are quite important in Sr_2RuO_4,[2] and the existence of enhanced spin fluctuations has been suggested by nuclear magnetic resonance (NMR).[3,4] On the other hand, the recent report has shown that enhanced magnetic excitations around $\mathbf{q}=0$ is not detected but sizeable excitations have been seen around finite $\mathbf{q}$ in Sr_2RuO_4 by inelastic neutron scattering.[5] This has stimulated debate on the mechanism of the spin-triplet superconductivity, which had been naively believed to have a close relation to FM ($\mathbf{q}=0$) spin excitations. Hence, it is desirable to investigate its related compounds as described below.

The simple perovskite (three-dimensional) metallic $SrRuO_3$ ($n=\infty$) has been well known to order ferromagnetically below 160 K with a magnetic moment $M=0.8 \sim 1.0\mu_B$/Ru.[6,7] FM perovskite oxides are relatively rare except for metallic manganites. For pure thin film $SrRuO_3$, analyses of quantum oscillations in the resistivity have given good evidence for the Fermi-liquid behavior.[8]

The double layered perovskite $Sr_3Ru_2O_7$ ($n=2$) is regarded as having an intermediate dimensionality between the systems with $n=1$ and $n=\infty$.[9] Investigations on polycrystalline $Sr_3Ru_2O_7$ showed a magnetic-susceptibility maximum around 15 K with Curie-Weiss-like behavior above 100 K and a metallic temperature dependence of the electrical resistivity.[10,11]

In the study presented here, we have succeeded in growing single crystals of $Sr_3Ru_2O_7$ by a floating-zone (FZ) method. Those single crystals (FZ crystals) do not contain any impurity phases (e.g., $SrRuO_3$) which was observed in polycrystals.[11] We report herein that the FZ crystal of $Sr_3Ru_2O_7$ is a nearly FM paramagnet (enhanced paramagnet) and a quasi-two-dimensional metal with a strongly correlated Fermi-liquid state. In addition, we have performed magnetization measurements under hydrostatic pressures up to 1.1 GPa in order to confirm whether the FM instability is susceptible to pressure. The results suggest that there is a changeover from paramagnetism to ferromagnetism, indicating a strong FM instability. Essential features of magnetism for FZ crystals[12] as well as polycrystals are inconsistent with the appearance of a FM ordering ($T_c = 104$ K) at ambient pressure for single crystals grown by a flux method[13] using $SrCl_2$ flux and Pt crucibles. We will argue that FZ crystals reflect the intrinsic behavior of $Sr_3Ru_2O_7$.

Details of the FZ crystal growth are explained elsewhere.[14] The crystal structure of the samples at room temperature was characterized by powder x-ray diffraction. Electrical resistivity $\rho(T)$ was measured by a standard four terminal dc-technique from 4.2 K to 300 K and by an ac method from 0.3 K to 5 K. Specific heat $C_P(T)$ was measured by a relaxation method from 1.8 K to 35 K (Quantum Design, PPMS). The temperature dependence of magnetic susceptibility $\chi(T) \equiv M/H$ from 2 K to 320 K was measured using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum Design, MPMS-5S). For magnetization measurements of FZ crystals at ambient pressure, we performed sample rotation around the horizontal axis, normal to the scan direction, using the rotator in MPMS-5S. We could align the crystal axes exactly parallel to a field direction within 0.2° using this technique. For high pressures, we measured magnetization using a long-type hydrostatic pressure microcell[15] with the SQUID magnetometer. Loaded pressures around 3 K were determined from the shift of superconducting transition temperature of Sn in the microcell in a 5 mT field.

The R-P type structure of $n=2$ for FZ crystals of $Sr_3Ru_2O_7$ was confirmed by the powder x-ray diffraction patterns with crushed crystals, which indicated no impurity peaks. Recently, the crystal structure of polycrystalline $Sr_3Ru_2O_7$ has been refined by neutron powder diffraction.[16,17] Although they have concluded that the symmetry of the structure is orthorhombic owing to the rotation of the RuO_6 octahedron about the c axis by about 7°, we deduced lattice parameters at room temperature by assuming tetragonal $I4/mmm$ symmetry as $a=3.8872(4)$ Å, and

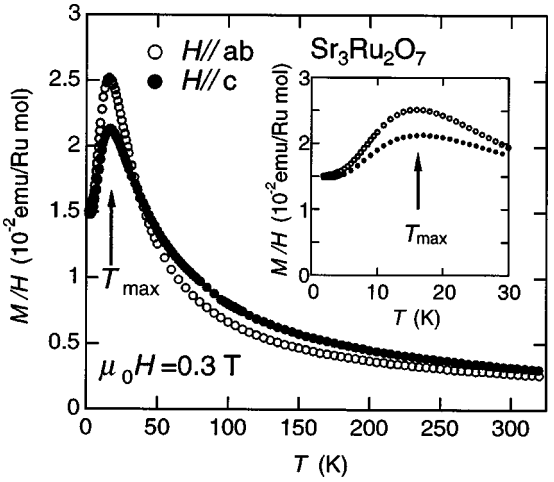

FIG. 1. The magnetic susceptibility of FZ crystals of $Sr_3Ru_2O_7$ under 0.3 T field above 2 K. The inset shows the low-temperature magnetic susceptibility against temperature T.

$c=20.732(3)$ Å. These values are in good agreement with those of polycrystals obtained by neutron diffraction[16,17] and x-ray diffraction.[11]

The temperature dependence of the magnetic susceptibility $\chi(T)=M/H$ in a field of 0.3 T is shown in Fig. 1. No hysteresis is observed between zero-field cooling (ZFC) and field cooling (FC) sequences, so we conclude that there is no ferromagnetic ordering. Little magnetic anisotropy is observed in contrast to large anisotropy ($\approx 10^2$) of flux-grown crystals.[13] The nearly isotropic susceptibility of $Sr_3Ru_2O_7$ is qualitatively similar to that of the enhanced Pauli-paramagnetic susceptibility in Sr_2RuO_4.[18] For an applied field of 0.3 T, there is no in-plane anisotropy of the susceptibility for the whole temperature range ($2\ K \leqslant T \leqslant 300$ K), within the precision of our equipment (1%).

The susceptibility for both $H\|ab$ and $H\|c$ exhibits Curie-Weiss behavior above 200 K. We have fitted the observed $\chi(T)$ from 200 to 320 K with $\chi(T)=\chi_0+\chi_{CW}(T)$, where χ_0 is the temperature independent term and $\chi_{CW}(T)=C/(T-\Theta_W)$ is the Curie-Weiss term. The effective Bohr magneton numbers p_{eff} deduced from C are $p_{eff}=2.52$ (2.99) and $\Theta_W=-39$ K (-45 K) for $H\|ab(H\|c)$. The negative values of Θ_W normally indicate antiferromagnetic (AFM) correlations in the case of localized-spin systems. However, we cannot conclude that AFM correlations play an important role solely by the negative Θ_W in an metallic system like $Sr_3Ru_2O_7$.[19]

Around $T_{max}=16$ K, $\chi(T)$ shows a maximum for both $H\|ab$ and $H\|c$. The maximum has been also observed in the polycrystals. The results of temperature dependence of specific heat, NMR,[20] and elastic neutron scattering[16,17] for polycrystals indicate that there is no evidence for any long-range order with definite moments. The FZ crystal shows nearly isotropic $\chi(T)$ for all crystal axes below T_{max}. Hence, the maximum cannot be accredited to the long-range AFM order. Therefore, we conclude $Sr_3Ru_2O_7$ to be a *paramagnet*. Concerning $\chi(T)$ under higher fields, T_{max} is suppressed down to temperatures below 5 K above 6 T.[21] Such a maximum in $\chi(T)$ and a field dependent T_{max} are often observed in a nearly ferromagnetic (enhanced paramagnetic) metal like $TiBe_2$ (Ref. 22) or Pd.[23] In addition, a similar

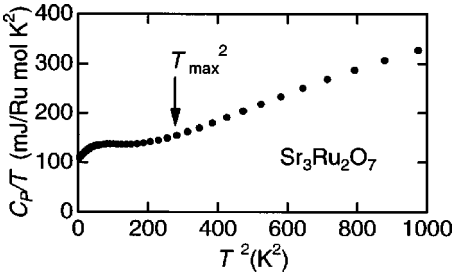

FIG. 2. The specific heat divided by temperature C_P/T of FZ crystals of $Sr_3Ru_2O_7$ above 2 K. C_P/T is plotted against T^2.

behavior in $\chi(T)$ has been observed in $(Ca,Sr)_2RuO_4$ (Ref. 24) and MnSi,[25] which are recognized as examples of a critical behavior by spin fluctuations. Similar critical behavior, originating especially from FM spin fluctuations, is also expected in $Sr_3Ru_2O_7$. Nevertheless, we cannot rule out the possibility of AFM correlations as observed in Sr_2RuO_4, caused by the nesting of its Fermi surfaces with the vector $\mathbf{Q}=(\pm 0.6\pi/a, \pm 0.6\pi/a, 0)$.[5]

As shown in Fig. 2, the specific heat coefficient of the FZ crystal of $Sr_3Ru_2O_7$ is $\gamma=110$ mJ/(K^2 Ru mol) somewhat larger compared to other R-P type ruthenates [$\gamma=80$ mJ/(K^2 Ru mol) for $CaRuO_3$, 30 mJ/(K^2 Ru mol) for $SrRuO_3$ (Ref. 7) and 38 mJ/(K^2 Ru mol) for Sr_2RuO_4 (Refs. 18 and 26)]. This suggests that $Sr_3Ru_2O_7$ is a strongly correlated metallic oxide. For polycrystalline $Sr_3Ru_2O_7$, we obtained the value $\gamma=63$ mJ/(K^2 Ru mol) using an adiabatic method.[11]

The temperature dependence of the electrical resistivity $\rho(T)$ is shown in Fig. 3 above 0.3 K. Both $\rho_{ab}(T)$ and $\rho_c(T)$ are metallic ($d\rho/dT>0$) in the whole region. The ratio of ρ_c/ρ_{ab} is about 300 at 0.3 K and 40 at 300 K. This anisotropic resistivity is consistent with the quasi-two-dimensional Fermi-surface sheets obtained from the band-structure calculations.[27] With lowering temperature below 100 K, a remarkable decrease of $\rho_c(T)$ is observed around

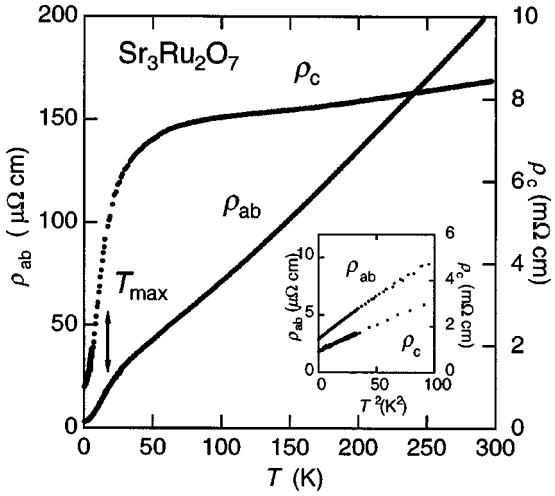

FIG. 3. The electrical resistivity of FZ crystals of $Sr_3Ru_2O_7$ above 0.3 K. Both ρ_{ab} and ρ_c are shown. The inset shows the low-temperature electrical resistivity against the square of temperature T^2.

50 K. This is probably due to the suppression of the thermal scattering with decreasing temperature between quasiparticles and phonons as observed in Sr_2RuO_4.[28,18,29] Thus, below 50 K, interlayer hopping propagations of the quasiparticle overcome the thermal scattering with phonons. This hopping picture for $\rho_c(T)$ is well consistent with the large value of $\rho_c(T)$ and nearly cylindrical Fermi surfaces. On the other hand, $\rho_{ab}(T)$ shows a change of the slope around 20 K. Such a change in $\rho_{ab}(T)$ has also been reported for Sr_2RuO_4 under hydrostatic pressure (≈ 3 GPa). That might be possibly due to the enhancement of ferromagnetic spin fluctuations.[28]

As shown in the inset of Fig. 3, the resistivity yields a quadratic temperature dependence below 6 K for both $\rho_{ab}(T)$ and $\rho_c(T)$, characteristic of a Fermi liquid as observed in Sr_2RuO_4.[18] We fitted $\rho_{ab}(T)$ by the formula $\rho_{ab}(T)=\rho_0+AT^2$ below 6 K and obtained $\rho_0=2.8\ \mu\Omega$ cm and $A=0.075\ \mu\Omega\,\mathrm{cm/K^2}$. Since the susceptibility is quite isotropic and temperature independent below 6 K, the ground state of $Sr_3Ru_2O_7$ is ascribable as a Fermi liquid. We now can estimate the Kadowaki-Woods ratio A/γ^2. Assuming that electronic specific heat $\gamma=110$ mJ/(K^2 Ru mol) is mainly due to the *ab*-plane component, we obtain $A/\gamma^2 \approx A_{ab}/\gamma^2=0.6\times10^{-5}\ \mu\Omega\,\mathrm{cm/(mJ/K^2\ Ru\ mol)^2}$ close to that observed in heavy fermion compounds.

Regarding $\chi(T)$ again, it is important to note that even at temperatures much lower than $T_{\max}$, $\chi(T)$ remains quite large. It appears that the ground state maintains a highly enhanced value of 1.5×10^{-2} emu/Ru mol, comparable to that obtained for typical heavy fermion compounds. Considering that the observed χ is dominated by the renormalized quasiparticles, we can estimate the Wilson ratio $R_W=7.3\times10^4\times\chi(\mathrm{emu/mol})/\gamma[\mathrm{mJ/(K^2\ mol)}]$ in the ground state. If we regard the observed values at $T=2$ K as that at $T=0$ K, we have $R_W=10(18)$ using γ for single crystals (polycrystals). Despite the difference in the γ value between polycrystals and single crystals, R_W is much greater than unity. This large value implies that FM correlations are strongly enhanced in this compound, especially when compared with the values of 12 for $TiBe_2$ and 6 for Pd.[30] Therefore, the ground state of $Sr_3Ru_2O_7$ is characterized by strongly correlated Fermi-liquid behavior with enhanced FM spin fluctuations, i.e., $Sr_3Ru_2O_7$ is a strongly correlated nearly FM metal.

Concerning these FM correlations, it should be noted that, using single crystals grown by a chlorine flux method with Pt crucibles,[31] Cao *et al.* have investigated remarkable magnetic and transport properties of R-P ruthenates[13] prior to our crystal growth. The ground state of $Sr_3Ru_2O_7$ was concluded to be an itinerant *ferromagnet* with $T_c=104$ K and an ordered moment $M=1.2\mu_B$/Ru. The flux-grown crystals were reported to have a residual resistivity ($\rho_0=3$ mΩ cm) 10^3 times greater than that of FZ crystals ($\rho_0=3\ \mu\Omega$ cm) for in-plane transport. In addition, FZ crystals reveal T-square dependent resistivities at low temperatures as already shown, which was not observed in flux-grown crystals. In general, the FZ method with great care can be impurity-free crystal growth, while the flux method tends to contaminate crystals due to impurity elements from both the flux and the crucible. This might be a main reason why the resistivity is much higher for flux-grown crystals. Thus, we suppose with assurance that the data from FZ crystals reflect the intrinsic nature of $Sr_3Ru_2O_7$ better than those from flux-grown crystals.

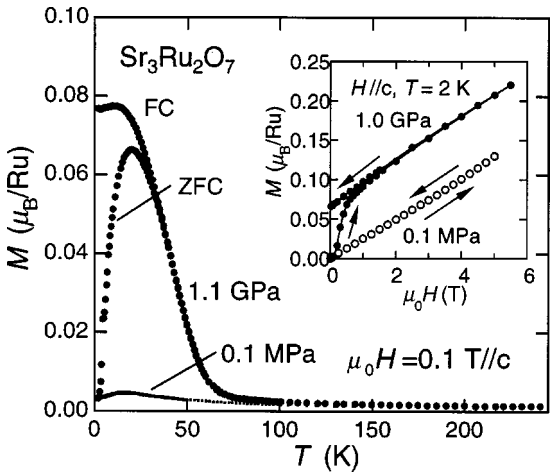

FIG. 4. The pressure dependence of magnetization $M(T)$ for $H\|c$. Obvious ferromagnetic ordering appears at about 70 K under 1 GPa pressure. The inset shows the field dependence of magnetization $M(H)$ under 0.1 MPa and 1 GPa pressures.

In order to acquire the information of the magnetic instability in the FZ crystal of $Sr_3Ru_2O_7$, we have measured magnetization under hydrostatic pressure up to 1.1 GPa. The temperature dependence of magnetization $M(T)$ is shown for several pressures under a 0.1 T field along the *c* axis in Fig. 4. Around 1 GPa, substantial increase is recognized below around 70 K with a clear FM component indicated by the difference between ZFC and FC sequences. Although the remanent moment at 2 K ($M\approx0.08\mu_B$/Ru) is much smaller than that expected for $S=1$ of Ru^{4+}, its susceptibility is quite large (0.4 emu/Ru mol). We infer that this transition is a FM ordering of itinerant Ru^{4+} spins. In Fig. 4, we also show the field dependence of magnetization $M(H\|c)$ at 2 K for $P=0.1$ MPa and $P=1$ GPa. An obvious ferromagnetic component appears at lower fields for $P=1$ GPa. Even at higher fields, an increase in magnetization by pressure is also present as at lower fields. This feature endorses the drastic changeover from paramagnetism to ferromagnetism induced by applied pressure. This is an example of the pressure-induced changeover from Fermi liquid to ferromagnetism.

For the purpose of understanding the observed behavior, we should begin with the Stoner theory. In the metallic state with correlated electrons, the ferromagnetic order is driven by the Stoner criterion $U_{\mathrm{eff}}N(E_F)\geqslant1$, where U_{eff} is an effective Coulomb repulsion energy. The systematics of bandwidth W and the density of states $N(E_F)$ in the R-P ruthenates is summarized by Maeno *et al.*[32] In this system, increasing n from 1 to ∞ causes enhancement of $N(E_F)$ as well as W. This is opposite to the single band picture, i.e., increasing $N(E_F)$ naively means decreasing W. In the case of R-P ruthenates, the anomalous variation might be due to the modifications of the degeneracy of three t_{2g} orbitals for Ru-4*d* electrons. According to the summary,[32] ferromagnetic $SrRuO_3$ is characterized by the highest $N(E_F)$ and W among them, satisfying the Stoner criterion. This implies that the enlargement of $N(E_F)$ and W reflects stronger three dimensionality in the R-P ruthenates. Hence, applying pressure probably makes $Sr_3Ru_2O_7$ closer to $SrRuO_3$, leading to FM

order. For further investigations, it is required that structural study, resistivity, and specific heat under pressures will be performed.

In conclusion, by using the floating-zone method we have succeeded in growing single crystals of $Sr_3Ru_2O_7$ with very low residual resistivity in comparison with that of flux-grown crystals reported previously. The results of magnetization, resistivity, and specific heat measurements suggest that $Sr_3Ru_2O_7$ is a strongly correlated Fermi liquid with a nearly ferromagnetic ground state, consistent with the observation of ferromagnetic ordering below 70 K under applied pressure ($P \sim 1$ GPa). This is an example of a pressure-induced changeover from Fermi liquid to ferromagnetism. This ferromagnetic ordering may guarantee the existence of the ferromagnetic spin fluctuations in $Sr_3Ru_2O_7$.

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