La impurity effects on quadrupolar ordering in $PrPb_3$

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We study low-temperature properties of $Pr_{1-x}La_xPb_3$ with the ground state of a non-Kramers Γ_3 for $0 \leqslant x \leqslant 0.8$. From the concentration dependence of the specific heat, quadrupolar ordering is expected to occur only up to $x \sim 0.02$. For a wide range of La concentrations where the ordering is absent, the specific heat shows a T linear variation, which is in an excellent agreement with the result obtained by the model for amorphous materials with a random configuration of a two-level system. Impurity effects on quadrupolar moments will be discussed.

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There has been a great deal of interest in a system with an orbital degeneracy in the crystal-electric-field (CEF) ground state. As temperature is decreased, a variety of interesting phenomena has been observed by lifting the degeneracy. A typical example is the cooperative Jahn-Teller effect, which is accompanied by a lattice distortion and is often observed in *d*-electron systems.[1] In *f*-electron systems, the orbital degree of freedom is given by quadrupolar moments, because the total angular momentum J is a good quantum number. Some $4f$ compounds with the degeneracy of the quadrupolar moments, e.g., CeB_6,[2] show a long-range ordering at low temperatures. A more attractive problem is the case when the quadrupolar ordering (QPO) does not occur down to 0 K. It has not been clarified, however, what lifts the degeneracy of the quadrupolar moments in such a case. A possible theoretical model could be based on the quadrupolar Kondo effect, which originates from the interaction between quadrupolar fluctuations of a nonmagnetic Γ_3 doublet and the charge of the conduction electrons, as introduced by Cox for the case of UBe_{13}.[3] This effect gives rise to a non-Fermi-liquid (NFL) behavior, such as the logarithmic temperature dependence of the quadrupolar susceptibility and the specific heat, and may explain NFL behavior in U-based compounds such as $Y_{0.8}U_{0.2}Pd_3$.[4]

The CEF level scheme of Pr^{3+} is the same as that of U^{4+} as long as they are in the same crystal-field symmetry. Therefore, a Pr-based compound is a good candidate for studying the quadrupolar Kondo effect. In the specific-heat measurements, Yatskar *et al.* found that $PrInAg_2$, which has a non-Kramers doublet Γ_3 as the CEF ground state, shows no QPO down to 50 mK, but has a Fermi-liquid-like ground state with a very large value of the Sommerfeld coefficient γ $(=C/T) \sim 6.5$ J/mol K^2.[5] Furthermore, the field dependence of the specific heat is very weak compared to the conventional heavy fermion materials arising from the Kondo effect.[6] These results suggest that the interaction between quadrupolar fluctuations of the Pr ions and the conduction electrons leads to a heavy fermion ground state in $PrInAg_2$, but does not cause the NFL behavior.

We focus on $PrPb_3$ with a $AuCu_3$-type cubic crystal structure. The CEF energy level of the $4f$ electron was determined by an inelastic neutron-scattering experiment. The ground state is a non-Kramers doublet Γ_3, and the first excited state is a triplet Γ_4 with an energy difference of 19 K.[7] Thus the magnetic and electronic properties at temperatures much lower than 19 K are mainly characterized by the Γ_3 state, suggesting that this compound can be a candidate for the quadrupolar Kondo system. It was shown that $PrPb_3$ exhibits an antiferro-QPO (AF-QPO) at 0.4 K,[8,9] which indicates that the fluctuation of the quadrupolar moments is entirely depressed at lower temperatures. By substituting nonmagnetic La ions for Pr ions, we have studied the impurity effects on QPO in $PrPb_3$ to compare to a rapid suppression of QPO as observed in $Ce_{1-x}La_xB_6$ (Ref. 10) and $Dy_{1-x}Y_xB_2C_2$ (Ref. 11). Moreover, in the region where QPO does not occur down to 0 K, we have carried out magnetic-susceptibility and specific-heat measurements in $Pr_{1-x}La_xPb_3$ with the CEF ground state of a non-Kramers Γ_3 in order to investigate how the degeneracy of the quadrupolar moments is lifted. In this paper we report a detailed study of the effects of the variation of the La-ion concentration in $Pr_{1-x}La_xPb_3$. We find that QPO disappears at concentration as low as $x \sim 0.02$. For a wide range of concentrations above $x \sim 0.02$, specific-heat measurements show that the system remains in a random configuration of two energy levels, i.e., a random two-level system (RTLS) attributed to the quadrupolar moments.

The samples of $Pr_{1-x}La_xPb_3$ are prepared by the Bridgeman method. Pr, Pb, and La of the required quantities in a Ta crucible are heated in a closed quartz tube under an Ar atomosphere. It is known that both $PrPb_3$ and $LaPb_3$ have a $AuCu_3$-type structure with lattice parameters $a = 4.867$ and 4.903 Å, respectively. In x-ray-diffraction spectra at room temperature, we observed signals not only from the

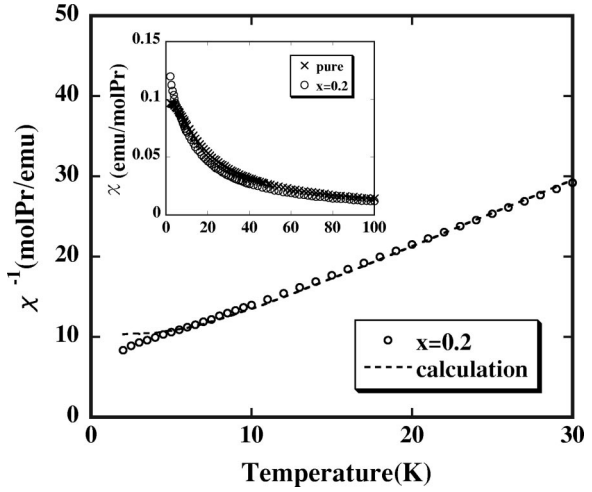

FIG. 1. Temperature dependence of the inverse susceptibility for $x=0.2$. The broken curve shows the calculated result based on the CEF level scheme; the ground state is Γ_3 and the first excited one is Γ_4, with an energy splitting of 19 K. The next excited state is Γ_5, with an energy splitting of 46 K from the ground state. Inset: temperature dependence of the susceptibility for $x=0$ and $x=0.2$.

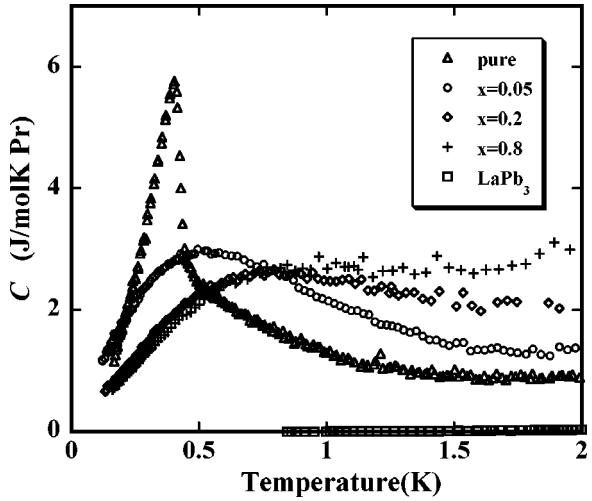

FIG. 2. Temperature dependence of the specific heat for pure and mixed systems with $x=0.05$, 0.2, and 0.8, where the specific heat is normalized by the Pr atomic concentration. The reference compound $LaPb_3$ is also shown.

$Pr_{1-x}La_xPb_3$ phase but also slightly from the Pb metal phase. In electrical resistivity measurements of $Pr_{1-x}La_xPb_3$, the rapid decrease due to the superconducting transition of Pb at 7 K was unavoidable. This is considered to be due to a thin layer of Pb metal phase formed on the sample surface by oxidation.[12] It is noted that the Pb phase does not affect the specific-heat measurements. A clear increase of the lattice parameter by La substitution could not be observed even at a La concentration $x=0.1$, where a remarkable feature is observed in the specific heat.

The susceptibility is measured down to 2 K in a static field of 1 kOe, using a Quantum Design superconducting quantum interference device magnetometer. The specific heat is measured by a semiadiabatic method using a dilution refrigerator. A small amount of Apiezon grease is mixed into some pieces of the single crystal to keep good thermal contact.

The temperature dependence of the susceptibility for all mixed systems was shown to be qualitatively similar to that in $PrPb_3$. The susceptibility obeys a Curie-Weiss law in the high-temperature region, and deviates from it in the low-temperature region. The temperature dependence of the susceptibility for the pure system and for a mixed system of $x=0.2$ are plotted in the inset of Fig. 1. This temperature dependence is explained by considering the CEF energy level of $4f$ electrons in a Pr^{3+} ion. In $PrPb_3$, the present experimental data are well reproduced by the CEF level obtained by the previous experiment.[7,9] At $x=0.2$, the best fit is obtained, as shown in Fig. 1, by assuming the same CEF scheme as that of pure $PrPb_3$, with an energy separation of 19 K between the ground and first excited states. We have estimated the CEF level at various concentrations, and found that the CEF energy level scheme does not change noticeably due to the substitution, i.e., the ground state remains a Γ_3 state. A small modification of the CEF levels, however, can be induced by the substitution. This may give rise to an increase of the susceptibility at very low temperatures, and make a small difference in the susceptibility between pure and mixed systems at high temperatures.

The temperature dependence of the specific heat normalized by the Pr atomic concentration for pure $PrPb_3$ and some typical La concentrations is shown in Fig. 2, along with the data for the reference compound $LaPb_3$. A sharp peak is seen at $T_Q=0.4$ K for $PrPb_3$. This peak was observed in the previous experiments, and explained as the occurrence of QPO.[8,9] In mixed systems, the specific heat changes drastically with an increase of the La concentration x. For $x=0.05$, the sharp peak due to QPO is no longer observed, and in place of it a broad maximum appears at around 0.5 K. This feature is also seen for La concentrations higher than $x=0.05$, where the broad maximum shifts to higher temperatures with the La concentration. The entropy reaches $R\ln 2(=5.9$ J/mol K) at $T\sim 2$ K for all systems, indicating that the ground state of the CEF level also remains at Γ_3 in mixed systems.

We plot C/T on a logarithmic scale of temperature for some lower and higher concentrations of La ions in Figs. 3 and 4, respectively. Assuming that the specific heat due to the phonon and electron parts is given by that of $LaPb_3$, we subtracted it from the measured specific heat to obtain the contribution from quadrupolar moments. Anomalies due to QPO can be clearly seen in the case of La concentrations of $x=0.01$ and 0.015. Conversely, no anomaly could be seen for the concentration $x\geqslant 0.02$ within the measured temperature region. Since the temperature dependence of $x=0.02$ is similar to that of $x=0.05$, the critical concentration is probably about $x=0.02$. Further measurements, however, are needed to determine the critical concentration precisely. We plot the concentration dependence of the ordering temperatures $T_Q(x)$ in the inset of Fig. 3. A strong suppression of $T_Q(x)$ can be seen. This suggests that the origin of the collapse of QPO is quite different from that of the magnetic ordering, because the magnetic ordering in three-dimensional

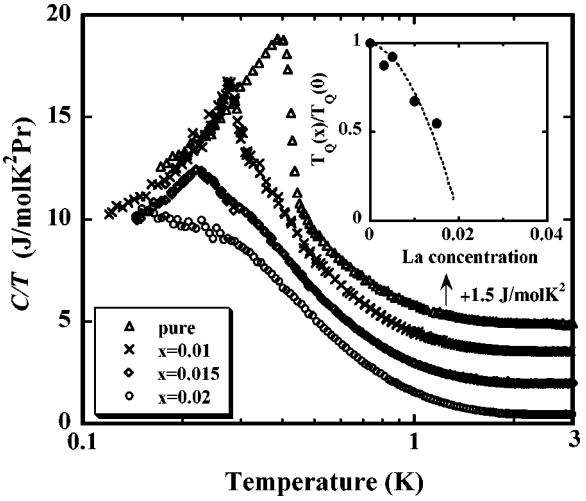

FIG. 3. C/T plotted on a logarithmic temperature scale for pure $x=0.01$, 0.015, and 0.02 cases. The data of the pure, 0.01 and 0.015 cases are shifted by 1.5 (J/mol K^2 Pr). The sharp peak due to the quadrupolar ordering is shifted to the lower temperatures with an increase of the La concentrations. Inset: the concentration dependence of $T_Q(x)/T_Q(0)$. The dotted line is a guide to the eye.

systems remains above dozen percent.[13] The reason for this will be discussed below.

For $x \geqslant 0.02$, only an enhancement of C/T can be seen in the low-temperature region without anomalies. In particular, the temperature dependence of the specific heat is approximately linear in the low-temperature region for a wide concentration range larger than $x=0.1$, suggesting that the origin of the enhancement is common to all concentrations. It is known that a heavy fermion compound shows a T linear dependence of the specific heat in the lower-temperature region, which is described by that of the Coqblin-Schrieffer model.[14] Although the origin of the enhancement is not due to the magnetic moments in the present system, we try to fit the data by a model with $J=1/2$. The predicted C/T curve increases only gently around the Kondo temperature T_K, as shown in Fig. 4, which differs considerably from the more abrupt increase in the experimental data.

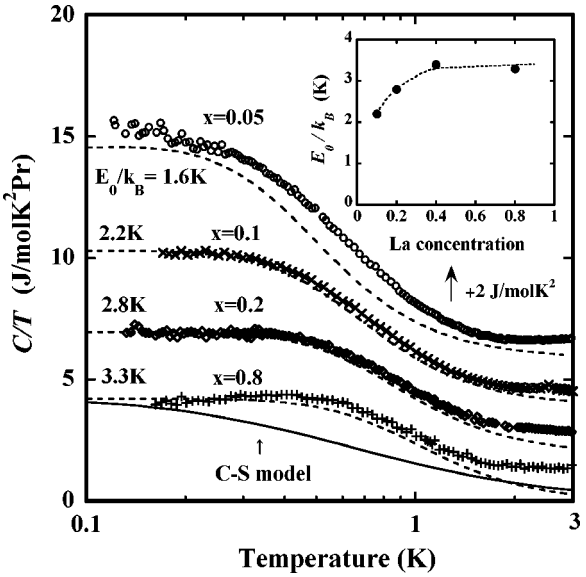

FIG. 4. C/T for $x=0.05$, 0.1, 0.2, and 0.8. The data for $x=0.05$, 0.1, and 0.2 are shifted by 2 (J/mol K^2Pr), The dotted lines are the curves obtained by Eq. (1) with $E_0=1.6$, 2.2, 2.8, and 3.3 K, respectively, where E_0 is defined in Eq. (2). The solid line for $x=0.8$ is the result obtained by the Coqblin-Schrieffer model with $J=1/2$ and $T_K=0.9$ K. We could not obtain a good fit by this model. Inset: the concentration dependence of the cutoff energy E_0/k_B, where E_0 is defined in Eq. (2). The dotted line is a guide to the eye.

It is well known that the specific heat in amorphous materials such as glasses shows a T linear dependence. The specific heat in such materials is understood by assuming the existence of two-level states resulting from random configurations of the potential barrier. The equal-weight superpose of the Schottky specific heat over such two-level systems is expressed by the following equation:[15,16]

$$C(T)=Nk_B\int_0^\infty n(E)\left(\frac{E}{k_BT}\right)^2\frac{e^{-E/k_BT}}{(1+e^{-E/k_BT})^2}dE, \qquad (1)$$

$$n(E)=\begin{cases}\dfrac{1}{E_0}, & 0\leqslant E\leqslant E_0\\ 0, & E_0\leqslant E.\end{cases} \qquad (2)$$

Here E is the energy difference between the two levels, and $n(E)$ is the constant density of states. E_0 is the cutoff of the energy difference. The specific heat for $x\geqslant 0.1$ is excellently reproduced by Eq. (1), choosing an optimum E_0 to fit the data as shown in Fig. 4. A small deviation at higher temperatures can be due to the tail of the Schottky contribution from the first excited state.

The measurements are done by using single crystals. In addition, the lattice distortion due to the Jahn-Teller effect has not been observed in $PrPb_3$. Thus the specific heat due to the RTLS does not come from a structural deviation in the crystal. Taking account of the entropy change, it is obvious that the enhancement of C/T is attributed to the two quadrupolar moments accompanied by Γ_3 doublet states in the CEF ground state, which split into two energy levels with random configurations.

A possible scenario for the appearance of two-level states due to quadrupolar moments is as follows. Let us consider Γ_3 doublet states, in the representation in which the quadrupole operator $O_2^0=3J_z^2-J(J+1)$ is diagonal, and denote them as $\Gamma_{3a}=-\sqrt{5/12}|0\rangle+\sqrt{7/24}(|4\rangle+|-4\rangle)$ and $\Gamma_{3b}=(1/\sqrt{2})(|2\rangle+|-2\rangle)$. O_2^0 turns positive or negative for Γ_{3a} and Γ_{3b} states, respectively. For pure $PrPb_3$, Γ_{3a} and Γ_{3b} states align alternatively in the AF-QPO state. However, in mixed systems, the CEF level of the Pr ion around the La ion might be distorted, since the diameter of the La ion is a little larger than that of the Pr ion. Thus the degeneracy of the Γ_3 doublet state should be lifted so as to screen the effect of the La ion. This can break the alignment of the AF-QPO, and lead to an energy splitting between Γ_{3a} and Γ_{3b}. Moreover, the next neighboring moments are also affected by the nearest moments. The La ion makes a random field at the Pr sites,

resulting in an energy splitting of Γ_{3a} and Γ_{3b} states which changes depending on the distance from the La ion.

In the inset of Fig. 4, we plot the concentration dependence of E_0/k_B, which corresponds to the maximum energy splitting of the two lifted moments. E_0/k_B is 2.2 K at $x=0.1$, it increases with increasing La concentration, and asymptotically approaches the value to ~ 3.3 K at high concentrations. Despite the large variation of the La concentration, the increase of E_0/k_B is smaller than 40%, implying that E_0/k_B is mainly determined by the stress of a Pr ion arising from neighboring La ions. This is consistent with our explanation that the distortion of the CEF due to the La ion brings about a lifting of the degeneracy of the Γ_3 moments. On the other hand, $x=0.05$ is near the critical concentration. The quadrupolar ordering and the two-level behavior are competing, which makes the meaning of $n(E)$ unclear. It may appear as an increase of C/T.

As shown in Fig. 3, $T_Q(x)$ in $PrPb_3$ is very sensitive to the La-ion substitution, which can be also explained by the distortion of the CEF due to the La ion. The maximum energy splitting due to the distortion is of the order of $E_0/k_B=2\sim 3$ K, which is much larger than $T_Q(0)$. This is the reason that QPO is strongly suppressed by the La impurity. If such a large energy splitting due to the distortion spreads around a La impurity over its third neighbors, it is not surprising that only $x\sim 0.02$ can break AF-QPO of $PrPb_3$. In the case of $Ce_{1-x}La_xB_6$ in which QPO is expected to exist up to $x\sim 0.3$ from the phase diagram, the critical temperature $T_Q(0)$ is 3.3 K.[10] In $Dy_{1-x}Y_xB_2C_2$, in which QPO survives up to $x=0.6$, $T_Q(0)$ is 25 K.[11] It is considered that the suppression of $T_Q(x)$ depends on the ordering temperature $T_Q(0)$.

Our results indicate that a distortion of CEF level due to La impurities gives rise to a drastic change of the low-temperature behavior of the quadrupolar moments. From the strong suppression of $T_Q(x)$, the influence of La is expected to reach over considerably more neighboring Pr sites. Thus it seems plausible that the internal field due to concentrated La impurities changes site by site, to yield a wide spread of density of states. In addition, the constant density of states observed in the specific heat suggests that long-distance correlation between the quadrupolar moments via the conduction electrons and phonons plays an important role.[17]

It is very important to investigate to what extent the RTLS due to the random potential of the quadrupolar moments is similar to a spin-glass system where the random interactions between spins are crucial. Judging from the temperature dependence of the specific heat, this system may be an ideal system by which to study the thermal properties of amorphous materials, e.g., thermal conductivity. In order to elucidate these problems, further experimental and theoretical studies are needed.

In summary, we have studied the low-temperature properties of $Pr_{1-x}La_xPb_3$, with the ground state of a non-Kramers Γ_3 for $0\leqslant x\leqslant 0.8$. From the concentration dependence of the specific heat, the ordering is expected to occur only up to $x\sim 0.02$. For a wide range of La concentrations where the ordering is absent, the specific heat is in an excellent agreement with the result obtained by the model for amorphous materials with a RTLS. These features can be understood by considering a distortion of the CEF level due to La impurities, and a long-distance correlation between the quadrupolar moments via the conduction electrons and phonons.

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[1] G.A. Gehring and K.A. Gehring, Rep. Prog. Phys. **38**, 1 (1975).
[2] P. Morin and D. Schmidt, in *Ferromagnetic Materials*, edited by K.H.J. Buschow and E.P. Wohlfarth (Elsevier, Amsterdam, 1990), Vol. 5, p. 1.
[3] D.L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[4] M.B. Maple, M.C. de Andrade, J. Herrmann, Y. Dalichaouch, D.A. Gajewski, C.L. Seaman, R. Chau, R. Movshovich, M.C. Aronson, and R. Osborn, J. Low Temp. Phys. **99**, 223 (1995).
[5] A. Yatskar, W.P. Beyermann, R. Movshovich, and P.C. Canfield, Phys. Rev. Lett. **77**, 3637 (1996).
[6] R. Movshovich, A. Yatskar, M.F. Hundley, P.C. Canfield, and W.P. Beyermann, Phys. Rev. B **59**, R6601 (1999).
[7] W. Gross, K. Knorr, A.P. Murani, and K.H.J. Buschow, Z. Phys. B **37**, 123 (1980).
[8] E. Bucher, K. Andres, A.C. Grossard, and J.P. Maita, J. Low Temp. Phys. **2**, 322 (1972).
[9] D. Aoki, Y. Katayama, R. Settai, Y. Inada, Y. Onuki, H. Harima, and Z. Kletowski, J. Phys. Soc. Jpn. **66**, 3988 (1997).
[10] T. Tayama, T. Sakakibara, K. Tenya, H. Amituka, and S. Kunii, J. Phys. Soc. Jpn. **66**, 2268 (1997).
[11] S. Sako, H. Onodera, H. Yamauchi, K. Indoh, A. Tobo, K. Ohoyama, and Y. Yamaguchi, J. Phys. Soc. Jpn. **69**, 1872 (2000).
[12] Z. Kletowski, P. Slawinski, and T. Cichorek, J. Magn. Magn. Mater. **162**, 277 (1996).
[13] R. B. Stinchcombe, in *Phase Transitions and Critical Phenomena*, edited by C. Domb and M.S. Green (Academic Press, New York, 1972), Vol. 1, p. 152.
[14] V.T. Rajan, Phys. Rev. Lett. **51**, 308 (1983).
[15] P.W. Anderson, B.I. Halperin, and C.M. Varma, Philos. Mag. **25**, 1 (1972).
[16] W.A. Phillps, J. Low Temp. Phys. **7**, 351 (1972).
[17] P.M. Levy, P. Morin, and D. Schmitt, Phys. Rev. Lett. **42**, 1417 (1979).