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Superconductivity and heavy fermion behavior in $PrOs_4Sb_{12}$

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Superconductivity has been observed in $PrOs_4Sb_{12}$ at $T_C = 1.85$ K and appears to involve heavy fermion quasiparticles with an effective mass $m^* \sim 50$ m_e as inferred from the jump in the specific heat at T_C, the upper critical field near T_C, and the normal state electronic specific heat. Thermodynamic and transport measurements suggest that the heavy fermion state has a quadrupolar origin, although a magnetic origin cannot be completely ruled out.

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A remarkable class of rare earth and actinide compounds containing Ce, Yb, and U ions undergo a continuous transition from a high temperature phase in which the *f*-electrons behave as if they are localized with well-defined magnetic moments to a low temperature heavy Fermi liquid phase in which the *f*-electrons appear to be delocalized with enormous effective masses m^* of the order of several hundred times the free electron mass m_e.[1,2] The heavy Fermi liquid ground state of these so-called "heavy fermion" *f*-electron materials is unstable to the formation of superconductivity and magnetically ordered states which sometimes coexist with one another. The superconducting specific heat jump ΔC at the superconducting critical temperature T_C is of the order of γT_C, where γ is the normal state electronic specific heat coefficient (i.e., $C_{el} \sim \gamma T$), showing that the superconductivity is a bulk phenomenon involving the heavy electrons that are responsible for the large value of γ, which can be as high as several J/mol K^2. In addition, the superconductivity in these materials appears to be anisotropic with an energy gap that vanishes at points or along lines on the Fermi surface, indicative of superconducting electron pairing of electrons with angular momentum greater than zero.[1,2] It is widely believed that the pairing of the superconducting electrons in these materials is mediated by magnetic fluctuations.

The subset of heavy fermion compounds currently known to exhibit superconductivity consists of Ce and U intermetallic compounds, such as $CeCu_2Si_2$ and UBe_{13}.[3,4] Recently, heavy fermion behavior has been reported in the Pr-based compounds $PrInAg_2$ and $PrFe_4P_{12}$ and attributed to the interaction of the electric quadrupole moments of a Pr^{3+} Γ_3 nonmagnetic doublet ground state in the crystalline electric field (CEF) with the charges of the conduction electrons.[5,6] In this paper, we report the observation of heavy fermion behavior and superconductivity in the compound $PrOs_4Sb_{12}$, which appears to be the first example of a Pr-based heavy fermion superconductor.[7] Thermodynamic measurements and recent inelastic neutron scattering experiments are consistent with a Pr^{3+} Γ_3 ground state in $PrOs_4Sb_{12}$, suggesting that the quadrupolar fluctuations are responsible for the heavy fermion state.

Single crystals of the filled skutterudite $PrOs_4Sb_{12}$ were grown in an Sb flux (Ref. 8). X-ray diffraction measurements revealed that $PrOs_4Sb_{12}$ crystallizes in the $LaFe_4P_{12}$-type BCC structure with a lattice parameter $a = 9.3017$ Å.[9] Electrical resistivity ρ, specific heat C, and magnetic susceptibility χ measurements between ~ 1 K and 300 K were made in a ^{4}He cryostat, in a semi-adiabatic ^{3}He calorimeter, and with a superconducting quantum interference device (SQUID) magnetometer, respectively. Measurements of $\rho(T)$ down to 60 mK in magnetic fields up to 30 kOe were performed in a transverse geometry in a ^{3}He-^{4}He dilution refrigerator.

The physical properties of $PrOs_4Sb_{12}$ are summarized in Fig. 1. The $\chi(T)$ data [Fig. 1(a)] exhibit a peak at ~ 3 K and saturate to a value of ~ 0.06 cm^3/mol as $T \rightarrow 0$, indicative of a nonmagnetic ground state. At temperatures above 50 K, $\chi(T)$ of $PrOs_4Sb_{12}$ can be described by a Curie-Weiss law with an effective moment $\mu_{eff} = 2.97$ μ_B, somewhat reduced from the free ion value $\mu_{eff} = 3.58$ μ_B, and a Curie-Weiss temperature $\theta_{CW} = -16$ K. The onset of superconductivity occurs at $T_C = 1.85$ K in a field of 20 Oe as revealed by the large diamagnetic signal shown in inset (ii) of Fig. 1(a). The ρ vs T curve, shown in Fig. 1(a) and inset (i), displays metallic behavior and a distinct decrease below ~ 7 K in the normal state before dropping abruptly to zero when superconductivity occurs at $T_C = 1.86$ K. The residual resistivity ratio (RRR$\sim$33) and transition width $\Delta T_C = 5$ mK reflect the high quality of the single crystals.

Evidence that strong electronic correlations are present in $PrOs_4Sb_{12}$ is provided by the magnitude of the superconducting specific heat jump as displayed in inset (iii) of Fig. 1. Although the superconducting transition is somewhat rounded, perhaps due to variations in the composition of the crystals or strain induced by compressing the powdered single crystals into a pellet, an equal entropy construction in which the entropy is conserved just above and below T_C, yields $\Delta C/T_C \sim 500$ mJ/mol K^2. The value of the electronic specific heat coefficient from the weak-coupling BCS prediction ($\Delta C/\gamma T_C = 1.43$) is $\gamma \sim 350$ mJ/mol K^2. The specific heat data can be described by the expression $C(T)/T = \gamma + \beta T^2$, where βT^2 is the lattice contribution (set equal to that of $LaOs_4Sb_{12}$ with $\theta_D = 304$ K), between 6.9 K $\leqslant T \leqslant$ 9.6 K (not shown), from which $\gamma = 750$ mJ/mol K^2 is obtained. A Schottky-like peak in the specific heat data of $PrOs_4Sb_{12}$ is visible at ~ 3 K.

Additional evidence for heavy fermion behavior in $PrOs_4Sb_{12}$ is provided by an analysis of the slope of the upper critical field H_{c2} near T_C similar to that described in

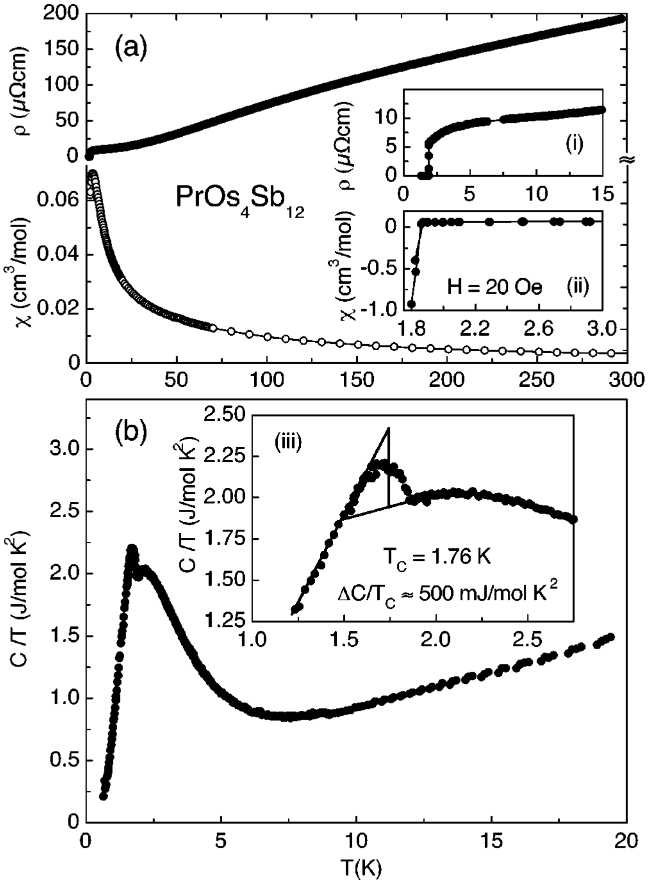

FIG. 1. Physical properties of $PrOs_4Sb_{12}$. Panel (a): ρ vs T (upper y axis). Inset (i): $\rho(T)$ below 20 K. χ vs T at $H=5$ kOe (lower y axis). Inset (ii): $\chi(T)$ at $H=20$ Oe. Panel (b): $C(T)/T$ below 20 K. Inset (iii): Expanded view of the superconducting specific heat jump. Solid lines represent an equal entropy construction yielding $\Delta C/T_C \sim 500$ mJ/mol K^2.

Ref. 14 for the heavy fermion superconductor UBe_{13}. Shown in Fig. 2 is the $H_{c2}(T)$ curve for $PrOs_4Sb_{12}$ derived from $\rho(T)$ measurements (inset of Fig. 2). Disregarding the slight positive curvature in $H_{c2}(T)$ near T_C, a linear fit to the data yields a value of ~ 19 kOe/K for the initial slope $(-dH_{c2}/dT)_{T_C}$. The zero temperature value of the orbital critical field can be determined from the relation $H^*_{c2}(0) = 0.693\ (-dH_{c2}/dT)_{T_C} T_C$,[15] yielding the value $H^*_{c2}(0) \sim 24.5$ kOe. The superconducting coherence length ξ_0 can be estimated from the relation $H^*_{c2}(0) = \Phi_0 / 2\pi\xi_0^2$,[16] yielding $\xi_0 \sim 116$ Å. A value for the Fermi velocity $v_F = 1.57 \times 10^6$ cm/s is then obtained from $\xi_0 = 0.18\hbar v_F / k_B T_C$[16] from which m^* and γ can be estimated as follows. Using a spherical Fermi surface approximation, the Fermi wave vector is given by $k_F = (3\pi^2 Z/\Omega)^{1/3}$, where Z is the number of electrons per unit cell and Ω is the unit cell volume. Assuming that Pr contributes 3 electrons ($Z=6$), we obtain $k_F = 6.05 \times 10^7$ cm^{-1}. The expression $m^* = \hbar k_F / v_F$ yields $m^* \sim 50$ m_e. From the relation $\gamma = \pi^2 (Z/\Omega) k_B^2 m^* / \hbar^2 k_F^2$, $\gamma \sim 350$ mJ/mol K^2 is obtained. These values of m^* and γ are comparable to the values estimated from the specific heat jump ΔC at T_C and the normal state specific heat.

The physical properties of $PrOs_4Sb_{12}$ can be analyzed within a localized or itinerant electron approach. In an ionic (localized) model, a cubic crystalline electric field (CEF) splits the $J=4$ Hund's rule multiplet of Pr^{3+} into a singlet (Γ_1), a doublet (Γ_3), and two triplets (Γ_4 and Γ_5). As shown by Lea, Leask, and Wolf (LLW),[10] the CEF Hamiltonian in cubic symmetry can be written in terms of the ratio of the fourth and sixth order terms of the angular momentum operators, x, and an overall energy scale factor W. The magnetic susceptibility data were fitted by a CEF model in which the ground state was chosen to be either a nonmagnetic Γ_1 singlet ($W>0$) or a nonmagnetic Γ_3 doublet ($W<0$). A peak in $\chi(T)$ is produced when the first excited state is a Γ_5 triplet with an energy <100 K above the ground state and corresponds to a position (x) close to the crossing points on the LLW diagram where Γ_1 or Γ_3 are degenerate with Γ_5. The best fits to the data are: (a) $x=0.50$, $W=1.85$, and (b) $x=-0.72$, $W=-5.44$, corresponding to level schemes displayed in Fig. 3 of Γ_1(0 K), Γ_5(6 K), Γ_4(65 K), Γ_3(111 K) and Γ_3(0 K), Γ_5(11 K), Γ_4(130 K),

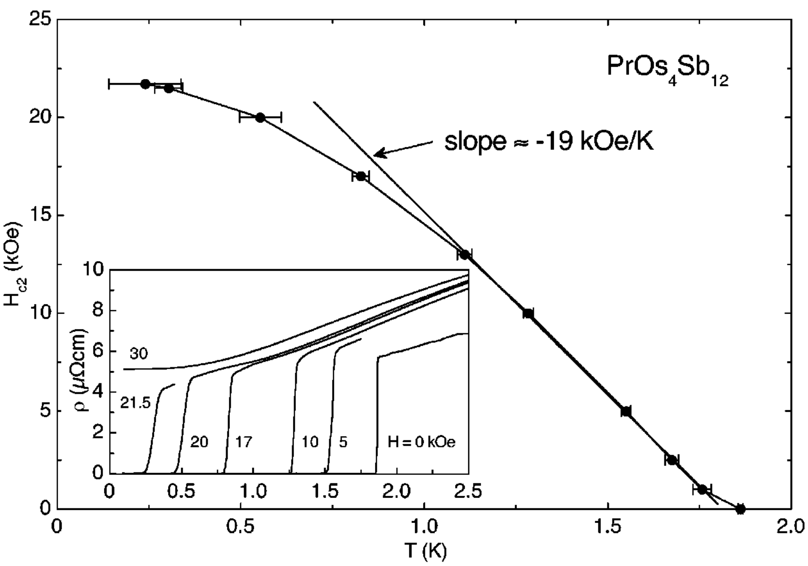

FIG. 2. Upper critical field H_{c2} vs T of $PrOs_4Sb_{12}$. The bars indicate the 10% and 90% values of the superconducting transitions. Inset: $\rho(T)$ in magnetic fields up to 30 kOe.

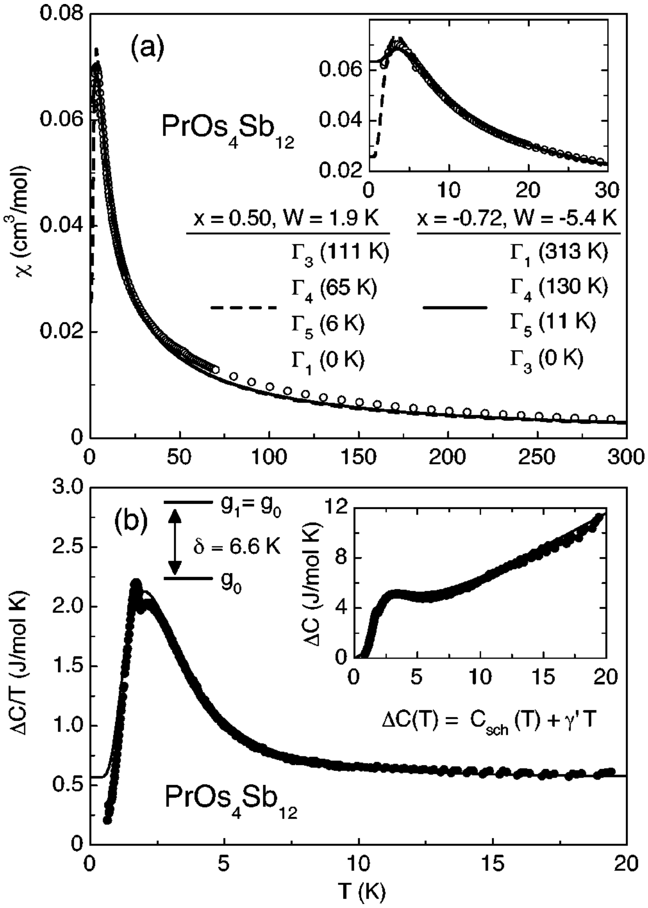

FIG. 3. Panel (a): Fits of $\chi(T)$ of $PrOs_4Sb_{12}$ to a CEF model in which the ground state is either Γ_3 (solid line) or Γ_1 (dashed line). Inset: $\chi(T)$ vs T below 30 K. Panel (b): $4f$ contribution to the specific heat $\Delta C = C(PrOs_4Sb_{12})$-$C_{latt}(LaOs_4Sb_{12})$, plotted as $\Delta C/T$ vs T. The solid line is a fit to a two-level Schottky anomaly and an additional $\gamma' T$ electronic contribution (see text for details). Inset: $4f$ contribution to the specific heat, plotted as ΔC vs T.

$\Gamma_1(313\ \mathrm{K})$, respectively. The fit based on the latter Pr^{3+} energy level scheme reproduced better the overall shape of the low temperature peak, and also the value of the Van Vleck paramagnetic susceptibility. The effective moment was allowed to vary in the analysis and a value of $\mu_{eff} = 2.6\ \mu_B$ was obtained in both scenarios. The reduced value of μ_{eff} could be due to incomplete filling of the Pr sites or Sb inclusions in the $PrOs_4Sb_{12}$ single crystals. Several Pr^{3+} energy level schemes can account for the broad peak in $C(T)$ just above the superconducting transition in $PrOs_4Sb_{12}$. The best fit of the $4f$ contribution to the specific heat [i.e., $\Delta C = C(PrOs_4Sb_{12})$-$C_{latt}(LaOs_4Sb_{12})$, where $C_{latt}(LaOs_4Sb_{12})$ is the lattice contribution of the isostructural compound $LaOs_4Sb_{12}$ (Ref. 8)], was to a system of two levels of equal degeneracy split by an energy $\delta = 6.6$ K, and an additional $\gamma' T$ electronic contribution with $\gamma' = 568$ mJ/mol K^2, as shown in Fig. 3(b). However, there are two problems associated with this interpretation. First, for a nonmagnetic Γ_1 or Γ_3 ground state, there are no excited states of degeneracy equal to that of the ground state. It is conceivable that the degeneracy of the Γ_3 ground state has been lifted by the CEF when the local site symmetry of the Pr^{3+} ions is not cubic as might be caused by some kind of local distortion. However, there is no indication for this distortion from refinements of x-ray diffraction data on $PrOs_4Sb_{12}$ single crystals.[11] Second, the amount of entropy associated with the two levels of equal degeneracy $S_{TLS} = R \ln 2 \approx 5.8$ J/mol K is too small to account for the total entropy $S_T = \int (C/T) dT \approx 10.3$ J/mol K at 10 K which includes the peak and the γT term. A more likely possibility is that the pronounced peak in $C(T)/T$ corresponds to a Γ_3 ground state and a low lying Γ_5 excited state. The entropy of this doublet-triplet ($\Gamma_3 - \Gamma_5$) scenario [$S_{\Gamma_3-\Gamma_5} = R \ln(5/2) \approx 7.6$ J/mol K] is large enough to account for most of the total entropy S_T at 10 K. The additional entropy may be due to contributions of the Γ_4 and Γ_1 excited states and/or lattice contributions that we were unable to remove completely using the procedure described above. Inelastic neutron scattering experiments reveal peaks in intensity at ~ 8 K and ~ 130 K that appear to be due to CEF excitations,[12] consistent with the Pr^{3+} CEF energy level scheme deduced from $\chi(T)$ and $C(T)$ which has a Γ_3 ground state and a low lying Γ_5 excited state.

The $\chi(T)$ and $C(T)$ data can also be analyzed within an itinerant electron approach. The peak in $C(T)/T$ would then arise from an electronic contribution with a low-degeneracy temperature $T_F^* \sim 10$ K, as observed in many heavy fermion compounds (e.g., $CeAl_3$, UBe_{13}), with a value of γ of ~ 2 J/mol K^2 at ~ 3 K. In this case, the Pr^{3+} excited CEF energy levels would be far removed from the ground state as, for example, in $PrInAg_2$ which has the Pr^{3+} energy level scheme: $\Gamma_3(0\ \mathrm{K})$, $\Gamma_4(71\ \mathrm{K})$, $\Gamma_5(96\ \mathrm{K})$, and $\Gamma_3(177\ \mathrm{K})$.[13] For a value of γ of ~ 2 J/mol K^2, the ratio $\Delta C/\gamma T_C \sim 0.2$ is reduced with respect to the BCS value of 1.43. In the superconducting state, the specific heat C_S has a power law T-dependence $C_S(T) \sim T^n$ with $n \sim 3.9$ for $0.6 \leqslant T \leqslant 1.1$; this value of n is somewhat larger than the values observed for other heavy fermion superconductors that lie within the range $2 \leqslant n \leqslant 3$.[2] The reduced specific heat jump and power law behavior of $C(T)$ are consistent with anisotropic superconductivity in which the electrons are paired in states with nonzero angular momentum (non–s-wave superconductivity). If the heavy fermion state is based on magnetic fluctuations, rather than quadrupolar fluctuations, one would expect a Wilson-Sommerfeld ratio $R_W = (\chi(0)/\gamma(0))(\pi^2 k_B^2/\mu_{eff}^2)$ of the order of unity. Using the values of $\chi(3\ \mathrm{K}) = 0.07$ cm^3/mol and $\gamma(3\ \mathrm{K}) \sim 2$ J/mol K^2, and $\mu_{eff} = 3\ \mu_B$, a value of $R_W \sim 0.9$, typical of many heavy fermion compounds, is obtained for $PrOs_4Sb_{12}$. However, conservation of entropy between the superconducting and normal states indicates that γ must decrease with decreasing temperature below ~ 3 K to a value ~ 500 mJ/mol K^2, consistent with the superconducting properties.

The electrical resistivity, however, does not exhibit typical f-electron heavy fermion behavior, in which $\rho(T)$ has a relatively weak T-dependence at high temperatures above a characteristic "coherence temperature" below which it decreases rapidly and then saturates as T^2, reminiscent of a Fermi liquid. The coefficient A of the T^2 term in $\rho(T)$ is often found to follow the Kadowaki-Woods (KW) relation $A/\gamma^2 = 1 \times 10^{-5}$ $\mu\Omega$cm (mol K/mJ)^2.[17] The resistivity of $PrOs_4Sb_{12}$ follows a T^2 dependence from 7.5 K $\lesssim T \lesssim 45$ K, with a T^2 coefficient $A = 0.009$ $\mu\Omega$cm/K^2. This is some two orders of magnitude smaller than the value ($A \sim 1$ $\mu\Omega$cm/K^2) expected from the KW relation, assuming $\gamma \sim 500$ mJ/mol K^2. The overall shape of the $\rho(T)$ curve and behavior at low temperatures (aside from the superconductivity), is very similar to that of $PrInAg_2$,[5,18] in which strong electronic correlations, perhaps due to quadrupolar fluctuations, are apparently responsible for the enormous electronic specific heat coefficient $\gamma \sim 6.5$ J/mol K^2. It is noteworthy that the value of A in this compound is also inconsistent with the KW relation.[5] The decrease in $\rho(T)$ below 7 K apparently reflects a decrease in scattering of conduction electrons by the electric quadrupole or magnetic dipole moments of a low lying Pr^{3+} energy level in the CEF. In a magnetic field of 30 kOe, $\rho(T)$ in the normal state varies as a power law $\rho \propto \rho_0 + BT^n$ in the range $0.1 \leqslant T \leqslant 1.1$ K with $B = 0.88$ $\mu\Omega$cm/K^3 and $n \sim 3$. A T^2 dependence of $\rho(T)$ is observed over a more limited temperature range from 0.5 to 1.0 K (with deviations outside this T range) with $A = 1.0$ $\mu\Omega$cm/K^2, in agreement with the KW relation.

If a Γ_3 nonmagnetic doublet ground state with a nonvanishing quadrupole moment is stabilized in a metallic compound, a quadrupolar Kondo effect can, in principle, be realized.[19] In the single-ion quadrupolar Kondo model, the quadrupolar moments of the *f*-electron ions are overscreened by the charges of the conduction electrons, leading to non-Fermi liquid (NFL) behavior in the physical properties at low temperatures. Single-ion NFL *T*-dependences, similar to those predicted, have been observed in the physical properties of the $M_{1-x}U_xPd_3$ (M = Y, Sc) systems.[20] However, it has not been possible to definitely establish that the quadrupolar Kondo effect is responsible for the NFL behavior in these systems. It seems possible that the heavy fermion behavior exhibited by $PrOs_4Sb_{12}$ is associated with a quadrupolar Kondo lattice, in analogy with the quadrupolar Kondo model.[19]

A lattice of Pr ions with a Γ_3 ground state may undergo a structural phase transition, which can be first or second order in nature, via a cooperative Jahn-Teller effect.[21] Such a transition is observed in cubic compounds such as $PrPb_3$.[22] While quadrupolar ordering at $T \sim 3$ K, producing a peak in $C(T)$, cannot be excluded in $PrOs_4Sb_{12}$, it is perhaps more likely that this type of ordering is suppressed by the Γ_3 quadrupolar fluctuations, analogous to the competition between the Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction and the magnetic Kondo effect.[23]

In summary, $PrOs_4Sb_{12}$ exhibits superconductivity with a $T_C = 1.85$ K that appears to involve heavy fermion quasiparticles with an effective mass $m^* \sim 50$ m_e, as inferred from the jump in specific heat at T_C, the slope of the upper critical field near T_C, and the electronic specific heat coefficient γ. The ground state of the Pr^{3+} ions in the cubic CEF appears to be the Γ_3 nonmagnetic doublet, suggesting the possibility that the heavy fermion behavior involves the interaction of the Pr^{3+} Γ_3 quadrupole moments and the charges of the conduction electrons. If this is indeed found to be the case, it raises the question of what role Pr^{3+} quadrupolar fluctuations play in the heavy fermion superconductivity of this compound.

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[1] Z. Fisk *et al.*, Nature (London) **320**, 124 (1986).
[2] R. Heffner and M. Norman, Comments Condens. Matter Phys. **17**, 361 (1996).
[3] F. Steglich *et al.*, Phys. Rev. Lett. **43**, 1892 (1979).
[4] H.R. Ott *et al.*, Phys. Rev. Lett. **50**, 1595 (1979).
[5] A. Yatskar *et al.*, Phys. Rev. Lett. **77**, 3637 (1996).
[6] H. Sato *et al.*, Phys. Rev. B **62**, 15 125 (2000).
[7] A brief report of this work was presented at the XII Symposium of Phase Transitions and Critical Phenomena, Ladik Zdroj, Poland, June 21-24, 2001, by M.B. Maple *et al.*, [Acta Phys. Pol. B **32**, 3291 (2001)].
[8] E.D. Bauer *et al.*, J. Phys.: Condens. Matter **13**, 4495 (2001).
[9] D.J. Braun and W. Jeitschko, J. Less-Common Met. **72**, 147 (1980).
[10] K.R. Lea, M.J.K. Leask, and W.P. Wolf, J. Phys. Chem. Solids **23**, 1381 (1962).
[11] P. Rogl (private communication).
[12] M. B. Maple *et al.*, International Conference on Strongly Correlated Electrons with Orbital Degrees of Freedom, Sendai, Japan, 2001 [J. Phys Soc. Jpn. (to be published)].
[13] T.M. Kelley *et al.*, Phys. Rev. B **61**, 1831 (2000).
[14] M.B. Maple *et al.*, Phys. Rev. Lett. **54**, 477 (1985).
[15] R.R. Hake, Appl. Phys. Lett. **10**, 189 (1967).
[16] See, for example, M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).
[17] K. Kadowaki and S.B. Woods, Solid State Commun. **58**, 307 (1986).
[18] H. Mitamura *et al.*, Physica B **284-288**, 1341 (2000).
[19] D.L. Cox, Phys. Rev. Lett. **59**, 1240 (1987).
[20] M.B. Maple *et al.*, J. Phys.: Condens. Matter **96**, 9773 (1996); D.A. Gajewski, R. Chau, and M.B. Maple, Phys. Rev. B **62**, 5496 (2000).
[21] G.A. Gehring and K.A. Gehring, Rep. Prog. Phys. **38**, 1 (1978).
[22] E. Bucher *et al.*, *Proceedings of the International Conference on Low Temperature Physics*, *LT13*, edited by K. D. Timmerhaus, W. J. O'Sullivan, and E. F. Hammel (Plenum, New York, 1974), Vol. 2, p. 322.
[23] S. Doniach, Physica B & C **91B**, 231 (1977).