Multipole and superconducting state in PrIr$_2$Zn$_{20}$ probed by muon spin relaxation

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We performed muon spin rotation and relaxation ($\mu$SR) measurements in the caged-structure heavy-fermion system PrIr$_2$Zn$_{20}$ to elucidate its magnetic and superconducting properties. Temperature-independent $\mu$SR 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$_2$Zn$_{20}$.

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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$_4$Sb$_{12}$. 1 In PrOs$_4$Sb$_{12}$, 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$_4$Sb$_{12}$, 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$_2$Zn$_{20}$. 3 PrIr$_2$Zn$_{20}$ belongs to the group of caged compounds $RT_2X_{20}$ having the cubic CeCr$_2$Al$_{20}$-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$_2$Zn$_{20}$, no magnetic phase transition is observed in magnetization measurements, which suggests a $\Gamma_3$ non-Kramers-doublet Pr ion. In addition, ac magnetic susceptibility measurements revealed superconductivity below 0.05 K in PrIr$_2$Zn$_{20}$. 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$_2$Zn$_{20}$, 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 ($\mu$SR) 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 $\mu$SR. In addition, unconventional superconductivity, e.g., superconductivity with broken time-reversal symmetry, is detectable. Since such superconductivity has been suggested in PrOs$_4$Sb$_{12}$, it is quite interesting to investigate the superconductivity in another Pr-based heavy-fermion superconductor PrIr$_2$Zn$_{20}$. We performed $\mu$SR experiments on PrIr$_2$Zn$_{20}$ to investigate the magnetic multipole ground state and the superconducting state.

II. EXPERIMENT

A conventional $\mu$SR 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$_2$Zn$_{20}$ were grown at Hiroshima University by the melt-growth method described elsewhere.5 Several pieces of a single-crystalline specimen...
(\sim 0.5 \text{ g}) \text{ of PrIr}_2\text{Zn}_{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 \( \mu \text{SR} \) spectrum in \text{PrIr}_2\text{Zn}_{20} at various temperatures. At 100 K, very slow muon spin relaxation, due to the nuclear dipolar moments of \( ^{141}\text{Pr} \) and \( ^{191,193}\text{Ir} \), was observed. Usually, if a system is nonmagnetic, its \( \mu \text{SR} \) 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 \( \mu \text{SR} \) 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.

The \( \mu \text{SR} \) spectra above 20 K were fitted using the following exponential muon spin relaxation function:

\[
P(t) = A_1 \exp(-\lambda_1 t).
\]  

For \( T < 20 \text{ K} \),

\[
P(t) = A_1 \exp(-\sigma_1^2 t^2) + A_2 \exp(-\lambda_2 t) + A_3 \exp(-\lambda_2 t) \cos(2\pi ft + \phi)
\]

was used for analyzing the \( \mu \text{SR} \) 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 \( \lambda \) and the precession frequency \( f \). \( \lambda \) 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 \( f \sim 0.65 \text{ MHz} \) at 3 K, which corresponds to \( \sim 50 \text{ Oe} \) of the local field at the muon site. The temperature dependence curve of \( \lambda \) smoothly connected with that of \( f \), and \( \lambda \) and \( f \) should have the same origin.

Below 1 K, there is no significant temperature dependence in the ZF \( \mu \text{SR} \) spectra. Figure 4 shows the temperature dependence of the fitting parameters \( \lambda_1, \lambda_2, \sigma_1, \) and \( f \) in
Thus, we propose that the muon spin relaxation in PrIr$_2$Zn$_{20}$ is quite different from the usual second-order phase transition. The spin relaxation or spontaneous muon spin precession is quite different from the usual second-order phase transition. The specific heat measurements, no phase transition is observed in a magnetically nonmagnetic PrIr$_2$Zn$_{20}$. Second, the temperature dependence of the muon relaxation occurs. It is also possible that there are other crystallographic muon sites. We note that such coupling is not seen in PrIr$_2$Al$_{30}$, probably due to the difference in the CEF level scheme.

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$_2$Zn$_{20}$. 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$_2$Sn (Ferroquadrupole (FQ) ordering), CeB$_6$ (Anti-ferroquadrupole ordering (AFQ) ordering), and PrIr$_2$Al$_{30}$ (AFQ ordering). 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 $T_Q$. They also discussed the quadrupole Kondo effect as a reason for the relatively low $T_Q$ in PrIr$_2$Zn$_{20}$. The quadrupole Kondo effect and non-Fermi-liquid behavior in non-Kramers-doublet systems has also been discussed for (Pr,La)Pb$_3$, PrMg$_3$, PrInAg$_2$, PrV$_2$Al$_{30}$, and PrNb$_2$Al$_{30}$.

Below 50 mK, superconductivity is observed in the resistivity and the ac magnetic susceptibility measurements. This superconductivity is observed not in a part of the specimen, but in the entire volume of the specimen. In Pr-based superconductors with a nonmagnetic CEF ground state, PrOs$_4$Sb$_{12}$ (Ref. 1 and 15) and PrPt$_4$Ge$_{12}$ (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. 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$_4$Sb$_{12}$ or PrPt$_4$Ge$_{12}$. 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 $\mu$SR 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 $\mu$SR measurements. In PrIr$_2$Zn$_20$, 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 $\mu$SR 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 PrIr$_2$Zn$_20$. However, we cannot exclude unconventional superconductivity of PrIr$_2$Zn$_20$ and further studies are required to determine the nature of the superconductivity.

### IV. CONCLUSIONS

The $\mu$SR measurements we conducted on a single-crystalline specimen of PrIr$_2$Zn$_20$ 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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