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Multipole and superconducting state in $PrIr_2Zn_{20}$ probed by muon spin relaxation

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We performed muon spin rotation and relaxation (μSR) measurements in the caged-structure heavy-fermion system $PrIr_2Zn_{20}$ to elucidate its magnetic and superconducting properties. Temperature-independent μSR spectra were observed below 1 K, indicating that the phase transition at 0.11 K is of a nonmagnetic origin, most probably pure quadrupole ordering. In the superconducting phase, no sign of unconventional superconductivity, such as superconductivity with broken time-reversal symmetry, was seen below $T_c = 0.05$ K. We also observed spontaneous muon spin precession in zero field in the paramagnetic phase below 15 K, suggesting that unusual coupling between ^{141}Pr nuclei and muons is realized in $PrIr_2Zn_{20}$.

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I. INTRODUCTION

f electrons of rare-earth and actinide ions support a variety of multipole degrees of freedom. In a highly symmetric crystalline-electric-field (CEF) potential, the multipole degrees of freedom survive even at low temperatures in some cases and a degenerate CEF ground state with multipoles (magnetic dipoles, electric quadrupoles, magnetic octupoles, or higher-order multipoles) is realized. Recent intensive research on localized f electrons has revealed that the high-order multipole interactions possibly overcome exchange interactions to realize a higher-order multipole ordering. Meanwhile, unconventional superconductivity is seen in several f-electron systems. In most of them, the origin of the superconductivity is believed to be a magnetic interaction. However, superconductivity occurs in a few systems with a nonmagnetic CEF ground state, and it has been suggested that the multipole fluctuation mediates the electron pairing interaction. Therefore, the interplay between superconductivity and a multipole in f-electron systems is important for the investigation of the mechanism of electron pairing.

Among f-electron systems, interest in Pr-based strongly correlated electron systems has been stimulated by the observations of attractive phenomena, such as heavy-fermion states, superconductivity, and multipole ordering. For example, unconventional superconductivity and magnetic-field-induced quadrupole ordering are observed in the Pr-based heavy-fermion system $PrOs_4Sb_{12}$.[1] In $PrOs_4Sb_{12}$, the superconducting phase is embedded in the quadrupole ordering phase in the B-T phase diagram. Since a nonmagnetic ground state is realized in $PrOs_4Sb_{12}$, it is arguable that the quadrupole fluctuation may play an important role in the mechanism of unconventional superconductivity.[2] Recently, another example of a Pr-based heavy-fermion system was found in $PrIr_2Zn_{20}$.[3] $PrIr_2Zn_{20}$ belongs to the group of caged compounds RT_2X_{20} having the cubic $CeCr_2Al_{20}$-type structure, where the R atoms are encapsulated in cages formed by 16 X atoms. In an RT_2X_{20} system, multipole phase transitions or strong hybridizations between $4f$ electrons and conduction bands are expected to occur owing to the highly degenerate ground state. In $PrIr_2Zn_{20}$, no magnetic phase transition is observed in magnetization measurements, which suggests a Γ_3 non-Kramers-doublet Pr ion. In addition, ac magnetic susceptibility measurements revealed superconductivity below 0.05 K in $PrIr_2Zn_{20}$. This system is the second example of a Pr-based heavy-fermion system in which superconductivity is observed. Since a nonmagnetic CEF ground state is suggested in $PrIr_2Zn_{20}$, quadrupole interactions may play an important role in its superconductivity. Furthermore, recent low-temperature specific heat measurements reveal a phase transition below 0.11 K, suggesting quadrupole ordering.[4] Therefore, the coexistence of superconductivity and quadrupole ordering may be realized; thus, it is quite interesting to investigate the possibility of superconductivity in a quadrupole ordered state.

The muon spin rotation and relaxation (μSR) technique is the ideal tool for investigating magnetic ground states and superconductivity. In particular, a muon detects only a local magnetic field. Therefore, pure quadrupole ordering and magnetic-multipole-related ordered states can be distinguished by μSR. In addition, unconventional superconductivity, e.g., superconductivity with broken time-reversal symmetry, is detectable. Since such superconductivity has been suggested in $PrOs_4Sb_{12}$, it is quite interesting to investigate the superconductivity in another Pr-based heavy-fermion superconductor $PrIr_2Zn_{20}$. We performed μSR experiments on $PrIr_2Zn_{20}$ to investigate the magnetic multipole ground state and the superconducting state.

II. EXPERIMENT

A conventional μSR measurement under zero magnetic field (ZF) above 2 K was carried out at the D1-area muon science facility (MUSE), J-PARC, Tokai, Japan. A low-temperature experiment using a dilution refrigerator was also carried out at the M15 beam channel, TRIUMF, Vancouver, Canada. At both these facilities, positive muons with a momentum of 29 MeV/c were implanted into the specimen, and the time evolution of the muon spin polarization was recorded.

Single-crystalline samples of $PrIr_2Zn_{20}$ were grown at Hiroshima University by the melt-growth method described elsewhere.[3] Several pieces of a single-crystalline specimen

(∼0.5 g) of $PrIr_2Zn_{20}$, from the same batch as the crystal of Ref. 4 used in the specific heat and magnetization measurements, were measured. A mosaic of aligned single crystals were glued to a silver sample holder by using Apiezon-N grease. The initial spin direction of the muon was along the (100) direction of the crystals.

III. RESULTS AND DISCUSSION

Figure 1 shows the time evolution of the ZF μSR spectrum in $PrIr_2Zn_{20}$ at various temperatures. At 100 K, very slow muon spin relaxation, due to the nuclear dipolar moments of ^{141}Pr and ^{191,193}Ir, was observed. Usually, if a system is nonmagnetic, its μSR spectra are expected to be independent of temperature. However, below approximately 70 K, the muon spin relaxation gradually became faster as the temperature decreased, indicating the appearance of a local magnetic field at the muon site. Moreover, below 15 K, spontaneous muon spin precession was seen under a ZF. This means that a static and homogeneous magnetic field existed at the muon site. We note that not all implanted muons showed the spontaneous muon spin precession. Approximately 16% of the muons were rotated by the homogeneous magnetic field, while the rest exhibited exponential or Gaussian relaxation. The fast Fourier transform (FFT) of the μSR spectrum at 1.6 K is shown in Fig. 2. It is evident that the spontaneous muon spin precession occurred with one frequency. This precession signal was observed right down to the lowest temperature (0.02 K). The origin of the local field will be discussed later.

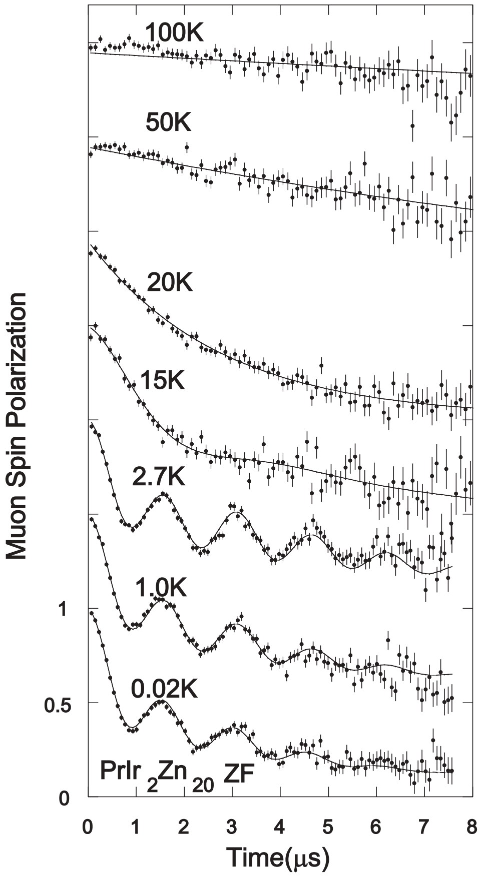

FIG. 1. μSR spectra for $PrIr_2Zn_{20}$ at various temperatures.

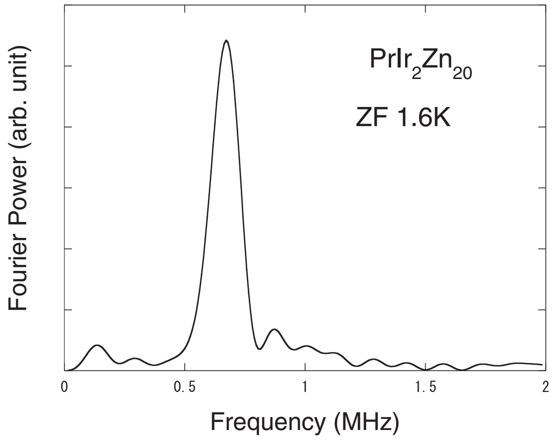

FIG. 2. Fast Fourier transform of the ZF-μSR spectrum (0.3–8.0 μs) for $PrIr_2Zn_{20}$ at 1.6 K. One peak is observed.

The μSR spectra above 20 K were fitted using the following exponential muon spin relaxation function:

$$P(t) = A_1 \exp(-\lambda t). \qquad (1)$$

For $T \leqslant 20$ K,

$$P(t) = A_1 \exp(-\sigma_1^2 t^2) + A_2 \exp(-\lambda_1 t) + A_3 \exp(-\lambda_2 t) \cos(2\pi f t + \phi) \qquad (2)$$

was used for analyzing the μSR spectra. The spectrum at 20 K can be fitted by using both functions. Figure 3 shows the temperature dependence of the muon spin relaxation rate λ and the precession frequency f. λ shows a steep increase when the temperature falls below approximately 70 K and f gradually increases as the temperature decreases down to 3 K. We obtained $f \sim 0.65$ MHz at 3 K, which corresponds to ∼50 Oe of the local field at the muon site. The temperature dependence curve of λ smoothly connected with that of f, and λ and f should have the same origin.

Below 1 K, there is no significant temperature dependence in the ZF μSR spectra. Figure 4 shows the temperature dependence of the fitting parameters λ_1, λ_2, σ_1, and f in

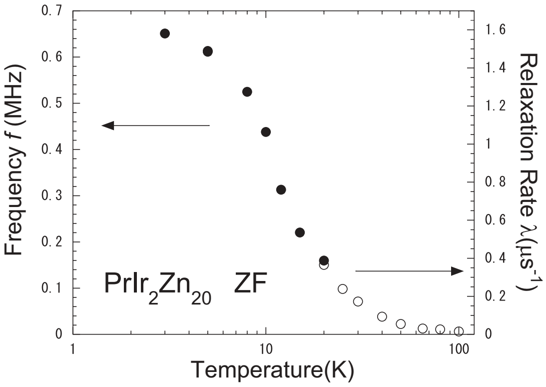

FIG. 3. Temperature dependence of the muon spin relaxation rate λ ($\geqslant$20 K) and the muon spin precession frequency f ($\leqslant$20 K) in $PrIr_2Zn_{20}$ under a zero magnetic field. The μSR spectrum at 20 K can be fitted by using both Eq. (1) and Eq. (2).

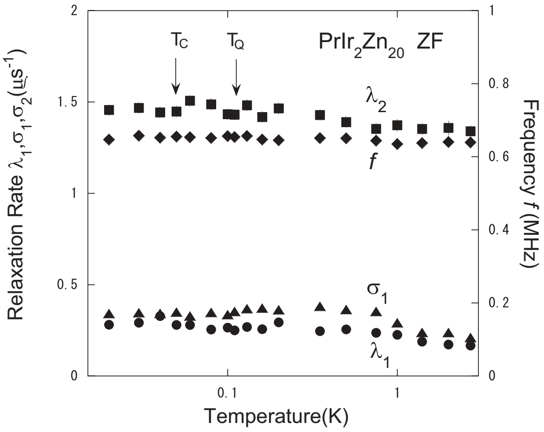

FIG. 4. Temperature dependence of the muon spin relaxation rates $\sigma_1,\lambda_1,\lambda_2$ and precession frequency f in Eq. (2) below 2 K in $PrIr_2Zn_{20}$. T_Q and T_c are the quadrupole ordering and superconducting transition temperatures, respectively.

Eq. (2) below 2 K. Here, the asymmetries (A_1, A_2, and A_3) were determined at 2.0 K and fixed for fitting by Eq. (2). As shown in Fig. 4, all the fitting parameters are independent of the temperature below 1 K, indicating no sign of anomalous behavior at the phase transition temperature $T_Q = 0.11$ K and the superconducting transition temperature $T_c = 0.05$ K.

We will now discuss the origin of the homogeneous local magnetic field at a muon site. Usually, spontaneous muon spin precession under ZF is observed in a magnetically ordered state. However, we believe that the spontaneous muon spin precession in $PrIr_2Zn_{20}$ is not due to magnetic ordering for the following reasons. First, no magnetic anomaly was observed in any bulk measurements. For example, the magnetic susceptibility shows a Van Vleck paramagnetic state and no trace of magnetic ordering is observed. In the specific heat measurements, no phase transition is observed above 0.11 K.[3,4] Furthermore, from these measurements, a nonmagnetic Γ_3 CEF ground state was proposed. These facts strongly suggest that a nonmagnetic ground state is realized in $PrIr_2Zn_{20}$. Second, the temperature dependence of the muon spin relaxation or spontaneous muon spin precession is quite different from the usual second-order phase transition. The muon spin relaxation rate starts to increase at approximately 70 K and, even at 3 K, the muon spin precession frequency is still increasing as the temperature decreases. This change in the muon spin relaxation over such a wide temperature range is quite different from the usual second-order phase transition. Thus, we propose that the muon spin relaxation in $PrIr_2Zn_{20}$ is due to the formation of spin coupling between the ^{141}Pr nuclei and the muons. In some Pr-based compounds, spin coupling between enhanced ^{141}Pr nuclear spins and muon spins occurs and anomalous spin relaxation is seen. Since the nuclear spin of ^{141}Pr and the muon spin are $I = 5/2$ and $I = 1/2$, respectively, multiple muon spin precession frequencies are expected. Indeed, five frequencies were seen in μSR measurements for $PrPb_3$.[5] However, we observed only one frequency of the muon spin relaxation, as shown in Figs. 1 and 2. Although it is expected that an unusual spin coupling system may form in $PrIr_2Zn_{20}$, the detailed state is unclear. The rotation component is ∼16% of the total signal and the state of the rest of the muons is not known. It may be possible that a combination of dipolar and isotropic couplings accidentally makes some frequencies nearly degenerate, and zero or much stronger muon spin relaxation occurs. It is also possible that there are other crystallographic muon sites. We note that such coupling is not seen in $PrTi_2Al_{20}$, probably due to the difference in the CEF level scheme.[6]

In the present measurements, the muon stopping site is not determined exactly. However, a coupling state between the muon and Pr is observed; hence we speculate that the muon stopping site is near the Pr ion, probably inside the Zn cage. In this case, the muon is close enough to the Pr ion to affect the crystal field. The temperature dependence of the muon spin relaxation frequency may reflect the locally perturbed CEF level scheme.

Next, we discuss the low-temperature properties of $PrIr_2Zn_{20}$. As is evident from Fig. 4, we observed no significant temperature variation of the muon spin relaxation below 1 K. This fact demonstrates that no additional magnetic field appeared at the phase transition temperature $T_Q = 0.11$ K. This proves that the transition at $T_Q = 0.11$ K is not magnetic in origin. In general, pure electric quadrupole ordering generates no additional local magnetic field under a ZF. A similar lack of variation of the muon spin relaxation in quadrupole ordering states is observed in UCu_2Sn (Ferroquadrupole (FQ) ordering),[7] CeB_6 (Antiferroquadrupole (AFQ) ordering),[8] and $PrTi_2Al_{20}$ (AFQ ordering).[6] Therefore, we conclude that the phase transition at 0.11 K is most probably due to pure quadrupole ordering. This is quite consistent with the recent ultrasonic measurement made by Ishii *et al.* that suggests AFQ ordering below T_Q.[9] They also discussed the quadrupole Kondo effect as a reason for the relatively low T_Q in $PrIr_2Zn_{20}$. The quadrupole Kondo effect and non-Fermi-liquid behavior in non-Kramers-doublet systems has also been discussed for (Pr,La)Pb_3,[10] $PrMg_3$,[11] $PrInAg_2$,[12] PrV_2Al_{20},[13] and $PrNb_2Al_{20}$.[14]

Below 50 mK, superconductivity is observed in the resistivity and the ac magnetic susceptibility measurements.[3,4] This superconductivity is observed not in a part of the specimen, but in the entire volume of the specimen.[4] In Pr-based superconductors with a nonmagnetic Γ_1 CEF ground state, $PrOs_4Sb_{12}$ (Refs. 1 and 15) and $PrPt_4Ge_{12}$ (Refs. 16 and 17), the appearance of additional weak local magnetic fields of a few oersteds is observed below the superconducting transition temperatures. In these systems, it is argued that the origin of the local magnetic fields below T_c is due to superconductivity with broken time-reversal symmetry. In the case of such superconductivity, there are several possible sources of a local field, depending on the spin and/or orbital parts of the Cooper pairs having nonzero values.[18] Usually, such a local magnetic field is averaged out in the whole system and is undetectable by bulk measurements. The muon is a local probe and can detect this type of weak field. However, in the present study, we did not observe such a field and no sign of superconductivity with broken time-reversal symmetry was evident. This result is in contrast with results for $PrOs_4Sb_{12}$ or $PrPt_4Ge_{12}$. For the appearance of such superconductivity, it may be important that the system be located quite close to a quantum critical point for quadrupole ordering.

Finally, let us now look at μSR in weak transverse magnetic fields. Generally, in the mixed state of a type-II superconductor, enhancement of muon spin relaxation due to vortex lattice formation, which reflects the magnetic penetration depth, is observed by transverse μSR measurements. In $\mathrm{PrIr_2Zn_{20}}$, however, no difference in muon spin relaxation under a transverse magnetic field of 20 Oe, which was applied perpendicular to the sample plane, was observed at 0.05 K ($\sim T_c$ at ZF) and 0.02 K ($<T_c$ at ZF). Probably this was because the critical field H_c was lower than 20 Oe. To obtain the magnetic penetration depth, a high-statistics μSR experiment under a weak field of a few oersteds is required.

In the present measurement, we have not observed any trace of unconventional superconductivity in $\mathrm{PrIr_2Zn_{20}}$. However, we cannot exclude unconventional superconductivity of $\mathrm{PrIr_2Zn_{20}}$ and further studies are required to determine the nature of the superconductivity.

IV. CONCLUSIONS

The μSR measurements we conducted on a single-crystalline specimen of $\mathrm{PrIr_2Zn_{20}}$ verify that no additional magnetic field appears at $T_Q = 0.11$ K, or at the superconducting transition temperature $T_c = 0.05$ K, suggesting that the phase transition at 0.11 K is most probably due to pure quadrupole ordering. Furthermore, no trace of superconductivity with broken time-reversal symmetry was observed. In the present study, no evidence of any unconventional superconductivity was obtained and so further microscopic studies are required.

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