Possible Observation of the Quadrupolar Kondo Effect in Dilute Quadrupolar System $\mathbf{Pr_xLa_{1-x}Pb_3}$ for $x \leq 0.05$

T. Kawae,* K. Kinoshita, Y. Nakaie, N. Tateiwa, and K. Takeda
Department of Applied Quantum Physics, Kyushu University, Fukuoka 812-8581, Japan

H. S. Suzuki
National Institute for Material Science, Sengen, Tsukuba, Ibaraki 305-0047, Japan

T. Kitai
Faculty of Engineering, Kyushu Insititute of Technology, Kitakyushu 804-8550, Japan

(Received 11 January 2005; published 19 January 2006)

We have studied non-Fermi-liquid (NFL) behavior in $Pr_xLa_{1-x}Pb_3$ with Γ_3 quadrupolar moments in the crystalline-electric-field ground state. The specific heat C/T shows NFL behavior in the very dilute region for $x \leq 0.05$, which is scaled by a characteristic temperature T^* in each Pr concentration. The application of a magnetic field leads to a sharp increase of C/T, demonstrating the shift of the entropy existing in the lower temperature region at $H = 0$ T. Moreover, Fermi-liquid behavior emerges at higher fields, in contrast with NFL behavior at lower fields. The observed features indicate that NFL behavior is caused by the quadrupolar Kondo effect.

DOI: 10.1103/PhysRevLett.96.027210 PACS numbers: 75.20.Hr, 71.27.+a, 75.40.Cx

The description of Fermi-liquid theory is the basis to understanding the electronic properties in various kinds of metals, while a large number of Ce- and U-based compounds have been found to show a non-Fermi-liquid (NFL) behavior. The multichannel Kondo effect [1] leads to the breakdown of the Fermi-liquid state and gives rise to NFL behavior [2,3]. As a special case of the two-channel Kondo effect (TCKE), the quadrupolar Kondo effect (QKE) is expected to be realized in f-electron compounds with the quadrupolar moments of a Γ_3 doublet in the crystalline-electric-field (CEF) ground state [4]. U^{4+} ion with the $5f^2$ configuration or Pr^{3+} ion with the $4f^2$ configuration under cubic symmetry can have the Γ_3 doublet in the CEF ground state. In this situation, the fluctuation of the quadrupolar moments would be quenched by the conduction electrons [4–6]. The scattering path between the Γ_3 doublet and the charge of the conduction electrons involves two electron channels, giving an overcompensation of the Γ_3 quadrupolar moment by conduction electrons below a characteristic temperature T_K. Since QKE corresponds to TCKE in the magnetic system, QKE causes the peculiar features such as NFL behavior, e.g., the logarithmic temperature dependence of the specific heat, $C/T \propto -\ln T$, and the residual entropy of $0.5R\ln 2$ at the ground state, where R is a gas constant. However, there has been no experimental evidence of QKE [7–13].

We have focused on $PrPb_3$ substituted by nonmagnetic La ions [14–16]. It is well established that the base-compound $PrPb_3$ has a Γ_3 doublet in the CEF ground state and exhibits the antiferroquadrupolar ordering at $T_Q = 0.4$ K [17]. We have demonstrated from the specific heat and susceptibility measurements that the Γ_3 doublet in the CEF ground state does not change by La substitution for the whole range of Pr concentration, implying that $Pr_xLa_{1-x}Pb_3$ is a good candidate to study QKE.

In this Letter, we report the specific heat study in $Pr_xLa_{1-x}Pb_3$ at the dilute region of the quadrupolar moments $x \leq 0.05$. The specific heat C/T shows NFL behavior, which is scaled by a characteristic temperature T^* in each Pr concentration. The magnetic field effect of C/T can be explained by the shift of the entropy at lower temperatures at $H = 0$ T predicted from the theories on QKE [2,18,19]. These facts provide strong support for the scenario that QKE is responsible for NFL behavior.

The samples of $Pr_xLa_{1-x}Pb_3$ were prepared by the same procedure reported in the previous papers [14,15]. The magnetization is measured by a Quantum Design SQUID magnetometer. The specific heat is measured by a quasiadiabatic heat-pulse method using a dilution refrigerator.

Prior to the results in the very dilute region of Pr ions, we summarize results in the higher concentrations. T_Q is strongly suppressed by La substitution, and the ordering exists only for the Pr concentration larger than $x \sim 0.98$ [14]. In a wide range for $0.1 \leq x \leq 0.95$, the specific heat shows a T-linear variation with a large γ coefficient ($= C/T$) at low temperatures, which is almost reproduced by the model for amorphous materials with a random configuration of a two-level system (RTLS) [14].

For $x \leq 0.05$, the low-temperature properties are changed dramatically as reported in our previous papers [15,16]. We show the concentration dependence of the electronic specific heat C_{el}/T at $H = 0$ T in Fig. 1. C_{el}/T shows NFL behavior with a monotonical enhancement, while that for $x = 0.1$ is almost constant at low temperatures. The data for $x \leq 0.05$ can be scaled by a characteristic temperature T^* as shown in the inset. These

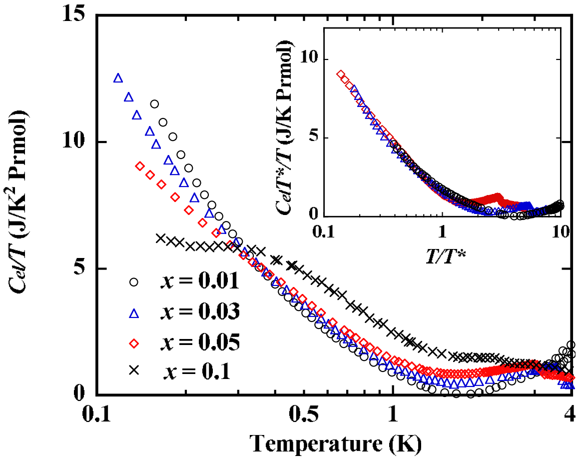

FIG. 1 (color online). C_{el}/T at $H = 0$ T plotted on a logarithmic temperature scale measured in a single crystal for $x = 0.05$ and polycrystals for $x = 0.1$, 0.03, and 0.01. C_{el}/T for $x = 0.1$ is almost constant at low temperatures, while that for $x \leq 0.05$ shows NFL behavior (see text). Inset: $C_{el}T^*/T$ versus log (T/T^*) at $H = 0$ T. T^* is taken to be 1 K for $x = 0.05$, 0.65 K for $x = 0.03$, and 0.40 K for $x = 0.01$.

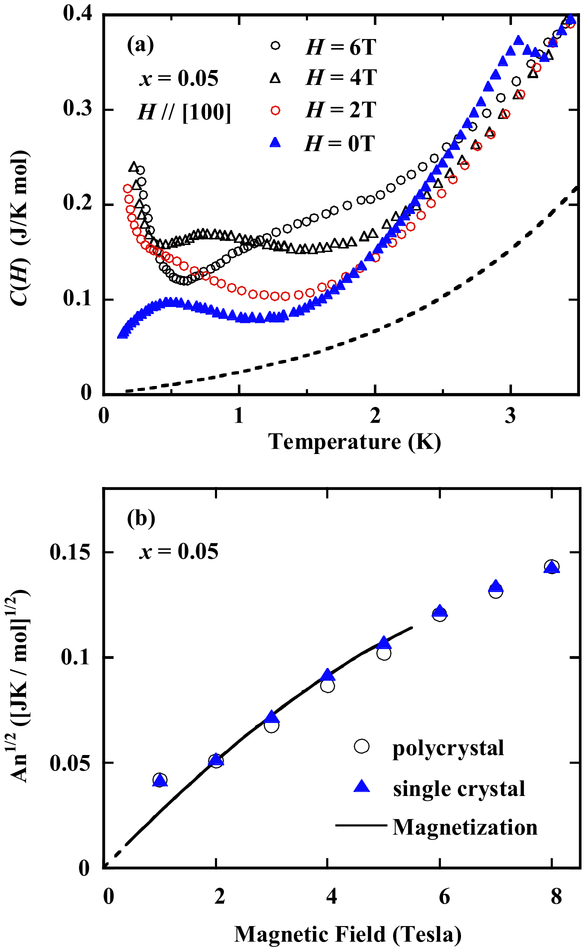

FIG. 2 (color online). (a) Temperature dependence of the specific heat for the single crystal in $H \parallel [100]$ at representative magnetic fields. The data from bottom to top at $T = 1$ K correspond to the results for $H = 0$, 2, 6, and 4 T, respectively. The dashed line shows the phonon contribution C_{ph} for $H \geq 1$ T estimated from the specific heat of LaPb$_3$. (b) Magnetic field dependence of $A_n^{1/2}$ in the nuclear specific heat obtained by the fitting from Eq. (1) and that calculated from the magnetization at $T = 2$ K for $x = 0.05$.

results represent two significant features: NFL behavior appears in *the dilute limit of the* Γ_3 *moments* and is understood as *the single-ion effect of the* Γ_3 *moments*. In addition, we observed important characteristics in the magnetic susceptibility and the electrical resistivity [15,16]. The susceptibility increases gradually below 5 K with decreasing temperature. The electrical resistivity $\rho(T)$ for $x \leq 0.05$ exhibits a marked decrease deviating from the Fermi-liquid behavior in the temperature region where NFL behavior was observed in the specific heat. These features for $x \leq 0.05$ suggest that NFL behavior comes from Kondo effect arising from the correlation between the Γ_3 moments and the conduction electrons.

Next we explore the magnetic field dependence of the specific heat $C(H)$. As mentioned above, there exists the residual entropy at low temperatures in the quadrupolar Kondo system. In this case, the peculiar features such as the enhancement of the γ coefficient should be observed when a magnetic field, lifting the degeneracy of the Γ_3 doublet, is applied [2,18,19].

We show the temperature dependence of $C(H)$ in $x = 0.05$ at representative fields in Fig. 2(a). The sharp peak at around 3.2 K at $H = 0$ T, which is due to the superconducting transition in LaPb$_3$ [15,20], shrinks rapidly by applying a small external field. Within the resolution of the measurements, the anomaly is indistinguishable above $H = 0.05$ T, which is lower than the upper critical field of the transition. Thus, we neglect the additional specific heat due to the superconducting transition in the following discussion above $H = 1$ T. The specific heat $C(H)$ is largely modified with increasing magnetic field. An upturn with $1/T^2$ dependence appears at low temperatures, and grows with increasing magnetic field. This upturn is caused by a nuclear Schottky specific heat. To extract the field dependence of C_{el}, we tentatively express $C(H)$ as

$$C(H) = \left(\frac{A_n}{T^2}\right) + C_{ph} + C_{el}. \qquad (1)$$

A_n/T^2 and C_{ph} represent the nuclear and lattice contributions, respectively. From the fit of the upturn with $1/T^2$ dependence, we estimate the coefficient A_n and plot the results in Fig. 2(b). The value of $A_n^{1/2}$ exhibits a huge nuclear specific heat, which leads to the increase of a thermal relaxation time between the nuclear spin and lattice system [21]. In the present experiments, the deviation from the $1/T^2$ dependence is detected at lowest temperatures in high field region, e.g., below $T = 0.25$ K at $H = 6$ T. The estimation of A_n, therefore, is carried out carefully in the region where the $1/T^2$ dependence is observed [22]. We emphasize that the ambiguity of A_n does not affect the qualitative features discussed later.

PrPb$_3$ is of the hyperfine enhanced system [23], meaning that the field at Pr nuclei is enhanced by $(1 + K)$ due to the hyperfine field generated by the Van Vleck susceptibility through the off-diagonal matrix element of the total angular momentum $\mathbf{J} = 4$, where K is the enhancement factor. Since $K \gg 1$, $A_n$is approximated by

$$A_n = R(A_{\mathrm{hf}}\chi^{VV}H/g_J\mu_B)^2 I(I+1)/3, \qquad (2)$$

where A_{hf}, χ^{VV}, g_J, μ_B, and I are the magnetic dipole hyperfine constant of Pr nuclei with the value of 0.052 K [24], the Van Vleck susceptibility, the Landé g factor, the Bohr magneton, and Pr nuclear spin moment of $I = 5/2$, respectively. We evaluated $A_n^{1/2}$ from the magnetization by using Eq. (2) as plotted in Fig. 2(b). The values of $A_n^{1/2}$ obtained from the specific heat and the magnetization measurements are in reasonable agreement above $H = 2$ T, reflecting the consistency of the two measurements. On the other hand, there is a discrepancy between them at $H = 1$ T, suggesting that the susceptibility at $H = 1$ T increases below 2 K. We observed the similar field dependence of the susceptibility in the dilute quadrupolar compound Pr$_x$La$_{1-x}$InAg$_2$ [25]. The susceptibility increases remarkably below 15 K at low fields, while the increase is suppressed with increasing magnetic field.

In Figs. 3(a) and 3(b) we show the magnetic field dependences of C_{el}/T for $x = 0.05$ estimated from Eq. (1) for the single crystal in $H \parallel [100]$ and for the polycrystal, respectively. When appropriate magnetic fields of $H = 2$ and 3 T are applied, the slope of C_{el}/T exhibits a sharp increase preserving NFL behavior as shown in the figures. The value of C/T in Ce- and U-based compounds reported to show NFL behavior so far is monotonically suppressed with increasing magnetic field up to the field at which Fermi-liquid behavior emerges [9,10,26]. Thus, the increase of C_{el}/T in the present compound demonstrates that the origin of NFL behavior is different from that in Ce- and U-based compounds, in which the origin is thought to be magnetic fluctuations.

As magnetic field is further increased, the breakdown of the NFL state becomes apparent. At $H = 4$ T, a round shape is seen at around 0.7 K, implying the beginning of the suppression of NFL behavior. Above $H = 6$ T, C_{el}/T is almost constant. Recalling the fact that $\rho(T)$ at $H = 6$ T follows approximately T^2 dependence for the observed temperature region, while a marked decrease of $\rho(T)$ is found below $H = 5$ T [15,16], we can conclude that Fermi-liquid state emerges above $H = 6$ T. This feature is extremely important for the evidence of *the nonlocal nature of the* Γ_3 *moments*. The application of the magnetic field leads to the energy splitting of the Γ_3 doublet due to the Van Vleck term through the off-diagonal matrix element, which is the same at every Pr site. Thus, if the Γ_3 moments were localized, NFL behavior should have been observed to higher fields, that is, the magnetic field could not have changed the qualitative feature of the ground state properties.

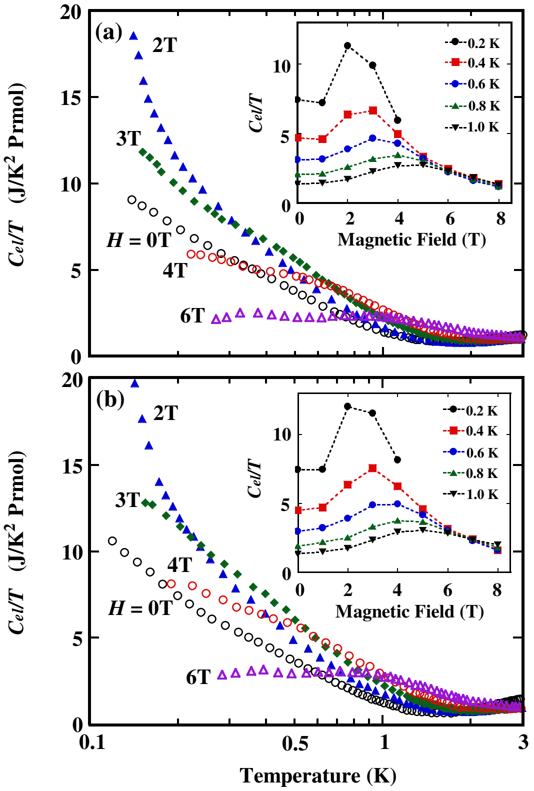

FIG. 3 (color online). (a) Magnetic field dependences of C_{el}/T in $H \parallel [100]$ in the single crystal. Inset: The magnetic field dependence of C_{el}/T at representative temperatures. The dashed lines are guides for eyes. (b) Magnetic field dependences of C_{el}/T in the polycrystal. The inset shows the magnetic field dependence of C_{el}/T at representative temperatures.

Here, we discuss the present results under magnetic fields based on the field effect on the two-channel Kondo model (TCKM) because the quadrupolar Kondo model (QKM) can be mapped on TCKM which has been extensively studied. The magnetic field in QKM acts as the channel field in TCKM [5]. In addition, the splitting of the Γ_3 doublet by magnetic field should be taken into account in real compounds, which corresponds to the case of the application of the spin field in TCKM. The application of the channel or spin field in TCKM brings about a large increase of the γ coefficient in the specific heat because of the residual entropy at the ground state [2,18]. In other words, the entropy, which exists in the lower temperature region, should shift to higher temperatures by applying the channel or spin field. Qualitatively, the same features have to be observed in QKM by applying magnetic field, because this situation corresponds to the case in the application of the channel and spin fields in TCKM as described above.

Indeed, the field dependence of C_{el}/T is consistent with that expected from QKM under magnetic fields as follows [2,18,19]. The sharp increase of C_{el}/T is observed at $H = 2$ T, which demonstrates the presence of the entropy in the lower temperature region. C_{el}/T at $H = 1$ T, on the other hand, seems to keep the value at $H = 0$ T as shown in each of the insets in Figs. 3(a) and 3(b), which implies that the field is insufficient to raise C_{el}/T, i.e., to shift the entropy up to the observed temperature region predicted in Fig. 2 or Fig. 6 in Ref. [2]. The entropy calculated by integrating C_{el}/T between $T = 0.2$ and 2 K in the single crystal is $0.64R\ln2$ at $H = 0$ T and changes to $0.82R\ln2$ at 2 T, $0.92R\ln2$ at 3 T and $0.87R\ln2$ at 4 T. Moreover, it will gradually decrease at higher fields. The field dependence of C_{el}/T reflects the shift of the entropy existing in the lower temperature region to higher temperatures as a function of the magnetic field. The calculated entropy at $H = 0$ T already exceeds the theoretical value of $0.5R\ln2$ in QKE. This can be ascribed to the distortion of CEF because of the difference of the ion radius between Pr^{3+} and La^{3+}, which causes lifting the degeneracy of the Γ_3 doublet even at zero field and raising C_{el}/T at low temperatures, which is discussed in the previous papers [14,15].

The suppression of NFL behavior at higher fields can be related with the crossover effect from NFL to Fermi-liquid state by decreasing temperature [5]. The crossover temperature is predicted to be about Δ^2/T_K in QKM for $\Delta \ll T_K$, where Δ is the effective field, which includes the contributions from both the channel field and the splitting of the Γ_3 doublet due to the Van Vleck term, and T_K is Kondo temperature. The first excited level in the present compound is at ~15 K, leading to the large splitting of the Γ_3 doublet, whereas the effect of the channel field is obscure. For simplicity, we take account of only the splitting due to the Van Vleck term in the present case. At $H = 4$ T, Δ in the [100] direction is evaluated to be ~1.8 K from the CEF scheme, while T_K is considered to be ~5 K from the electrical resistivity results [15,16]. The evaluated value is in reasonable agreement with the crossover temperature of ~0.7 K at $H = 4$ T, although Δ is close to T_K. The crossover temperature shifts to higher temperatures with increasing magnetic field, resulting in the emergence of Fermi-liquid behavior for a wide temperature region above $H = 6$ T.

As shown above, the observed features indicate that QKE is responsible for NFL behavior for $x \leq 0.05$. In addition, the correlation between the Γ_3 moments and the conduction electrons may play the crucial role for the novel features even in the Pr concentration for $x \geq 0.1$. In $PrPb_3$, the correlation may bring about a nonsquare modulated structure in the quadrupolar ordering as reported by Onimaru *et al.* [17]. For $0.1 \leq x \leq 0.95$, the T-linear specific heat reproduced by the model for amorphous materials with RTLS suggests appearance of a glasslike state of the Γ_3 moments [14]. This state seems to be realized due to the competition of two kinds of correlations, (i) the correlation between the Γ_3 moments and the conduction electrons and (ii) the intersite correlation between the Γ_3 moments. Further experimental and theoretical studies are needed to clarify the novel features arising from the correlation between the Γ_3 moments and the conduction electrons.

In conclusion, we have revealed the following features on NFL behavior in $Pr_xLa_{1-x}Pb_3$. NFL behavior of C_{el}/T appears in the dilute limit of the Γ_3 moments for $x \leq 0.05$, and is understood as the single-ion effect of the Γ_3 moments. With increasing magnetic field, the sharp increase of C_{el}/T is observed for $x = 0.05$, which reflects the shift of the entropy existing at lower temperatures at $H = 0$ T. In contrast to NFL behavior at lower fields, Fermi-liquid behavior emerges above $H = 6$ T. The observed features indicate that NFL behavior for $x \leq 0.05$ is caused by QKE due to the correlation between the Γ_3 moments and the conduction electrons.

We would like to express our sincere thanks to M. Koga, H. Ishii, O. Sakai, Y. Shimizu, K. Miyake, T. Onimaru, and T. Sakakibara for valuable comments and helpful discussion. This work was partly supported by the Grant-Aid for Scientific Reserch from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

---

*Electronic address: kawaetap@mbox.nc.kyushu-u.ac.jp

[1] P. Nozières and A. Brandin, J. Phys. (Paris) **41**, 193 (1980).
[2] P.D. Sacramento and P. Schlottmann, Phys. Rev. B **43**, 13 294 (1991).
[3] I. Affleck and A.W.W. Ludwig, Phys. Rev. B **48**, 7297 (1993).
[4] D.L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[5] For a review, D.L. Cox and A. Zawadowski, Adv. Phys. **47**, 599 (1998).
[6] M. Koga and H. Shiba, J. Phys. Soc. Jpn. **64**, 4345 (1995).
[7] M.B. Maple *et al.*, J. Low Temp. Phys. **99**, 223 (1995).
[8] H. Amitsuka and T. Sakakibara, J. Phys. Soc. Jpn. **63**, 736 (1994).
[9] B. Andraka and A.M. Tsvelik, Phys. Rev. Lett. **67**, 2886 (1991).
[10] H. Amitsuka *et al.*, Physica (Amsterdam) **281–282B**, 326 (2000).
[11] A. Yatskar *et al.*, Phys. Rev. Lett. **77**, 3637 (1996).
[12] Y. Aoki *et al.*, Phys. Rev. B **65**, 064446 (2002).
[13] E.D. Bauer *et al.*, Phys. Rev. B **65**, 100506(R) (2002).
[14] T. Kawae *et al.*, Phys. Rev. B **65**, 012409 (2002).
[15] T. Kawae *et al.*, J. Phys. Soc. Jpn. **72**, 2141 (2003).
[16] T. Kawae *et al.*, Physica (Amsterdam) **329-333B**, 493 (2003).
[17] T. Onimaru *et al.*, Phys. Rev. Lett. **94**, 197201 (2005), and references therein.
[18] N. Andrei and A. Jerez, Phys. Rev. Lett. **74**, 4507 (1995).
[19] Y. Shimizu *et al.*, J. Phys. Soc. Jpn. **68**, 2994 (1999).
[20] E. Bucher *et al.*, Helv. Phys. Acta **41**, 723 (1968).
[21] R. Vollmer *et al.*, Phys. Rev. Lett. **90**, 057001 (2003).
[22] Y. Aoki *et al.*, J. Phys. Soc. Jpn. **71**, 2098 (2002).
[23] H. Ishii, J. Low Temp. Phys. **135**, 579 (2004).
[24] B. Bleany, J. Appl. Phys. **34**, 1024 (1963).
[25] T. Kawae *et al.*, J. Phys. Soc. Jpn. **74**, 2332 (2005).
[26] H. v. Löhneysen *et al.*, Phys. Rev. Lett. **72**, 3262 (1994).