Orbital-Degenerate Paramagnetic Metal Sr$_2$MoO$_4$: An Electronic Analogue to Sr$_2$RuO$_4$

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We present the first systematic study on polycrystalline Sr$_2$MoO$_4$ as an electronic analogue to the spin-triplet superconductor Sr$_2$RuO$_4$. The Pauli paramagnetic susceptibility and metallic behaviors of specific heat and electrical resistivity have been observed. The density of states at the Fermi level $D(E_F)$ deduced from the results is about three times smaller than that of Sr$_2$RuO$_4$. Any indication of superconductivity intrinsic to Sr$_2$MoO$_4$ has not been observed down to 25 mK, which may correspond to the smaller $D(E_F)$. We discuss the origin of the difference in electronic states between Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$.

KEYWORDS: molybdate, Sr$_2$RuO$_4$, strongly-correlated electron system

The manifestation of spin-triplet superconductivity (SC) in the quasi-two-dimensional Fermi liquid state of Sr$_2$RuO$_4$ has marked an epoch in the study of SC in strongly-correlated electron systems. One might expect that ferromagnetic spin fluctuations are essential for the origin of the spin-triplet SC, as observed in superfluid (p-wave) $^3$He. Rice and Sigrist suggested the p-wave pairing in Sr$_2$RuO$_4$ immediately after the discovery of SC.

Their idea was based on the existence of ferromagnetism in SrRuO$_3$, the three-dimensional (3D) analogue to Sr$_2$RuO$_4$, and similar values of the Landau parameters to those of Fermi liquid $^3$He.

Concerning the electronic configuration in Sr$_2$RuO$_4$, the formal valence number of Ru ion is 4+ with four 4d electrons in three $t_{2g}$ orbitals ($4d_{xy}$, $4d_{yz}$, $4d_{zx}$). The strong crystalline field for 4d electrons causes the Ru ion to have a low spin state with spin degree of freedom $S=1$, which means triple degeneracy and ferromagnetic correlations due to the Hund coupling. The normal state properties of Sr$_2$RuO$_4$ are well described quantitatively by the Fermi surface parameters obtained from the quantum oscillation measurements.

They confirmed that two cylindrical sheets of $4d_{yz}$ and $4d_{zx}$ orbitals and a cylindrical sheet of $4d_{xy}$ orbitals consist of four 4d electrons of Ru$^{4+}$, which had been derived from the band-structure calculation.

A recent inelastic neutron scattering measurement on Sr$_2$RuO$_4$ has shown that incommensurate peaks of dynamical magnetic susceptibility $\chi(Q)$ with $q_0 = (\pm 0.6\pi/a, \pm 0.6\pi/a, 0)$ exist instead of a ferromagnetic peak ($Q \approx 0$). The incommensurate peaks are ascribed to nesting vectors between Fermi surfaces with one-dimensional (1D) $4d_{yz}$ and $4d_{zx}$ orbitals. This provides a new physical aspect, the relation between the spin-triplet SC and the incommensurate spin fluctuations. If the SC mainly corresponds to this incommensurate spin fluctuation, the 1D $4d_{yz}$ and $4d_{zx}$ orbitals may play a vital role in the spin-triplet SC of Sr$_2$RuO$_4$. On the other hand, if the incommensurate spin fluctuation contributes negligibly to the spin-triplet SC, the 2D $4d_{xy}$ orbital is more important. Since the partial density of states for the $4d_{xy}$ orbital is the highest among three $t_{2g}$ orbitals, most theoretical studies on the spin-triplet SC are based on this 2D $4d_{xy}$ orbital. Recently, Takimoto has indicated the possibility of spin-triplet pairing symmetry in Sr$_2$RuO$_4$ originating from the orbital fluctuations together with the incommensurate spin fluctuation observed by the inelastic neutron scattering. The orbital fluctuations are supposed to be driven by the on-site Coulomb interaction between electrons in different $4d-t_{2g}$ orbitals, which are almost degenerate. At present, the important problem is whether or not the incommensurate spin fluctuation can induce the spin-triplet pairing. In addition, the role of the orbital degeneracy must be understood to clarify the mechanism of the spin-triplet SC in Sr$_2$RuO$_4$.

An alternative route to understand the spin-triplet SC is provided by studying other compounds related to Sr$_2$RuO$_4$. Several metallic ruthenates were expected to reveal SC and were intensively examined. However, such ruthenates have not shown SC, unlike cuprates, where many charge-transfer-type insulators can be made superconductive by ionic substitutions. Hence, it is intriguing to find a ruthenium-free electronic analogue to Sr$_2$RuO$_4$. In order to provide a new system to be compared with Sr$_2$RuO$_4$, we have focused on Sr$_2$MoO$_4$ because it is isostructural to Sr$_2$RuO$_4$ and has a similar electronic configuration. Mo ions in Sr$_2$MoO$_4$ formally possess the valence 4+ and have two 4d electrons in three $t_{2g}$ orbitals ($4d_{xy}$, $4d_{yz}$, $4d_{zx}$) with an equivalent orbital degeneracy ($S=1$) to Sr$_2$RuO$_4$. Moreover, Sr$_2$MoO$_4$ is expected to have three Fermi surfaces with the same topology as those of Sr$_2$RuO$_4$. These Fermi surfaces for the 1D orbitals with smaller Fermi wave vectors than those of Sr$_2$RuO$_4$ may also produce incommensurate spin fluctuations at $q$ closer to the ferromagnetic wave vector ($Q \approx 0$). Therefore, Sr$_2$MoO$_4$ is a good candidate not only for a new superconductor but also for a
counterpart to clarify the mechanism of the spin-triplet SC in Sr$_2$RuO$_4$. In this Letter, we report the successful synthesis of polycrystalline Sr$_2$MoO$_4$ and the results of magnetic susceptibility $\chi$, electrical resistivity $\rho$ and specific heat $C$. We have no evidence for SC ascribable to Sr$_2$MoO$_4$ down to 25 mK in the present results.

As for the synthesis of Sr$_2$MoO$_4$, there was a controversy over whether or not the phase actually existed. To our knowledge, Balz and Plieth first reported on Sr$_2$MoO$_4$, but McCarthy and Gooden could not obtain any Sr$_2$MoO$_4$ phase in their research. Lindblom and Rosen reported successful synthesis and deduced the lattice parameters by assuming I4/mmm symmetry. Very recently, Steiner and Reichelt performed X-ray Rietveld analysis on a multi-phase sample including Sr$_3$MoO$_4$. They concluded that the crystal structure is the K$_2$NiF$_4$ type (Fig. 1), which is the same as that of Sr$_2$RuO$_4$. Nevertheless, systematic investigations on physical properties of Sr$_2$MoO$_4$ as well as definitive structural refinements have not yet been carried out since the synthesis of single-phase samples is extremely difficult.

The procedure for the sample synthesis is explained below. First, we prepared polycrystalline Sr$_3$MoO$_6$ from mixed raw materials of SrCO$_3$ (99.99%) and MoO$_3$ (99.99%) by firing in an Ar flow atmosphere at 1273 K for 24 h with intermediate grindings. Then, Sr$_3$MoO$_6$ and Mo metal powder (99.9%) were ground together in a dry N$_2$ atmosphere so that the total composition was Sr$_2$MoO$_4$. The resultant mixture was pressed into pellets and then sintered in a quartz tube under controlled oxygen partial pressure at 1273 K to 1473 K. Details of the synthesis will be explained elsewhere.

We characterized the obtained samples at room temperature by powder X-ray diffraction with Cu-Kα radiation. DC magnetization above 2 K was measured using a SQUID magnetometer (Quantum Design, MPMS) and that between 25 mK and 2 K was measured using a SQUID magnetometer (SHE) installed in a dilution refrigerator. Data below 2 K were collected by moving the sample through the pickup coil under a field of 0.1 Oe. Electrical resistivity $\rho(T)$ was measured by the ac method from 80 mK to 300 K. The samples for $\rho(T)$ and magnetization below 1 K were covered with epoxy resin in order to avoid exposure to air. Specific heat measurement between 0.7 K and 60 K were performed by the quasi-adiabatic heat-pulse method. In Fig. 2, we show the powder X-ray pattern of Sr$_2$MoO$_4$ along with that for a single phase of Sr$_2$RuO$_4$. The pattern of Sr$_2$MoO$_4$ without unidentified peaks indicates that the obtained polycrystal is single-phased, except for a very weak peak of Mo metal. Moreover, these patterns suggest that both compounds share a common crystal structure. Indeed, the structural symmetry of Sr$_2$MoO$_4$ has been concluded to be I4/mmm from the electron diffraction analysis by Shirakawa et al. The calculated lattice parameters of tetragonal Sr$_2$MoO$_4$ for the powder X-ray pattern are $a = 3.9168(4)$ Å and $c = 12.859(2)$ Å and those of Sr$_2$RuO$_4$ are $a = 3.87073(2)$ Å and $c = 12.7397(1)$ Å. The values of Sr$_2$MoO$_4$ are in good agreement with those of previous work. Both $a$ and $c$ parameters are larger than those of Sr$_2$RuO$_4$ by about 1%, owing to the larger ionic radius of Mo$^{4+}$ than Ru$^{4+}$. We should note that the current samples still contain very small amounts of Mo metal and Mo$_2$C because the condition of the synthesis is highly subtle. Nevertheless, we could synthesize the samples with the amount of those phases less than 1%. Temperature dependence of magnetic susceptibility $\chi(T) = M/H$ is shown in Fig. 3 for both Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ between 2 K and 300 K. Sr$_2$MoO$_4$ reveals enhanced Pauli paramagnetic susceptibility, which is almost temperature independent except for the Curie-like increase with lowering temperature below 20 K. This probably corresponds to the existence of a small amount of magnetic impurities. Such Curie-like behavior is also observed in CaVO$_3$. The difference in the absolute value between Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ will be discussed later together with that of the electronic specific heat coefficient. No hysteresis is observed between zero-field-
cooling (ZFC) and field-cooling (FC) sequences. Hence, a ferromagnetically ordering component or a spin-glass state does not exist. In addition, there is no indication of a long-range magnetic ordering.

The temperature dependence of specific heat $C_P(T)$ for Sr$_2$MoO$_4$ is ordinary metallic behavior below 10 K with a relatively large Sommerfeld coefficient $\gamma$, as shown in Fig. 4. The temperature dependence of $C_P(T)$ almost follows the relation $C_P(T) = \gamma T + \beta T^3$. The obtained electronic specific heat coefficient $\gamma$ is 12 mJ/(K$^2$ mol) for Sr$_2$MoO$_4$. Considering its Pauli paramagnetic susceptibility and normal metal behavior of $C_P(T)$, the ground state of Sr$_2$MoO$_4$ is probably dominated by renormalized quasi-particles, as observed in the Fermi liquid state. We did not observe the relevant anomaly in $C_P(T)$ below 10 K to the Curie-type increase in $\chi(T)$. This is also consistent with the fact that the increase in $\chi(T)$ is due to a tiny amount of the magnetic impurity.

For Sr$_2$MoO$_4$, we try to evaluate the Wilson ratio, a dimensionless parameter concerned with correlation among electrons. It is necessary to determine the precise contributions of the Landau diamagnetic susceptibility especially when we have small mass enhancement of electrons. Hase has calculated the band structure for Sr$_2$MoO$_4$ based on the atomic coordinates obtained by the prior X-ray Rietveld analysis. According to their results, the density of states $D(E_F)$ and electronic specific heat coefficient $\gamma_{\text{calc}}$ are 2.1 states/eV and 5 mJ/(K$^2$ Mo mol), respectively. The ratio of $\gamma/\gamma_{\text{calc}}$ should be nearly equal to the mass enhancement $m^*/m$, thus $m^*/m \approx \gamma/\gamma_{\text{calc}} \approx 2$. The reduction factor by the Landau diamagnetism $1 - (1/3)(m/m^*)^2$ is about 0.92 in the present case. Considering this diamagnetism and core diamagnetic susceptibility, we obtain the Pauli contribu-
tion $\chi_{\text{Pauli}} = (\chi_{\text{obs}} - \chi_{\text{core}})/0.92 \approx 3.2 \times 10^{-4}$ emu/mol, where $\chi_{\text{obs}}$ is the observed susceptibility and $\chi_{\text{core}} = -0.95 \times 10^{-4}$ emu/mol. This value of $\chi_{\text{Pauli}}$ is three times smaller than that of Sr$_2$RuO$_4$.

We obtained the Wilson ratio $R_W = 7.3 \times 10^4 \times \gamma(\text{emu/mol})/\gamma_{\text{Pauli}} (\text{emu/mol}) = 1.9$, using the above value of $\chi_{\text{Pauli}}$. This ratio is almost the same as that of Sr$_2$RuO$_4$. The important point is that the value of $R_W$ is considerably larger than unity, which is the value for the non-interacting free-electron system. This reflects the existence of substantial electron-electron correlation in Sr$_2$MoO$_4$, although it possesses smaller $D(E_F)$ than that of Sr$_2$RuO$_4$.

The electrical resistivity $\rho(T)$ of Sr$_2$MoO$_4$ presented in Fig. 5 shows metallic $(d\rho/dT \geq 0)$ behavior for the entire temperature range (80 mK $\leq T \leq 300$ K). The ground state is supposed to be Fermi liquid, as recognized in Sr$_2$RuO$_4$ because of the temperature dependence of $C_P(T)$ and the Pauli paramagnetic $\chi(T)$. On the basis of the data of $\rho(T)$ for polycrystals, we cannot draw any conclusions about its absolute value and the precise temperature dependence because of grain-boundary resistance and the mixing of both in-plane and out-of-plane behaviors. It would be necessary to grow single-crystalline Sr$_2$MoO$_4$ to confirm whether the ground state is the Fermi liquid by observing the $T^2$-law in resistivity.

We have paid a great deal of attention to the behavior of Sr$_2$MoO$_4$ below 4 K to observe SC. In Fig. 6, we show $\rho(T)$ and $\chi(T)$ below 1 K. Two drops of $\rho(T)$ at 0.9 K and 0.4 K are evident. The change at 0.9 K is also present in the $\chi(T)$ data with a superconducting response. The volume fraction of this signal is at, most, about 1%. We have concluded that this superconducting signal is in accordance with the existence of Mo metal as a trace amount of impurity in the Sr$_2$MoO$_4$ sample. On the other hand, the other drop at 0.4 K in $\rho(T)$ does not accompany any anomaly in $\chi(T)$. The negative value of $\chi(T)$ above 0.9 K is probably due to superconducting molybdenum carbides with $T_c = 3-4$ K, which was also found in $\chi(T)$ measured by the MPMS SQUID magnetometer. These results indicate that polycrystalline Sr$_2$MoO$_4$ is not superconducting above 25 mK.

Now we suggest the reasons why the polycrystalline Sr$_2$MoO$_4$ we obtained does not exhibit SC. The substantial difference between Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ is the density of states $D(E_F)$. The absolute values of $\chi(T)$ and $C_P(T)$, proportional to $D(E_F)$, of Sr$_2$MoO$_4$ are both about three times smaller than those of Sr$_2$RuO$_4$. This is nearly consistent with the preliminary results of band-structure calculations for Sr$_2$MoO$_4$. 

![Fig. 3. Magnetic susceptibility of Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ (ref. 25) before subtracting the Landau and the core diamagnetic contributions. The data of Sr$_2$RuO$_4$ was derived from the susceptibility of single crystals by calculating $(\Sigma_{\chi(H\parallel b)} + \chi(H\parallel c))/3.$](image)

![Fig. 4. Temperature dependence of specific heat of Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ (ref. 25). Data of $C/T$ are shown against $T^2$.](image)
The origin of the difference of $D(E_F)$ between Sr$_2$MoO$_4$ and Sr$_2$RuO$_4$ is proposed below. The ratio $d_c/d_a$, where $d_c$ ($d_a$) is the distance between the transition-metal ion and the neighboring oxygen ion along the $c$-axis ($a$-axis), plays an essential role in energy-level splitting of the three $t_{2g}$ orbitals. According to Steiner and Reichelt, the MoO$_6$ octahedron is more elongated along the $c$-axis than the RuO$_6$ octahedron in Sr$_2$RuO$_4$. The ratio $d_c/d_a$ for Sr$_2$MoO$_4$ is 1.13$^{19}$ while $d_c/d_a$ for Sr$_2$RuO$_4$ is 1.07. The larger $d_c/d_a$ will lead to the decreased population of 4d electrons in the 2D-4d$_{xy}$ orbital ($\gamma$ Fermi surface described in ref. 5). In other words, more dispersion along the $c$-axis is introduced and smaller $D(E_F)$ is expected. This smaller $D(E_F)$ is probably the main reason why Sr$_2$MoO$_4$ is not superconductive. Another important feature of strontium molybdates is paramagnetism in SrMoO$_3$ with a similar value of $\chi$ to that of Sr$_2$MoO$_4$. This shows a great contrast to the ferromagnetism in SrRuO$_3$, which satisfies the Stoner criterion with the largest $D(E_F)$ in its paramagnetic state among ruthenates. The absence of significant ferromagnetic spin fluctuation in SrMoO$_3$ may be related to the absence of SC in Sr$_2$MoO$_4$. Despite our argument over the smaller $D(E_F)$ above, further investigations on Sr$_2$MoO$_4$, such as single-crystal studies are highly anticipated, since Sr$_2$MoO$_4$ is the best system to verify the importance of the orbital degeneracy or multiple Fermi surfaces to the spin-triplet SC in Sr$_2$RuO$_4$.

In summary, we have succeeded in synthesizing single-phase polycrystalline Sr$_2$MoO$_4$. The first systematic studies of magnetic susceptibility, electrical resistivity and specific heat measurements have been performed down to low temperatures around $10^{-2}$ K. We did not observe any signs of superconductivity intrinsic to Sr$_2$MoO$_4$. The value of the Wilson ratio shows remarkable electron-electron correlations.

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