Antiferroquadrupolar Ordering in a Pr-Based Superconductor $PrIr_2Zn_{20}$

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An antiferroquadrupolar ordering at $T_Q = 0.11$ K has been found in a Pr-based superconductor $PrIr_2Zn_{20}$. The measurements of specific heat and magnetization revealed the non-Kramers Γ_3 doublet ground state with the quadrupolar degrees of freedom. The specific heat exhibits a sharp peak at $T_Q = 0.11$ K. The increment of T_Q in magnetic fields and the anisotropic $B - T$ phase diagram are consistent with the antiferroquadrupolar ordered state below T_Q. The entropy release at T_Q is only 20% of $R\ln 2$, suggesting that the quadrupolar fluctuations play a role in the formation of the superconducting pairs below $T_c = 0.05$ K.

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Orbital degrees of freedom in d-electron as well as f-electron systems have attracted much attention. An abundance of unusual phenomena in d-electron systems such as metal-insulator transition, high-temperature superconductivity, and colossal magnetoresistance have been discussed on the basis of underlying correlation and/or ordering of the orbital degrees of freedom [1,2]. In $4f$-electron systems, however, strong intra-atomic spin-orbit coupling forces the magnetic and orbital degrees of freedom to be described in terms of the total angular momentum $\boldsymbol{J}$. For instance, an orbitally degenerate state carries quadrupole moments (rank-2 irreducible tensor operators in $\boldsymbol{J}$). The quadrupole moments often play an important role in forming exotic electronic ground states such as the antiferroquadrupolar (AFQ) state with a staggered quadrupolar component [3] and a non-Fermi liquid (NFL) state attributed to two-channel (quadrupole) Kondo effect [4–8]. Furthermore, the feasibility of superconductivity mediated by quadrupolar fluctuations in the heavy-fermion superconductor $PrOs_4Sb_{12}$ with $T_c = 1.5$ K [9] has been pointed out by neutron scattering and nuclear quadrupole resonance measurements [10,11].

The AFQ ordering gives rise to a spontaneous lifting of the orbital degeneracy without uniform structural distortion characterized by the $k = 0$ propagation vector [3]. It is therefore a phase transition of the quadrupole moments. The quadrupole moments are active in the ground state or low-lying state of the $4f$ ions under the crystalline electric field (CEF). A well-known example of a $4f^2$ cubic system is $PrPb_3$, which undergoes the AFQ transition at $T_Q = 0.4$ K [12,13]. In this case, the CEF splits the ninefold multiplet with $J = 4$ into four multiplets. The CEF ground state of the nonmagnetic Γ_3 doublet carries electric quadrupole moments $O_2^0 = (3J_z^2 - \boldsymbol{J}^2)/2$ and $O_2^2 = \sqrt{3}(J_x^2 - J_y^2)/2$. The former has been found to be the AFQ order parameter by the combined analysis of magnetization and neutron scattering experiments [14,15]. The quadrupole moments are aligned with an incommensurate sinusoidally modulated structure even in the ground state. Thereby, the indirect RKKY-type interaction between the quadrupoles plays the essential role. On the other hand, substituting La for Pr in $PrPb_3$ destroys the AFQ order at $x = 0.03$ in $Pr_{1-x}La_xPb_3$ [16]. NFL behavior appearing for $x \geq 0.95$ arises from the quadrupole Kondo effect. The absence of AFQ order in $PrInAg_2$ [17] and $PrMg_3$ [18,19] with the Γ_3 doublet was discussed by taking the quadrupole Kondo effect into consideration. However, the NFL behavior and absence of AFQ order might be attributed to the atomic disorder effect inherent to the diluted systems and to the Heusler structure compounds. Quadrupole moments are active in the CEF ground states in uranium-based systems, such as $U_xY_{1-x}Pd_3$ [20,21], UBe_{13} [22] $U_xTh_{1-x}Be_{13}$ [23], and $U_xTh_{1-x}Ru_2Si_2$ [24], none of which show AFQ order.

In Ce- and Yb-based compounds, NFL behaviors and/or superconductivity often appear in the vicinity of quantum critical points [8,25–28]. In certain cases, the intersite RKKY magnetic interaction competes with the on-site Kondo effect. In analogy, a new type of quantum critical point due to the quadrupolar degrees of freedom may exist when the RKKY-type interaction between the quadrupoles competes with the quadrupolar Kondo effect.

We have recently reported that $PrIr_2Zn_{20}$ undergoes a superconducting transition at $T_c = 0.05$ K [29]. The superconductivity was indicated by the large diamagnetic signal in the ac magnetic susceptibility. This compound crystallizes in the cubic $CeCr_2Al_{20}$-type structure with the space group $Fd\bar{3}m$ and $Z = 8$ [30], where Pr atoms are encapsulated in the highly symmetric Frank-Kasper cages formed by 16 zinc atoms. On cooling below 2 K, the specific heat divided by the temperature, C/T, continuously increases and reaches 5 $\mathrm{J/(K^2\,mol)}$ at 0.4 K, suggesting that Pr $4f^2$ electrons are involved in the heavy-fermion state. It should be recalled that heavy-fermion behaviors are found in the isostructural Yb-based compounds $\mathrm{YbT_2Zn_{20}}$ (T = Fe, Co, Ru, Rh, Os, and Ir) which locate in the vicinity of a quantum critical point [31,32].

In this Letter, we report the first observation of AFQ ordering in a superconductor $\mathrm{PrIr_2Zn_{20}}$. Our analysis of magnetic anisotropy in the paramagnetic state and a Schottky peak in the specific heat reveals that the CEF ground state of $\mathrm{PrIr_2Zn_{20}}$ is the non-Kramers Γ_3 doublet. The twofold degeneracy is found to be released by the AFQ ordering at 0.11 K. The entropy at T_Q is reduced to $0.2R\ln 2$ from $R\ln 2$ expected for twofold degeneracy of the Γ_3 state. This fact leads one to speculate that quadrupolar fluctuations would play an important role in the formation of the superconducting pairs.

Single crystals of $\mathrm{PrIr_2Zn_{20}}$ used in the present work were grown by the melt-growth method described in the previous paper [29]. Magnetization was measured by using a commercial SQUID magnetometer (Quantum Design MPMS) between 1.9 and 350 K in magnetic fields up to 5 T. Magnetization measurements at low temperatures down to 0.045 K were performed by a capacitive Faraday method with a high-resolution capacitive force-sensing device installed in a ^{3}He-^{4}He dilution refrigerator [33]. Specific heat was measured by a relaxation method between 0.4 and 300 K and by a quasiadiabatic method down to 0.06 K. Thereby, a horizontal magnetic field was generated by a split-pair superconducting magnet. The ac magnetic susceptibility was measured down to 0.02 K by using a Hartshorn bridge installed in a ^{3}He-^{4}He dilution refrigerator. The samples of $\mathrm{PrIr_2Zn_{20}}$ and the reference superconductor $\mathrm{LaIr_2Zn_{20}}$ of the same dimensions $0.5 \times 1 \times 4\ \mathrm{mm^3}$ were loaded, respectively, into two pickup coils wound in reverse.

In order to determine the CEF ground state, we have analyzed the results of magnetization and specific heat. Figure 1 shows the temperature dependence of the inverse magnetic susceptibility χ^{-1} at a magnetic field of B = 0.1 T applied along the [100] direction. At $T > 30$ K, χ^{-1} follows the Curie-Weiss law with the effective magnetic moment of 3.49(2) μ_B/f.u., in agreement with the value of the trivalent Pr ion. On cooling below 30 K, χ^{-1} gradually approaches a constant value, which is a characteristic of Van Vleck paramagnets. As the $\mathrm{Pr^{3+}}$ ion in $\mathrm{PrIr_2Zn_{20}}$ is on a site of the T_d point group, the CEF splits the ninefold multiplet into four multiplets: Γ_1 singlet, Γ_3 doublet, and Γ_4 and Γ_5 triplets. If the CEF ground state is either Γ_1 or Γ_3, the ground state can be nonmagnetic. The magnetic part of the specific heat C_m shows a Schottky anomaly at 10 K, as shown in the lower inset in Fig. 1. The height and

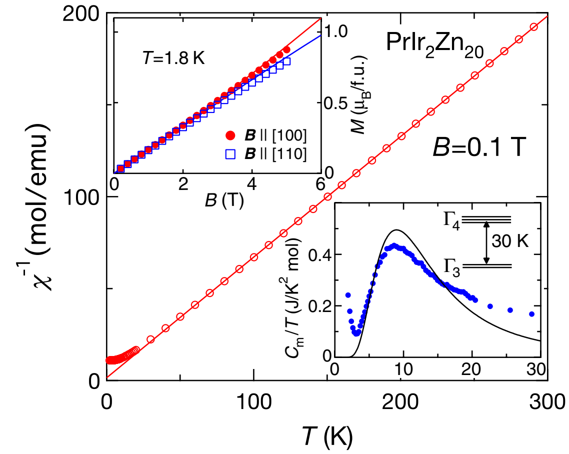

FIG. 1 (color online). Temperature dependence of the inverse magnetic susceptibility $\chi^{-1}(T)$ at a magnetic field of $B = 0.1$ T for $\boldsymbol{B}\|[100]$. At $T > 30$ K, $\chi^{-1}(T)$ follows the Curie-Weiss law with the effective magnetic moment of a free $\mathrm{Pr^{3+}}$ ion. The lower inset displays the temperature dependence of the magnetic part of the specific heat divided by the temperature, C_m/T. The solid line is the calculation for a CEF level scheme with the ground state of a Γ_3 doublet and an excited state of magnetic Γ_4 triplet lying at 30 K. The upper inset shows the isothermal magnetization in $\boldsymbol{B}\|[100]$ and $\boldsymbol{B}\|[110]$ at 1.8 K. The lines are the $M(B)$'s calculated for the CEF scheme as shown in the lower inset.

width of the peak are rather well reproduced by a two-level model of doublet and triplet separated by $\Delta E = 30$ K (see the solid line). Given that the ground state was a Γ_1 singlet, the peak height would be twice as large as the experimental data. The Γ_3 doublet ground state is further supported by the observation of the anisotropic behavior in the isothermal magnetization $M(B)$ as is shown in the upper inset in Fig. 1. At 1.8 K, $M(B)$'s for $\boldsymbol{B}\|[100]$ and $\boldsymbol{B}\|[110]$ are almost the same up to 1.5 T, above which $M(B)$'s gradually diverge. This anisotropic behavior of $M(B)$'s can be reproduced by the calculation for the Γ_3–Γ_4 CEF level scheme (see the solid lines). This magnetic anisotropy is indeed consistent with that of the Pr-based AFQ compound $\mathrm{PrPb_3}$ [13]. In addition to $\mathrm{PrPb_3}$, the Γ_3 ground state has been reported for a few Pr-based compounds such as $\mathrm{PrInAg_2}$, $\mathrm{PrMg_3}$, PrPtBi (ferroquadrupolar ordering at 1.35 K) [34], and $\mathrm{PrInNi_4}$ (ferromagnetic ordering at 0.75 K) [35]. The issue is how to lift the twofold degeneracy of the Γ_3 doublet. On cooling $\mathrm{PrIr_2Zn_{20}}$, C/T continuously increases and reaches 5 $\mathrm{J/(K^2\,mol)}$ at 0.4 K. This behavior should result from the gradual release of the entropy in the Γ_3 doublet because the C_m/T deviates upwards from the curve calculated for the CEF scheme, as shown in the lower inset in Fig. 1.

Keeping this in mind, we extended the temperature range of the measurements of M and C for $\mathrm{PrIr_2Zn_{20}}$ down to 0.045 and 0.06 K, respectively. Figure 2 shows a sharp peak in $C(T)$ at 0.11 K. The inset in Fig. 2 shows the temperature dependence of M/B at various magnetic fields up to 10 T applied along the [100] direction. Because no magnetic anomaly was observed at around 0.11 K in M/B,

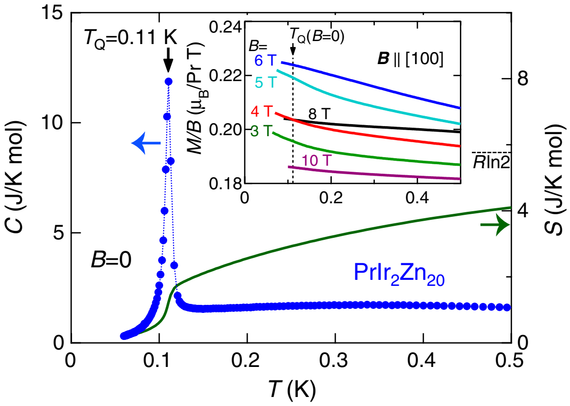

FIG. 2 (color online). The solid circles and solid line, respectively, show the temperature dependences of the specific heat C (left-hand scale) and the entropy S (right-hand scale) of $PrIr_2Zn_{20}$. C shows a sharp peak at $T_Q = 0.11$ K, at which temperature S is only 20% of $R\ln 2$. The inset shows the temperature dependence of M/B at various magnetic fields of $\boldsymbol{B}\|[100] = 3$, 4, 5, 6, 8, and 10 T.

this phase transition should result from a nonmagnetic origin. The continuous decrease in $C(T)$ for $T < 0.11$ K further supports the nonmagnetic ordered state, because the Pr nuclear contribution would be strongly enhanced by a large internal magnetic field at the Pr sites if a magnetic order occurred. The entropy release up to 0.11 K was estimated to be $0.2R\ln 2$ as shown with the solid line. We may discard the possibility of ordering of nuclear spins of $I = 5/2$ for ^{141}Pr nuclei which should release the entropy of $R\ln 6$. Therefore, the phase transition is likely to be the ordering of the multipolar degrees of freedom in the Γ_3 doublet. We denote the ordering temperature at 0.11 K as T_Q, hereafter.

The data of $C(T)$ in magnetic fields for $\boldsymbol{B}\|[100]$ are shown in Fig. 3(a). Once a magnetic field is applied, the peak is split in two. The higher transition temperature T_{Q1} increases with increasing magnetic fields up to 5 T. The lower one T_{Q2} decreases to 0.095 K at 2 T but increases at $B > 2$ T and disappears at $B \geq 3.5$ T. On the other hand, in $\boldsymbol{B}\|[110]$ as shown in Fig. 3(b), the peak does not split but shifts to higher temperatures. These variations of $C(T)$ in magnetic fields must reflect the anisotropic responses of the order parameter to the magnetic field.

The $B - T$ phase diagrams for $\boldsymbol{B}\|[100]$ and $\boldsymbol{B}\|[110]$ are summarized in Fig. 4. The transition temperatures were determined as the temperature at the maximum of $C(T)$. Note that both T_{Q1} for $\boldsymbol{B}\|[100]$ and T_Q for $\boldsymbol{B}\|[110]$ are increased in the magnetic field. The AFQ state in $PrPb_3$ has a similar phase diagram [13–15], where the increment of T_Q was explained by taking account of the interaction between field-induced multipoles [36] and/or fluctuations of the quadrupole moments [37]. The phase diagram of $PrIr_2Zn_{20}$ is circumstantial evidence of the AFQ order. Further evidence for AFQ order has been given by ultrasonic measurements, which revealed a negative coupling constant between the quadrupole moments and

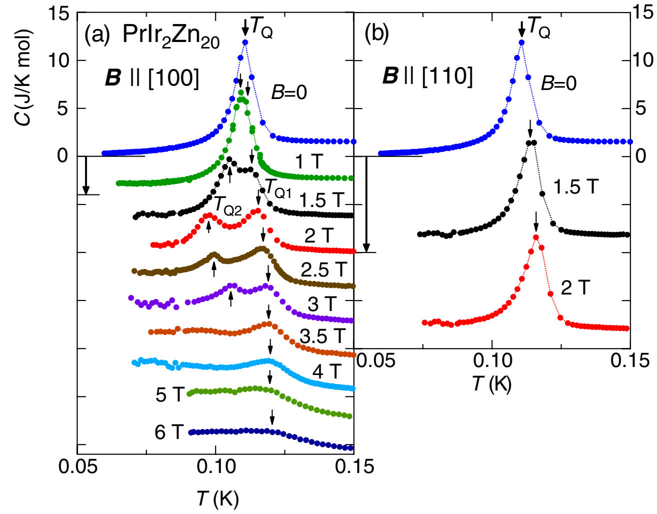

FIG. 3 (color online). Temperature dependence of the specific heat of $PrIr_2Zn_{20}$ in $\boldsymbol{B}\|[100]$ and $\boldsymbol{B}\|[110]$. Each data point in the magnetic field is vertically offset for clarity. In $B = 0$, a sharp peak appears at 0.11 K, which splits into two at T_{Q1} and T_{Q2} in $\boldsymbol{B}\|[100] \geq 1$ T. The upper temperature T_{Q1} increases with increasing magnetic fields. In $\boldsymbol{B}\|[110]$, however, the peak shifts to higher temperatures without being split.

disappearance of the quadrupolar degrees of freedom at $T < T_Q$ [38]. To determine the order parameter, alignment of field-induced magnetic moments reflecting the quadrupole ordered structure should be observed by the neutron diffraction technique.

The superconducting transition of $PrIr_2Zn_{20}$ was studied by the ac magnetic susceptibility and electrical resistivity measurements. As shown in the inset in Fig. 4, the Meissner signal of $PrIr_2Zn_{20}$ below 0.05 K fully compensates the opposite signal from the reference superconductor $LaIr_2Zn_{20}$ with $T_c = 0.6$ K [29], confirming the bulk nature of the superconductivity in $PrIr_2Zn_{20}$. As displayed in

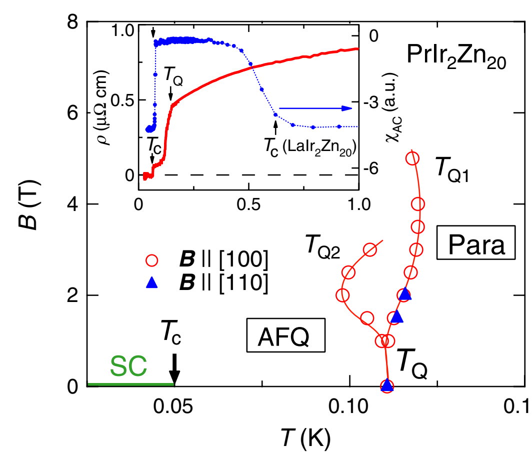

FIG. 4 (color online). $B - T$ phase diagram of $PrIr_2Zn_{20}$ for $\boldsymbol{B}\|[100]$ (open circles) and $\boldsymbol{B}\|[110]$ (solid triangles). T_c and SC denote the superconducting transition temperature and the superconducting phase, respectively. The inset shows the temperature dependence of the ac magnetic susceptibility and electrical resistivity.

the diagram, the superconducting state with $T_c = 0.05$ K exists in the AFQ ordered phase. Thus, $PrIr_2Zn_{20}$ is the first example where a superconducting transition occurs in the AFQ phase.

There are several Pr-based superconductors such as $PrOs_4Sb_{12}$ [9], $PrPt_2B_2C$ [39,40], and $PrPt_4Ge_{12}$ [41]. However, their CEF ground states are the nonmagnetic singlet. Among them, the heavy-fermion compound $PrOs_4Sb_{12}$ undergoes a superconducting transition at $T_c = 1.85$ K. Upon applying a magnetic field, the superconductivity vanishes at 2 T, which is followed by the appearance of an AFQ ordering at $B > 4$ T, where the quadrupole moments are induced by the Zeeman effect. Although the interplay between the quadrupolar degrees of freedom and the superconductivity was pointed out [10,11], the AFQ phase is away from the superconducting phase in the $B - T$ phase diagram. In contrast, the quadrupole moments of the Γ_3 ground state in $PrIr_2Zn_{20}$ are active even in zero magnetic field. The reduced entropy of $0.2R\ln 2$ at T_Q indicates that the fluctuations of the quadrupole moments remain below T_Q. Therefore, the fluctuations of the quadrupole moments possibly play the essential role in the formation of the superconducting pairs.

It is interesting to compare the present system with iron pnictide superconductors showing critical d-orbital fluctuations. The orbital fluctuations induced by the electron-phonon interaction due to the Fe-ion oscillation are thought to stabilize the superconducting state [42]. Strong electron-phonon interaction in $LaIr_2Zn_{20}$, $PrRu_2Zn_{20}$, and $LaRu_2Zn_{20}$ has been suggested by the observation of structural distortions above 100 K [29]. The role of the orbital degrees of freedom in the superconducting state in $PrIr_2Zn_{20}$ would be revealed by comprehensive studies using microscopic techniques.

In summary, we performed the magnetization M and specific heat C measurements on the Pr-based superconductor $PrIr_2Zn_{20}$ with a caged structure. The CEF ground state of the trivalent Pr ion was found to be the non-Kramers Γ_3 doublet. We observed a sharp peak in $C(T)$ at $T_Q = 0.11$ K, whereas no anomaly appears in $M(T)$ at around T_Q. Moreover, the anisotropic variations of $C(T)$ and the increment of the transition temperatures in magnetic fields strongly support the AFQ ordering. The entropy at T_Q is only 20% of $R\ln 2$, suggesting the possible interplay between quadrupolar fluctuations and the superconductivity. In order to explore it, transport and magnetic measurements under high pressures as well as microscopic measurements such as neutron scattering, μSR, and NMR at $T < 0.1$ K are in progress.

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