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Evidence for magnetic ordering associated with metal-insulator transition in $SmRu_4P_{12}$ studied by muon spin relaxation

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Muon spin relaxation measurements on the filled skutterudite compound $SmRu_4P_{12}$ have been carried out in zero and longitudinal fields. The temperature dependence of both the initial asymmetry and the muon spin depolarization rate shows the appearance of a magnetically ordered state below the metal-insulator transition temperature T_{MI}. The present study indicates that the ordering below T_{MI} is not a nonmagnetic antiferroquadrupolar ordering but a magnetic one, which supports a scenario that magnetic octupolar ordering occurs below T_{MI} in $SmRu_4P_{12}$.

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I. INTRODUCTION

Filled skutterudite compounds with the general formula RT_4X_{12} (R, rare earth, actinoid; T, Fe, Ru, Os; X, P, As, Sb) crystallize in a body-centered cubic structure of the space group $Im\,\bar{3}$ (T_h^5, no. 204).[1] A lot of remarkable phenomena have been observed in these systems.[2–10] Among them, $PrRu_4P_{12}$ and $SmRu_4P_{12}$ exhibit metal-insulator (MI) transitions at T_{MI} of 62 and 16.5 K, respectively.[5,11] They have attracted much attention because of the different features of each MI transition. $PrRu_4P_{12}$ shows no sign of magnetic ordering below T_{MI}; on the contrary, a magnetization anomaly was observed in $SmRu_4P_{12}$ at T_{MI}.[12]

The nesting of the Fermi surface may be a common feature of the RRu_4P_{12} system. Indeed, band structure calculations have shown the existence of an approximately cube-shaped holelike Fermi surface with the nesting wave vector $\boldsymbol{q}=(1,0,0)$.[13,14] The band has a roughly flat dispersion at the Fermi level, which indicates that a slight displacement causes a substantial difference in the Fermi surface topologies. The interplay of the Fermi surface instability and the $4f$ orbital degree of freedom which is coupled to the local lattice distortion is a unique characteristic in this system. The lattice distortion lifts the angular momentum degeneracy within the cubic structure, and sometimes induces a multipolar ordering.[14]

In $PrRu_4P_{12}$, lattice distortions open a gap everywhere on the Fermi surface.[13,15] However, the structural phase transition at T_{MI} does not change the local symmetry of the Pr $4f$ state, which causes the system to remain in a paramagnetic state. In $SmRu_4P_{12}$, magnetic susceptibility measurements show that the Sm ions are in a trivalent state with the total angular momentum of $J=5/2$.[11] In the body-centered cubic structure with point group of T_h symmetry, the crystalline electric field splits a sixfold-degenerate multiplet into the doublet Γ_5 and the quartet Γ_{67}. Specific heat measurements show that the magnetic entropy at T_{MI} is close to $R\ln 4$.[16] This result means that the ground state is Γ_{67} which corresponds to Γ_8 in the ordinary O_h symmetry having both a magnetic and an orbital degree of freedom.

In $SmRu_4P_{12}$, an additional phase transition at T_N of 15 K was observed below T_{MI}. T_{MI} exhibits the characteristic magnetic field dependence.[17] T_{MI} increases with increasing field up to 200 kOe, and then the field dependence saturates at fields up to 300 kOe. Reentrant behavior is expected at higher fields. On the contrary, T_N decreases with increasing field. Though the anomaly at T_N is vague in zero field (ZF), it becomes apparent with increasing field.[12,17] The behavior is quite similar to that in CeB_6 where an antiferroquadrupolar (AFQ) ordering and a subsequent antiferromagnetic (AFM) one occur.[18] Hence, the succeeding transitions in $SmRu_4P_{12}$ have been expected to be an AFQ ordering below T_{MI} and an AFM one below T_N.[12,17]

On the other hand, recent ultrasonic measurements have shown that the elastic constants C_{44} and $\frac{1}{2}(C_{11}-C_{12})$ exhibit a slight and a large elastic softening above T_{MI} and below T_{MI} toward T_N, respectively.[19,20] The softening above T_{MI} is much less than that expected for the case of an AFQ ordering in which the quadrupole-quadrupole interaction plays an important role.[20] From group-theoretical considerations, an octupolar ordering (Γ_{5u}) below T_{MI} and an AFM one (Γ_{4u}) below T_N are considered as the most probable candidates.[20] To date, an octupolar ordering in NpO_2 is widely accepted.[21–23] $SmRu_4P_{12}$ would be another candidate.

In ZF, there is a clear difference between an AFQ ordering and an octupolar one. An AFQ ordering is nonmagnetic and holds time-reversal symmetry (TRS); on the contrary, an octupolar one is magnetic and breaks TRS. In the case of an AFQ ordering in an applied magnetic field, it is noted that TRS can be broken by the appearance of an internal field from an AFM component induced by the external field. In the case of an octupolar ordering, TRS is broken even in an applied field because it is essentially a magnetic ordering. As a result, TRS is broken in both cases in an applied field. It is impossible to distinguish a magnetic-field-induced AFQ ordering from a magnetic octupolar one under an external field. A magnetization anomaly at T_{MI} in $SmRu_4P_{12}$ was observed in applied fields of 10–90 kOe.[12] Hence, further microscopic ZF measurements are strongly required to clarify whether the phase transition at T_{MI} is "nonmagnetic" or "magnetic." Neutron diffraction experiments on this system are difficult because of the large absorption of neutrons by Sm nuclei. Though a ^{31}P NMR measurement has already been performed,[24] information in ZF could not be obtained since this experiment cannot be performed in ZF. A muon spin relaxation (μSR) measurement is the best method for the present purpose because the μSR experiment can be performed in ZF and sensitively detects only magnetic components. Therefore, ZF μSR measurements on $SmRu_4P_{12}$ have been carried out in order to clarify the transition at T_{MI}. In this Brief Report, we report the results of μSR measurements in ZF and longitudinal fields (LFs).

II. EXPERIMENT

Single-phase polycrystalline $SmRu_4P_{12}$ was synthesized by using the high-pressure and high-temperature method.[11] The sample was crushed to powder for the measurements. The μSR experiments were performed by implanting pulsed surface positive muons at the RIKEN-RAL Muon Facility in the U.K. The direction of the initial muon spin is parallel to the beamline. Forward and backward counters were located on the upstream and the downstream sides in the direction of the beamline. The asymmetry parameter $A(t)$ was defined as $A(t)=[F(t)-\alpha B(t)]/[F(t)+\alpha B(t)]-A_{BG}$, where $F(t)$ and $B(t)$ are the total muon events counted by the forward and the backward counters at time t, respectively. A_{BG} is the background. α is the calibration factor reflecting the relative counting efficiencies of both counters. In ZF experiments, stray fields at the sample position were compensated within 0.05 Oe by using correction coils; this is a small enough value for our ZF μSR measurement. The LF μSR experiments were performed by applying magnetic fields up to 500 Oe along the beamline.

III. RESULTS AND DISCUSSION

Figure 1 shows the ZF μSR time spectra at several temperatures T. $A(t)$ gradually decreases with increasing t above T_{MI}, where the muon spin depolarizes slowly because of transferred magnetic fields from dynamically fluctuating Sm moments and nuclear moments. The decrease of $A(t)$ becomes rapid below about 17 K. Muon spin precession was observed at low temperatures below about 5 K, which indicates that the ground state of the Sm moments is a magnetically ordered state.

In order to clearly show the change of the spectrum shown in Fig. 1, the spectra were analyzed by a multicomponent function expressed by the formula

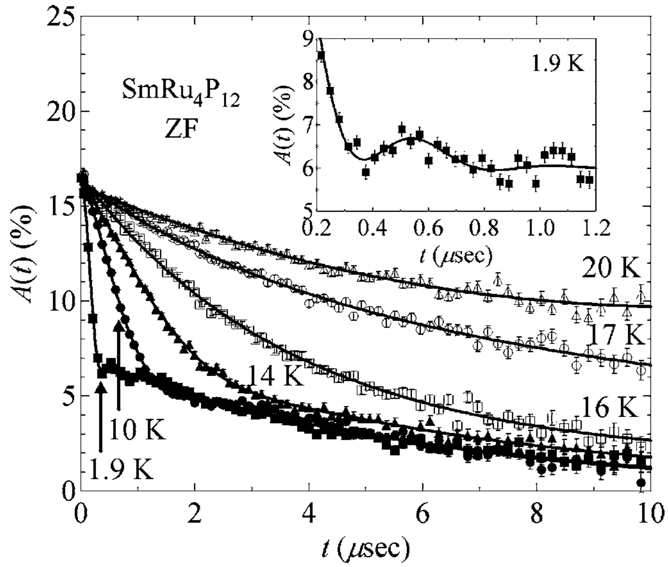

FIG. 1. ZF μSR time spectra at several temperatures. The inset shows the muon spin precession at 1.9 K. The solid lines show the best-fit results by the formula (1).

$$A(t)=A_1e^{-\lambda_1 t}+A_2e^{-\lambda_2 t}+A_3e^{-\lambda_3 t}\cos(\omega t+\theta). \qquad (1)$$

The first and second terms simply represent the components of the rapid and the slow depolarizations, respectively. The third term describes the precession component. The parameters A_1, A_2, and A_3 are the initial asymmetries at $t=0$, λ_1, λ_2, and λ_3 are the muon spin depolarization rates, and ω and θ are the frequency and phase of the precession. In the analysis of spectra below about 5 K, which include the muon spin precession component, the third term was taken into account. The spectra above that temperature, which have no precession, were analyzed without this term.

Figure 2 shows the T dependence of A_2 and λ_2. At T_{MI}, A_2 rapidly decreases, and λ_2 shows a peak. The decrease of A_2 means the increase of A_1, which corresponds to the appearance of fast relaxation behavior with a magnetic origin. The peak in λ_2 arises from the critical slowing-down behavior of the Sm moments around T_{MI}. These results strongly support the appearance of a magnetically ordered state below

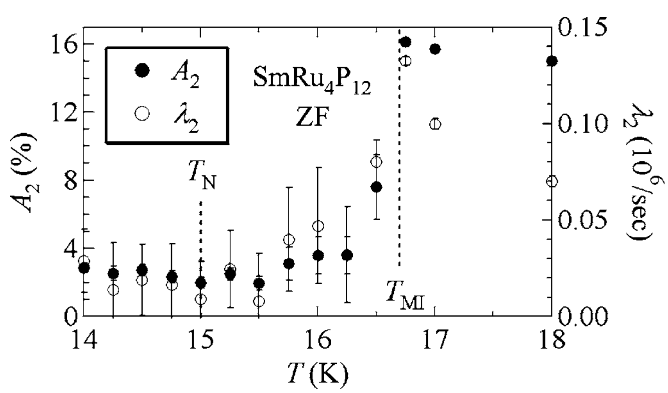

FIG. 2. Temperature dependence of A_2 (closed circles) and λ_2 (open circles) obtained from the best-fit results by the formula (1) shown as the solid lines in Fig. 1.

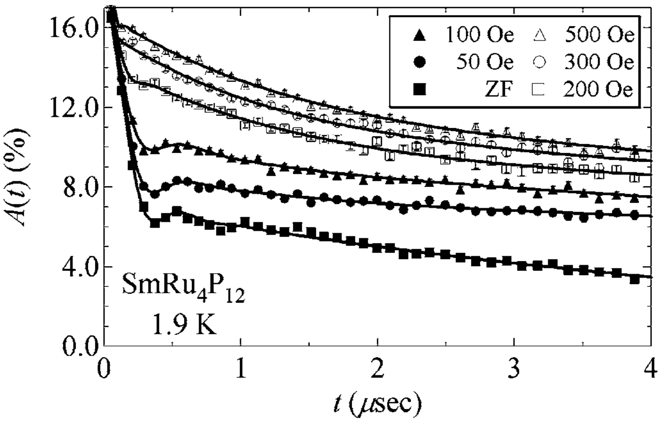

FIG. 3. LF μSR time spectra at 1.9 K in several longitudinal fields. The solid lines show the best-fit results by the formula (1).

T_{MI}.[25,26] On the contrary, no remarkable anomaly was observed around T_N.

Since the muon spin precession was not clearly observed above about 5 K, LF μSR measurements were performed at several temperatures in order to clarify whether the anomaly at T_{MI} is due to a static or a dynamical internal field. Figure 3 shows the LF μSR time spectra at 1.9 K in several longitudinal fields H_{LF}. The tail of the spectrum longer than about 1 μs increases with increasing H_{LF}. Spectral overlap exists below about 0.3 μs. This behavior is typical in the presence of a static internal field at the muon site.[27] Long-term depolarizations were observed in each field due to the contribution from the fluctuations of the Sm moments at 1.9 K.

Figure 4 shows the H_{LF} dependence of A_2 at 1.9 K obtained from the spectra by adopting the formula (1). In LFs, the muon spins rotate around the total field of the internal field and the LF at the muon site. The spectra change with increasing H_{LF}, which is well represented by the increase of the A_2 fraction in formula (1). This means that the muon spin is gradually decoupled by a LF from the static internal field, which causes fast depolarization below T_{MI}. The static internal field H_{int} at this temperature was estimated from the H_{LF} dependence of A_2 by using the formula

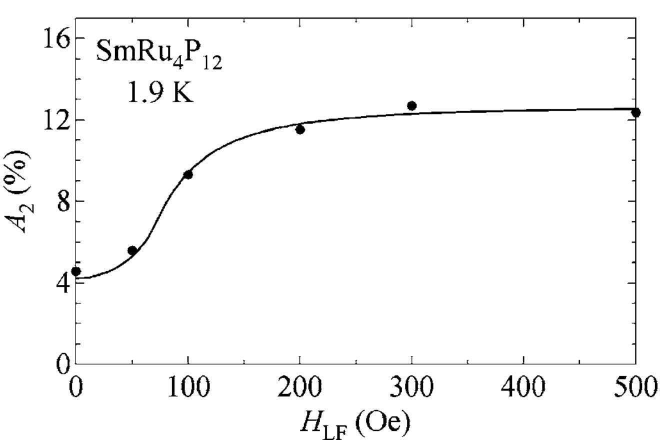

FIG. 4. Longitudinal field dependence of A_2 at 1.9 K obtained from the best-fit results by the formula (1) shown as the solid lines in Fig. 3. The solid line shows the best-fit result by the formula (2).

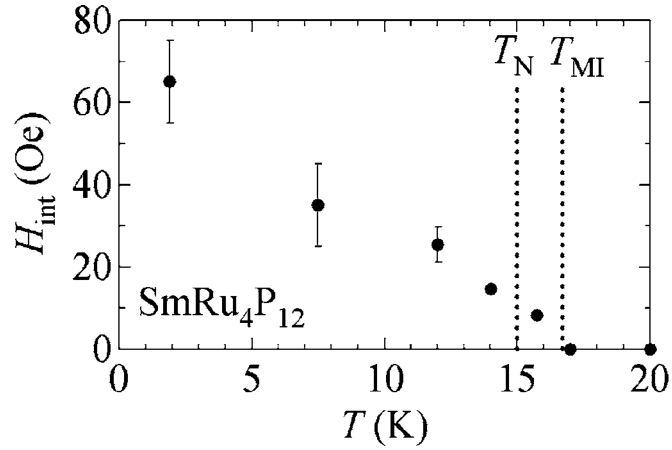

FIG. 5. Temperature dependence of H_{int} obtained from the decouplings of the LF μSR spectra.

$$A_2 = \frac{3}{4} - \frac{1}{4x^2} + \frac{(x^2-1)^2}{16x^3} \ln \frac{(x+1)^2}{(x-1)^2}, \tag{2}$$

where $x = H_{LF}/H_{int}$. This formula is derived from the assumption that H_{int} has a unique magnitude but random directions to H_{LF}.[28,29] Then, $H_{int} \simeq 65$ Oe was evaluated at this temperature. This field is much higher than that expected for nuclear dipole moments.

Figure 5 shows the T dependence of H_{int} obtained by the same procedures. H_{int} appears below T_{MI}. Together with the ZF μSR results which suggest the appearance of a magnetic transition at T_{MI}, these results indicate that a static internal field appears below T_{MI} but not below T_N. This leads to the conclusion that the ordering below T_{MI} is not a nonmagnetic AFQ ordering but a magnetic one with TRS breakdown.

TRS breakdown in NpO_2 was also confirmed by observing the muon spin precession below the transition temperature of 25 K.[30] Compared with the case of NpO_2, the precession in $SmRu_4P_{12}$ shows a fast dumping, which means that the spin alignment is not so coherent. Although the origin of the low coherency is not clear at the moment, it might be guessed that the fluctuating Sm moments smear out the precession.

A clear anomaly was not observed around T_N, which is consistent with other experiments.[10,12,17,19,20] From a group-theoretical consideration based on Landau theory, this ambiguous transition can be explained by the coupling of an octupolar (Γ_{5u}) and a dipolar (Γ_{4u}) order parameter.[20] The strength of the coupling depends on the separation of the transition temperatures. This is supported by the result that Γ_{5u} and Γ_{4u} belong to the same irreducible representation in the T_h symmetry. In ZF and low fields, the coupling can smear out the anomaly at T_N because the separation between each transition temperature is small.[20] In this case, the anomaly around T_N becomes ambiguous. On the other hand, with increasing field, the anomaly around T_N becomes clear. Hence, the present result is consistent with the expected behavior in the octupolar-dipolar (AFM) scenario.[20] In addition, it is noted that a magnetic dipole moment has been excluded as a candidate for the order parameter below T_{MI} because a discontinuous transition is expected at T_N in this case.[20] Therefore, the probable order parameter for this MI transition is a magnetic octupolar ordering.

It is also pointed out from multiorbital Anderson model calculations that a Γ_{5u} and Γ_{4u} octupolar fluctuation can become significant in Sm-based filled skutterudite systems.[31] In the case of NpO_2, it is reported that the hyperfine interactions at O sites obtained from ^{17}O NMR can be well explained by a longitudinal triple-$\vec{q}$ multipolar structure.[22,23] In order to establish the octupolar scenario in $SmRu_4P_{12}$, angle-resolved NMR with single-crystal and neutron diffraction experiments using a sample without an isotope of the ^{149}Sm nucleus are strongly required in future works. In conjunction with these results, an octupolar structure can be specified in $SmRu_4P_{12}$.

IV. SUMMARY

In summary, ZF and LF μSR measurements on $SmRu_4P_{12}$ have been performed. The T dependence of both A_2 and λ_2 obtained from the ZF μSR spectra has an anomaly around T_{MI}. The appearance of a static internal field below T_{MI} was confirmed from the decouplings of the LF μSR spectra. These results are direct evidence for magnetic ordering with TRS breakdown below T_{MI} but not a nonmagnetic AFQ ordering, which supports the scenario that magnetic octupolar ordering occurs below T_{MI} in $SmRu_4P_{12}$.

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