Observation of Modulated Quadrupolar Structures in $PrPb_3$

T. Onimaru,[1,*] T. Sakakibara,[1] N. Aso,[2] H. Yoshizawa,[2] H. S. Suzuki,[3] and T. Takeuchi[4]

[1]*Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan*

[2]*Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, Tokai 319-1106, Japan*

[3]*National Institute for Materials Science, Tsukuba 305-0047, Japan*

[4]*Low Temperature Center, Osaka University, Toyonaka 560-0043, Japan*

(Received 12 November 2004; published 16 May 2005)

Neutron diffraction measurements have been performed on the cubic compound $PrPb_3$ in a [001] magnetic field to examine the quadrupolar ordering. Antiferromagnetic components with $q = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0)$, $(\frac{1}{2}\ \frac{1}{2} \pm \delta\ 0)$ $(\delta \approx \frac{1}{8})$ are observed below the transition temperature T_Q (0.4 K at $H = 0$) whose amplitudes vary linear with H and vanish at zero field, providing the first evidence for a modulated quadrupolar phase. For $H < 1$ T, a nonsquare modulated state persists even below 100 mK suggesting quadrupole moments associated with a Γ_3 doublet ground state to be partially quenched by hybridization with conduction electrons.

DOI: 10.1103/PhysRevLett.94.197201 PACS numbers: 75.25.+z, 61.12.Ld, 75.20.Hr, 75.30.Kz

In recent years, there has been a growing interest in the role of orbital degrees of freedom in d as well as f electron systems. A number of unusual properties in transition metal compounds have been discussed on the basis of underlying orbital orders. In the case of $4f$ electron systems, the 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 level carries quadrupole moments (rank-2 irreducible tensor operators in $\boldsymbol{J}$). In a cubic (O_h) system, up to five independent quadrupole moments are defined (two Γ_3-type and three Γ_5-type operators) [1,2]. The orbital ordering in f electron systems, i.e., a spontaneous lifting of the orbital degeneracy by interactions, therefore is a phase transition of quadrupole moments. In reality, active quadrupole moments depend on the low-lying crystalline field levels of the $4f$ ions.

Following magnetic orderings, one refers to uniform alignment of the quadrupole moment as a ferroquadrupolar state, whereas an ordering having a staggered quadrupolar component is called an antiferroquadrupolar (AFQ) state. To date, however, the number of AFQ systems whose ordering structures and the order parameter (OP) are identified is still limited. They include CeB_6 [3,4], TmTe [5], DyB_2C_2 [6,7], UPd_3 [8], and $PrFe_4P_{12}$ [9]. Because of a lack of an internal magnetic field (time reversal symmetry is conserved) and the smallness of the associated lattice distortion, there are only a few experimental methods to explore the AFQ structure microscopically. Among them, neutron diffraction in a magnetic field is a powerful method to investigate the AFQ OPs as well as the ordering wave vectors. In an AFQ phase, a uniform magnetic field applied along a suitable direction generates a staggered magnetic moment which has the same periodicity with the underlying AFQ structure. Note that the direction of the induced staggered component is closely related to the symmetry of the OP [2]. This technique has been applied successfully to many of the AFQ compounds mentioned before to identify their OPs.

So far, all the AFQ structures known have simple $\boldsymbol{q}$ vectors (simple alternations of the quadrupole moments) [3–9]. One of the reasons for this could be the short range nature of quadrupolar interactions. Nevertheless, it has been argued theoretically that an indirect quadrupolar interaction of RKKY-type might exist in some intermetallic systems [1,10] and as a matter of fact, as pointed out recently, these indirect multipole interactions are responsible for the unusual properties of CeB_6 [2,11,12]. In metallic systems, the existence of long range quadrupolar interactions would not rule out the possibility of modulated or incommensurate AFQ structures.

In the present study, we focus our attention on the intermetallic compound $PrPb_3$ with the $AuCu_3$-type cubic structure. The crystalline field ground state of $PrPb_3$ is a Γ_3 non-Kramers doublet [13,14], with a magnetic Γ_4 triplet lying 15–19 K above the ground state [14–16]. Since the Γ_3 doublet carries quadrupole moments $O_2^0 = (3J_z^2 - \boldsymbol{J}^2)/2$ and $O_2^2 = \sqrt{3}(J_x^2 - J_y^2)/2$, $PrPb_3$ is a good candidate for a quadrupolar transition. The compound exhibits a second-order transition at 0.4 K with a lambda-type anomaly in the specific heat [13,17]. Absence of a magnetic superlattice reflection and a lattice distortion in the neutron diffraction measurement performed in zero magnetic field [14] suggests the phase transition to be of AFQ-type [18].

The idea of an AFQ ordering has further been strengthened by the H-T diagram study [16], in which reentrant behavior with a significant enhancement of the transition temperature T_Q is observed for $H \parallel [100]$, as is often the case for AFQ ordering systems. A mean-field analysis based on a simple two-sublattice model succeeded in reproducing the overall features of the reentrant phase diagrams of $PrPb_3$ with an alternating alignment of the Γ_3-type quadrupole moments as the possible OP. Shortly after, angle-resolved magnetization measurements revealed characteristic field-angular oscillations of $T_Q(H)$, which can be interpreted by assuming an O_2^0-type AFQ moment and its equivalents to be the OPs at low H (<7 T) [19].

So far, no microscopic verification for an AFQ ordering has been obtained in this system. Our preliminary neutron diffraction measurement in a [110] magnetic field [(110) scattering plane] could not detect any field-induced antiferromagnetic reflection in the AFQ phase below 3 T [20]. In the present work, we have continued the experiment in a magnetic field applied parallel to the [001] direction using a larger crystal of higher quality and succeeded in observing field-induced superlattice reflections which, as we discuss below, to our surprise are associated with modulated quadrupole structures.

Single crystalline $PrPb_3$ was grown by the Bridgeman method. In the present study, a specimen with 10 mm diameter by 24 mm long was used. Neutron diffraction measurements were performed using the Institute for Solid State Physics (ISSP) triple-axis spectrometer GPTAS (4G) installed at the JRR-3M research reactor in Japan Atomic Energy Research Institute. More details of the experimental procedure will be published elsewhere.

Figure 1 shows the results of $\boldsymbol{Q}$ scans along the $(h\frac{1}{2}0)$ line carried out in a field of $H = 4$ T at various temperatures ranging from 0.125 to 0.8 K. On cooling below the transition temperature $T_Q = 0.65$ K, where quadrupolar ordering has been reported [16], strong superlattice reflections appear at $\boldsymbol{q}_1 = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0)$ with $\delta \sim 1/8$. On further cooling below $T_t = 0.45$ K, i.e., the first-order transition temperature found in magnetization [21] and specific heat measurements [22], the third-order harmonic $\boldsymbol{q}_1' = (\frac{1}{2} \pm 3\delta\ \frac{1}{2}\ 0)$ with much weaker intensity is found to develop. Similar reflections were also observed at $\boldsymbol{q}_2 = (\frac{1}{2}\ \frac{1}{2} \pm \delta\ 0)$ and $\boldsymbol{q}_2' = (\frac{1}{2}\ \frac{1}{2} \pm 3\delta\ 0)$ as well. The inset of Fig. 1 shows the $(hk0)$ reciprocal plane ($\perp H$) investigated, where open and closed circles represent the nuclear and the magnetic reflections, respectively, observed in a field of $H = 4$ T at $T = 0.125$ K. We observed that the integrated intensity of the superlattice reflections has no significant dependence on the angular direction of the scattering vector. We also carried out a similar $\boldsymbol{Q}$-scan experiment at several fields but could not observe any noticeable change in the relative intensity between the reflections at $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$. Hence a change in a domain population, if any, is confirmed to be very small.

Knowing that the domain population change is negligible, we may estimate the field variation of the staggered component from the intensity of the $(\frac{3}{8}\frac{1}{2}0)$ reflection. In Fig. 2, we plot the square root of the scattering intensity (background subtracted) at $T = 0.32$ K as a function of H. Keeping in mind that the peak width is virtually independent of H, the square root intensity is proportional to the staggered component. The intensity vanishes at $H = 0$, consistent with the previous work reporting the absence of antiferromagnetic scattering in zero field [14]. The important point is that the staggered component develops *proportional to H* up to 2 T. This fact strongly indicates that the observed superlattice reflections arise from an induced antiferromagnetic moment in the presence of an underlying AFQ ordering [23]. The present experiment thus confirms the AFQ ordering in $PrPb_3$, and to the best of our knowledge, provides the first evidence of a modulated ($\delta \neq 0$) quadrupolar ordering.

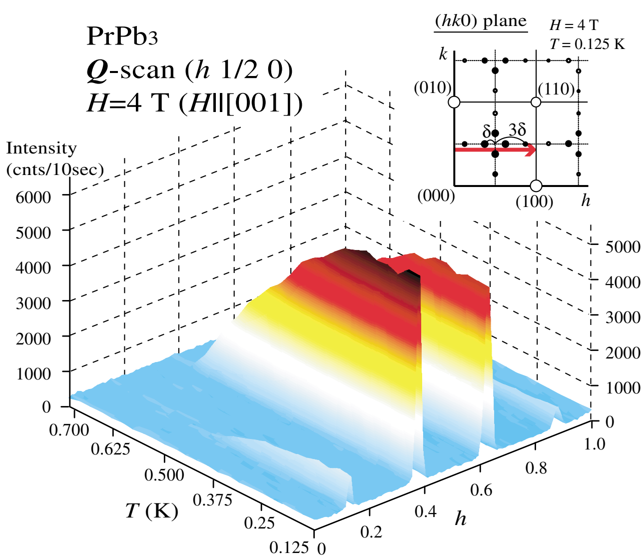

FIG. 1 (color). Evolution of the magnetic scattering in a field of $H = 4$ T applied along the [001] direction, obtained in a temperature interval of $0.125\ \text{K} < T < 0.81$ K. The $\boldsymbol{Q}$ scans were performed along the line $(h\frac{1}{2}0)$, as indicated by a red arrow in the $(hk0)$ reciprocal plane (inset), where open and closed circles represent the nuclear and the magnetic reflections observed at $T = 0.125$ K, respectively.

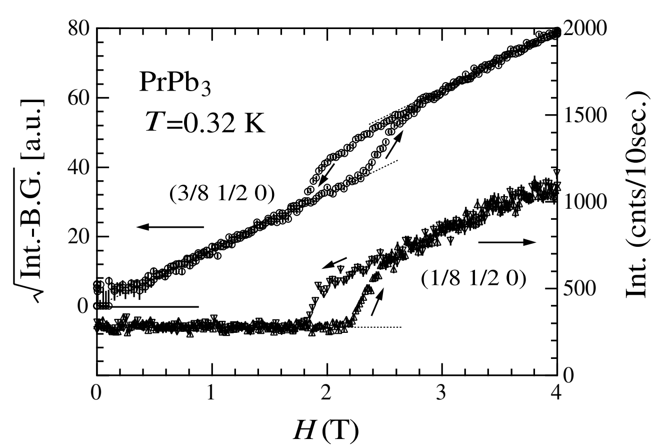

FIG. 2. Field dependence of the square root of the $(\frac{3}{8}\frac{1}{2}0)$ reflection intensity (circles) at $T = 0.32$ K. The background was subtracted from the data. The intensity of the $(\frac{1}{8}\frac{1}{2}0)$ peak (triangles) is also shown as a function of H. The small arrows indicate the direction of the field scan.

At around 2.1 T, we observed a jump in the scattering intensity with an apparent hysteretic behavior, indicating an occurrence of a first-order transition at this field. Associated with this transition is the third-order harmonic $\boldsymbol{q}_1'$ as shown in Fig. 2. We found that this transition field remains finite (≥ 1 T) on cooling down to below 100 mK. It is important to note that no harmonic component is observed in the low field phase.

Figure 3 shows the H-T phase diagram of $PrPb_3$ for $\boldsymbol{H}$ parallel to [001] obtained by the present experiment. The quadrupolar transition line is defined by the onset of the $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ superlattice reflections. The obtained phase boundary $T_Q(H)$ agrees well with the phase line reported in the specific heat and magnetization measurements [16,21,22]. Within the AFQ phase, we observed a first-order phase transition characterized by the appearance of the $\boldsymbol{q}_1'$ and $\boldsymbol{q}_2'$ harmonic reflections. This transition line $T_t(H)$ again agrees with the results of previous thermodynamical measurements [21,22]. The inset of Fig. 3 shows the temperature dependence of the position of the $(\frac{1}{2} - \delta\ \frac{1}{2}\ 0)$ superlattice reflections in a field of 4 T. In the temperature range $T_t < T < T_Q$, δ takes a value slightly below 1/8. Upon the first-order transition at T_t, δ exhibits a jump to a value very close to 1/8. Although more careful study would be needed, we expect that the phase below T_Q is an incommensurate state and T_t is a lock-in temperature into the commensurate state with $\delta = 1/8$. It is noteworthy that the $T_t(H)$ line does not intersect with the abscissa for low T and the modulated phase continues to exist to $T \to 0$ at low fields below 1 T.

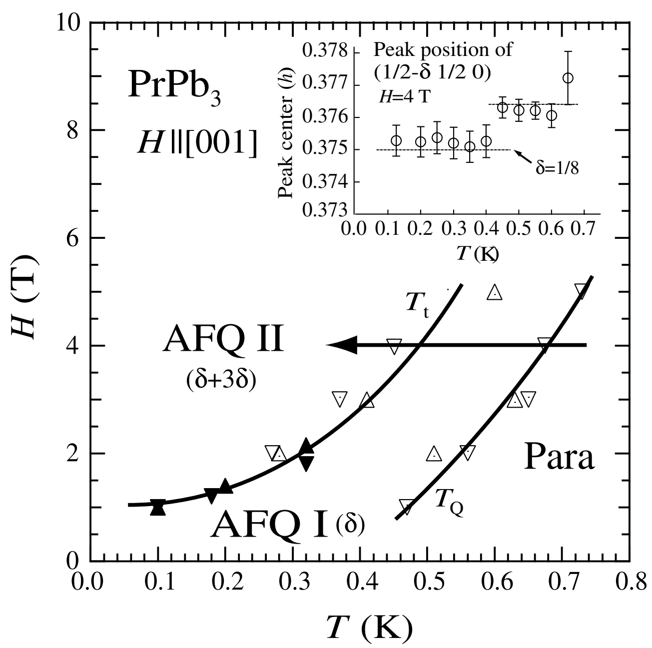

FIG. 3. H-T phase diagram of $PrPb_3$ in a [001] magnetic field. Open and closed triangles denote the transition points determined from the T- and H-scan measurements, respectively. For both cases, the upward and downward triangles represent the increasing and decreasing $T(H)$ scans, respectively. AFQ I denotes the possible incommensurate structure with the wave vectors $\boldsymbol{q} = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0)$ and/or $(\frac{1}{2}\ \frac{1}{2} \pm \delta\ 0)$, $(\delta \sim \frac{1}{8})$. AFQ II denotes the antiphase structure as discussed in the text. The inset shows the temperature dependence of the center position of the magnetic reflection at around $\boldsymbol{q} = (\frac{1}{2} - \delta\ \frac{1}{2}\ 0)$ in a field of $H =$ 4 T, obtained on cooling below 0.75 K as shown by the arrow.

We now discuss possible magnetic and quadrupole structures of $PrPb_3$ in a [001] field. While the field independence of the relative intensity of the $\boldsymbol{q}_1$ and $\boldsymbol{q}_2$ reflections favors a double-$\boldsymbol{q}$ structure, we cannot rule out the possibility of a single-$\boldsymbol{q}$ structure with two equally populated Q domains. The direction-independent scattering intensity within the $(hk0)$ plane leaves two possibilities regarding the polarization of the field-induced antiferromagnetic component μ_{AF}; μ_{AF} is either parallel to [001] or rotating in the (001) plane. Although the latter structure cannot be excluded from the present neutron scattering data alone, it is incompatible with the quadrupole OPs in the Γ_3 doublet state and therefore we do not discuss this possibility here [2]. In the former case, the alignment of μ_{AF} along the [100] axis is given in Fig. 4 by the thick arrows, where we assume $\delta = 1/8$ for simplicity. The observed superlattice reflections below T_Q (AFQ I) are best described by a sinusoidally modulated antiferromagnetic structure as shown in Fig. 4(a). The amplitude of the staggered moment is determined to be $|\mu_{AF}| = 0.48 \pm 0.17\mu_B$ at 4 T and 0.50 K assuming a single-$\boldsymbol{q}$ structure. Below $T_t(H)$, this state undergoes a first-order transition into an antiphase structure (AFQ II) as shown in Fig. 4(b) which is accompanied by third harmonic reflections at $\boldsymbol{q}_1'$ and $\boldsymbol{q}_2'$. The polarization of $\mu_{AF} \parallel [001]$ (angular momentum operator J_z) is compatible with the quadrupole moment O_2^0 [2], being consistent with the analysis of the recent angle-resolved $T_Q(H)$ measurement [19]. Since the

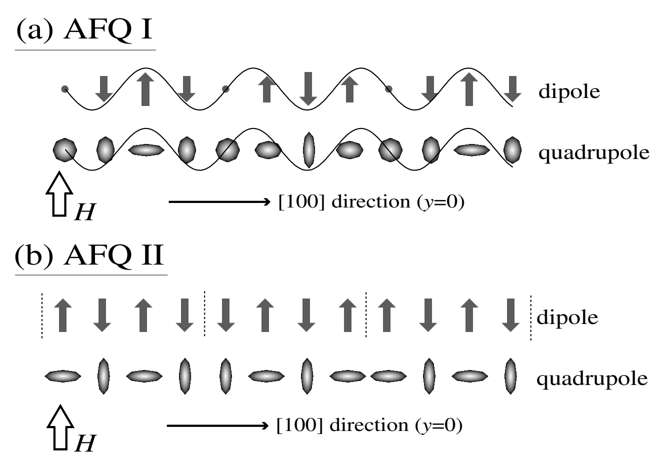

FIG. 4. Field-induced antiferromagnetic moments and the possible quadrupole structures along the [100] axis $(y = 0)$ in a [001] field. (a) Sinusoidal structure with $\boldsymbol{q} = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0)$, and (b) antiphase structure with $\boldsymbol{q} = (\frac{1}{2} \pm \delta\ \frac{1}{2}\ 0)$ and $(\frac{1}{2} \pm 3\delta\ \frac{1}{2}\ 0)$. We assume that $\delta = \frac{1}{8}$ for simplicity. Uniform components are not included. The solid lines denote the amplitude of the staggered components, whose phase factor is arbitrarily chosen.

field-induced μ_{AF} is proportional to the AFQ OP [23], it is concluded that the O_2^0 moment should show a similar sinusoidal oscillation in this phase as schematically illustrated in Fig. 4(a) where the solid line represents the amplitude of the O_2^0 moment. Below T_t, the O_2^0 moment would also take the antiphase structure as shown in Fig. 4(b).

Recalling that $PrPb_3$ is a Γ_3 non-Kramers doublet ground state system, it is reasonable that the system undergoes a phase transition from the sinusoidal to the antiphase structure at low T. In general, the sinusoidal structure is stable only at a high temperature region below T_Q, where thermal fluctuations are dominant, and gives way to the antiphase (square) structure in the ground state to reduce the entropy, as is often seen in magnetic ordering systems. Recalling the phase diagram in Fig. 3, however, we find that the nonsquare modulated phase persists down to the experimental accessible temperature of 100 mK in low fields below 1 T, without any indication of further transition. This observation is hardly understood within the framework of a localized f electron model in which the (pseudo) degeneracy with respect to the Γ_3 doublet would remain in a part of Pr sites. Similar phenomena of non-antiphase modulated structures persisting toward $T \to 0$ have also been reported in magnetic Kramers compounds, in which a Kondo screening effect is considered to be relevant for stabilizing such states at $T = 0$ [24,25]. The analogy to those magnetic systems strongly suggests that the local quadrupole moment in $PrPb_3$ should be partly quenched in the modulated phase at very low T due to the *quadrupole* Kondo effect [26]. The possibility of the Kondo effect associated with the orbital degeneracy has been discussed in several U- and Pr-based systems [27–29] but is still not well established experimentally. Very recently, it was recognized that the strong hybridization effect between Pr $4f$ and conduction electrons does exist in some of the Pr-based skutterudites, leading to heavy fermion behavior and unconventional superconductivity [30,31]. The present results on $PrPb_3$ provide another piece of evidence for the Kondo effect in Pr ($4f^2$) systems [32]. It would be interesting to examine the low energy excitation of this system at very low temperatures.

In summary, neutron diffraction experiment in a magnetic field has revealed a modulated quadrupole strucuture in $PrPb_3$ which persists as $T \to 0$ at low field. The results suggest a Kondo screening of the quadrupole moments of Pr^{3+} in the ground state.

We thank Y. Ōnuki, D. Aoki, T. Kawae, T. Kitai, and T. Tayama for helpful discussions and collaboration in the initial stage of the work. We are also grateful to J. Custers for useful comments. The present work was supported by Grants-in-Aid for Scientific Research from the JSPS and the MEXT of Japan.

*Electronic address: onimaru@issp.u-tokyo.ac.jp

[1] D. Schmitt and P. M. Levy, J. Magn. Magn. Mater. **49**, 15 (1985).
[2] R. Shiina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **66**, 1741 (1997).
[3] J. M. Effantin *et al.*, J. Magn. Magn. Mater. **47&48**, 145 (1985).
[4] H. Nakao *et al.*, J. Phys. Soc. Jpn. **70**, 1857 (2001).
[5] P. Link, A. Gukasov, J.-M Mignot, T. Matsumura, and T. Suzuki, Phys. Rev. Lett. **80**, 4779 (1998).
[6] Y. Tanaka *et al.*, J. Phys. Condens. Matter **11**, L505 (1999).
[7] K. Hirota *et al.*, Phys. Rev. Lett. **84**, 2706 (2000).
[8] D. F. McMorrow, K. A. McEwen, U. Steigenberger, H. M. Rønnow, and F. Yakhou, Phys. Rev. Lett. **87**, 057201 (2001).
[9] K. Iwasa *et al.*, Physica (Amsterdam) **312B–313B**, 834 (2002).
[10] P. M. Levy, P. Morin, and D. Schmitt, Phys. Rev. Lett. **42**, 1417 (1979).
[11] R. Shiina, O. Sakai, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. **67**, 941 (1998).
[12] H. Shiba, O. Sakai, and R. Shiina, J. Phys. Soc. Jpn. **68**, 1988 (1999).
[13] E. Bucher, K. Andres, A.C. Gossard, and J.P. Maita, J. Low Temp. Phys. **2**, 322 (1972).
[14] M. Niksch, W. Assmus, B. Lüthi, H. R. Ott, and J. K. Kjems, Helv. Phys. Acta **55**, 688 (1982).
[15] W. Gross, K. Knorr, A. P. Murani, and K. H. J. Buschow, Z. Phys. B **37**, 123 (1980).
[16] T. Tayama *et al.*, J. Phys. Soc. Jpn. **70**, 248 (2001).
[17] D. Aoki *et al.*, J. Phys. Soc. Jpn. **66**, 3988 (1997).
[18] P. Morin, D. Schmitt, and E. du Tremolet de Lacheisserie, J. Magn. Magn. Mater. **30**, 257 (1982).
[19] T. Onimaru *et al.*, J. Phys. Soc. Jpn. **73**, 2377 (2004).
[20] T. Onimaru *et al.*, Physica B (Amsterdam) (to be published).
[21] T. Sakakibara *et al.*, J. Phys. Condens. Matter **15**, S2055 (2003).
[22] R. Vollmer *et al.*, Physica (Amsterdam) **312B–313B**, 855 (2002).
[23] In an AFQ phase, a coupling $Q_{AF}\mu_{AF}M$ is allowed by symmetry in the Landau free energy expansion, where Q_{AF} is the AFQ OP and M is a uniform magnetization proportional to H. Because of this term, μ_{AF} compatible to Q_{AF} is induced in proportion to H and Q_{AF} in the AFQ state; T. Sakakibara *et al.*. J. Phys. Soc. Jpn. **69**, Suppl. A, 25 (2000).
[24] C. Vettier, P. Morin, and J. Flouquet, Phys. Rev. Lett. **56**, 1980 (1986).
[25] P. Bonville *et al.*, Europhys. Lett. **51**, 427 (2000).
[26] D. L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[27] M. B. Maple *et al.*, J. Low Temp. Phys. **95**, 225 (1994).
[28] D. L. Cox and M. Jarrell, J. Phys. Condens. Matter **8**, 9825 (1996).
[29] A. Yatskar, W. P. Beyermann, R. Movshovich, and P. C. Canfield, Phys. Rev. Lett. **77**, 3637 (1996).
[30] Y. Aoki *et al.*, Phys. Rev. B **65**, 064446 (2002).
[31] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506 (2002).
[32] The possibility of a quadrupole Kondo effect in the diluted alloys $Pr_xLa_{1-x}Pb_3$ has recently been discussed by T. Kawae *et al.*, J. Phys. Soc. Jpn. **72**, 2141 (2003).