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Quadrupole ordering and multipole interactions in Pr-based compounds

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Abstract

Field–temperature phase diagrams of cubic compounds $PrPb_3$ and $PrOs_4Sb_{12}$ with non-magnetic crystalline electric field (CEF) ground state have been examined by means of low-temperature magnetization measurements. $PrPb_3$ is a typical Γ_3 doublet CEF ground state system which undergoes an antiferro-quadrupole (AFQ) transition at $T_Q = 0.4$ K. In a magnetic field $T_Q(H)$ exhibits re-entrant behaviour depending on the field direction, which can be interpreted in terms of interactions between induced dipole (and possibly octupole) moments in the AFQ phase. In the heavy-electron superconductor $PrOs_4Sb_{12}$, a field-induced ordered state has been observed above 4 T for all the principal directions. The results are in favour of a Γ_1 CEF ground state model in which a level crossing with a Γ_5 triplet excited state induces a long-range (possibly quadrupolar) ordering in a magnetic field.

1. Introduction

In cubic Pr compounds, the ground state of the crystalline-electric-field (CEF) splitting of Pr^{3+} ($J = 4$) very often becomes a non-magnetic level, with orbital degeneracy (quadrupole moments) remaining in the ground state itself or in the low-lying levels. These systems may therefore provide an interesting situation where orbital (quadrupole) degrees of freedom play an important role in the low-temperature properties. Among these, antiferro-quadrupole (AFQ) transitions in which a quadrupole moment aligns alternately have received much attention in recent years because of a variety of interesting field–temperature (H–T) phase diagrams. In particular, many of the AFQ ordering systems exhibit re-entrant behaviour in the H–T phase diagram; the AFQ transition temperature increases in a magnetic field [1–4], which behaviour has been discussed by several authors on the basis of mixing with CEF excited states [5], fluctuations in the order parameter [6, 7] and the effect of magnetic (multipole) interactions [4, 8–10].

In this paper, we compared the H–T phase diagrams of two Pr-based cubic compounds $PrPb_3$ and $PrOs_4Sb_{12}$, through dc magnetization measurements at very low temperatures down to 50 mK [11]. The former is a typical Γ_3 nonmagnetic doublet ground state system that undergoes an AFQ transition [12–15]. The AFQ phase diagrams exhibit re-entrant behaviour [3, 4], which can be interpreted in terms of magnetic interactions between the induced (multipole) moments. The latter compound is considered to be the first Pr-based heavy-electron superconductor and has been discussed in relation to a quadrupolar Kondo effect assuming a Γ_3 doublet ground state of Pr^{3+} [16, 17]. Identification of the CEF ground state of this system, however, seems to be still controversial [18, 19]. Unlike the case of $PrPb_3$, we found that this compound exhibits a *field-induced* ordering (possibly an AFQ phase) for all the principal directions. The results are hard to understand in terms of the Γ_3 doublet ground state model, and rather suggest that the CEF ground state is a Γ_1 singlet that undergoes a level crossing with the Zeeman split triplet excited state.

2. Antiferro-quadrupolar ordering in a Γ_3 doublet ground state system $PrPb_3$

$PrPb_3$ crystallizes in the cubic $AuCu_3$ type structure. The CEF ground state of Pr^{3+} in this compound is known to be a Γ_3 non-Kramers doublet which carries quadrupole moments O_2^0 ($=[2J_z^2 - J_x^2 - J_y^2]/2$) and O_2^2 ($=\sqrt{3}[J_x^2 - J_y^2]/2$), with a magnetic Γ_4 triplet excited state lying $\sim$15 K above the ground state [13, 14]. This compound is therefore a very simple system in which the low-temperature properties are mainly governed by the quadrupolar degrees of freedom. This compound actually exhibits a second-order transition at 0.4 K [12], which is considered to be an AFQ ordering [15]. We have been examining the H–T phase diagram of Pr^{3+} [4], and the results for a high-quality single crystal are given in the following.

In figure 1, we show the magnetization divided by field M/H at various fields applied parallel to [100]. The AFQ transition manifests itself as an upward bending in M/H, by which the critical temperature $T_Q(H)$ can be defined. As can be seen in the figure, $T_Q(H)$ increases with H from 0.43 K at 1 T to 0.61 K at 4 T. We observed another anomaly in M/H below $T_Q(H)$ as indicated by upward arrows in figure 1, which implies a certain change in the AFQ ordered structure. We continued similar magnetization measurements for the other field directions at various fields, and the H–T phase diagrams confirmed so far are shown in figure 2, where the open circles are the data points obtained by the $M(T)$ measurements in fixed magnetic fields. The solid circles in the figure are the transition fields determined by the $M(H)$ measurements in fixed T, where a weak jump or a kink was observed in the magnetization curves. The AFQ phase appears to close in high fields for $H \parallel [100]$ and [111]. The upper phase boundary for $H \parallel [110]$, however, has not been determined yet. While no further transition has been observed in the $M(H)$ data for $H \parallel [110]$ above 8 up to 13 T at the base temperature, we have a feeling that the ordered phase extends to much higher fields. In all the directions, we newly observed first-order transition lines within the AFQ phase as shown in the figure.

One of the important features of the phase diagrams is the re-entrant behaviour of $T_Q(H)$, which is most pronounced for $H \parallel [001]([100])$. $T_Q(H)$ is strongly anisotropic, showing no enhancement for $H \parallel [111]$. The main origin of the enhancement in $T_Q(H)$, we consider, is the antiferromagnetic (AF) interactions [4]. First of all, it is important to point out that the order parameter (OP) at $H = 0$ is expected to be a pure quadrupole one; no magnetic component can in general mix into the quadrupolar OP upon the second-order transition because of a difference in symmetry. This means that at $H = 0$ the system cannot benefit from inherent magnetic interactions. When a magnetic field is applied in the AFQ phase, magnetic dipole moment with a staggered component is induced by a Van Vleck mechanism because the orbital

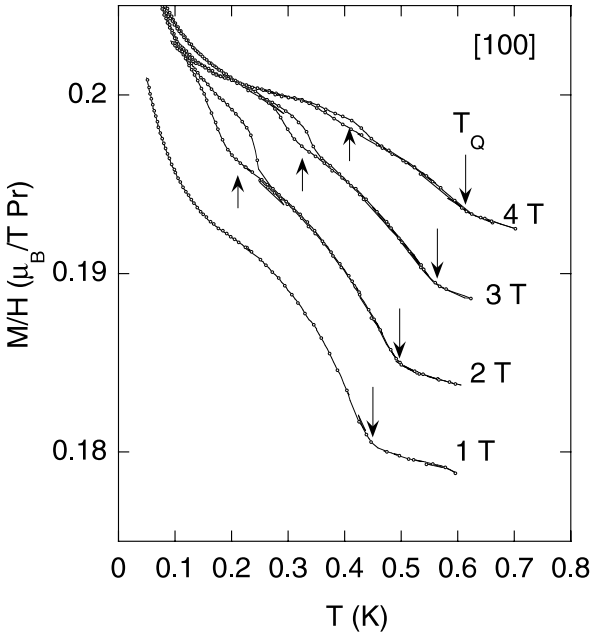

Figure 1. Magnetization divided by field M/H of $PrPb_3$ for $H \parallel [100]$. The downward arrows indicate the AFQ transition. The upward arrows indicate a first-order transition within the AFQ state. The upturn of the magnetization below 0.2 K is probably due to the Pr nuclear spin contribution.

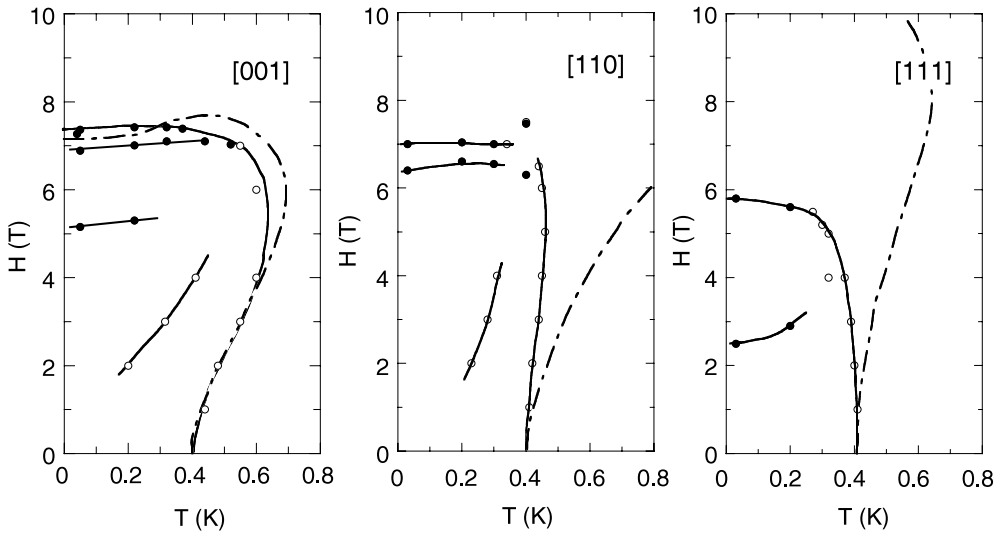

Figure 2. Phase diagram of $PrPb_3$ for the three principal field directions. The upper phase boundary for $H \parallel [110]$ has not been determined yet. The dot–dashed curves are the AFQ transition lines calculated by the mean field model (1) with parameters $K_{\Gamma 3} = -22.4$ mK, $K_1 = -0.73$ K and $K_2 = -0.37$ K.

is alternately ordered. The system can then gain the AF interaction energy through the induced AF moment, and the AFQ state is stabilized in a magnetic field. This scenario can be shown

more quantitatively by solving the following mean-field model:

$$\mathcal{H}_{\mathrm{A(B)}} = \mathcal{H}_{\mathrm{CEF}} - g_J \mu_{\mathrm{B}} \boldsymbol{J}\boldsymbol{H} - K_{\Gamma 3}[\langle O_2^0 \rangle_{\mathrm{B(A)}} O_2^0 + \langle O_2^2 \rangle_{\mathrm{B(A)}} O_2^2] - (K_1 \langle \boldsymbol{J} \rangle_{\mathrm{B(A)}} + K_2 \langle \boldsymbol{J} \rangle_{\mathrm{A(B)}}) \boldsymbol{J}, \quad (1)$$

where we assumed the simplest two-sublattice model since microscopic information on the ordered structure is still lacking. Here $\mathcal{H}_{\mathrm{CEF}}$ is the CEF Hamiltonian and $K_{\Gamma 3}$ the quadrupole interaction coefficient. K_1 and K_2 are the inter- and intra-sublattice AF interaction coefficients, respectively. The two parameters in $\mathcal{H}_{\mathrm{CEF}}$, W and x in the notation of [20], are chosen to best fit the susceptibility data as $W = -0.45$ K and $x = 0.39$ which give the CEF splitting of $\Gamma_3(0)$–$\Gamma_4(15\ \mathrm{K})$–$\Gamma_5(28\ \mathrm{K})$–$\Gamma_1(35\ \mathrm{K})$.

The dot–dashed curves in figure 2 are the calculated results of the AFQ phase boundaries with the interaction coefficients $K_{\Gamma 3} = -22.4$ mK, $K_1 = -0.73$ K and $K_2 = -0.37$ K. The stable OPs are O_2^0 and O_2^2 for $H \parallel [001]$ and [110], respectively. It is remarkable that the re-entrant behaviour in $T_{\mathrm{Q}}(H)$ can be reproduced quite well for $H \parallel [001]$. This re-entrant behaviour is largely due to the AF interactions because no significant enhancement of $T_{\mathrm{Q}}(H)$ was obtained when $K_1 = K_2 = 0$. We found, however, that the above model has a difficulty in explaining the observed anisotropy of the phase diagram; $T_{\mathrm{Q}}(H)$ is much overestimated for $H \parallel [110]$ and [111] as shown in the figure. This discrepancy might be resolved to some extent by introducing the anisotropic quadrupole interactions which are not included in the above simple model. However, we consider that the absence of enhancement in $T_{\mathrm{Q}}(H)$ for $H \parallel [111]$ is still hard to explain even by the anisotropic quadrupole interactions.

Another possible extension of the model would be to incorporate an octupolar interaction. In the AFQ phase of the Γ_3 quadrupoles in a magnetic field, it is shown by symmetry consideration that a staggered component of Γ_5 type octupole moments $(T_x^\beta, T_y^\beta, T_z^\beta)$ is induced for certain field direction [21]. Here the operators are defined as $T_x^\beta \equiv \frac{\sqrt{15}}{6} \overline{J_x(J_y^2 - J_z^2)}$, etc, where the bar means a symmetrized product. In fact, we found that large octupoles (T_x^β and T_y^β components) are induced for $H \parallel [110]$ and [111], but not for $H \parallel [001]$ if the OP is O_2^0 for this direction. Thus, the anisotropy of $T_{\mathrm{Q}}(H)$ may be explained if there is a weak ferro-octupolar interaction of order 5 mK in the system [4]. As shown in the figure, however, we observed some new transition lines within the AFQ phase, which imply that the actual AFQ structure might be more complex than what we assumed here. For more quantitative argument, we do need information about the ordered structure and, to this end, we are planning a neutron scattering experiment in a magnetic field.

3. Field-induced ordering in $PrOs_4Sb_{12}$

In $PrOs_4Sb_{12}$, the Van Vleck behaviour of the magnetic susceptibility data suggests that the CEF ground state is either a non-magnetic Γ_3 doublet or a Γ_1 singlet in the O_h notation [16, 17]. Identification of the CEF ground state of this system is of importance for understanding the the heavy-electron formation in this system, but the situation seems to be still controversial [18, 19]. In order to gain further insight into this issue, we are focusing our attention on the field-induced ordering (FIO) in $PrOs_4Sb_{12}$ which has recently been revealed for $H \parallel [100]$ by the specific heat measurements [18, 19]. Since this type of phase diagram has never been observed in Ce-based heavy-fermion compounds, the origin is considered to be specific to the Pr 4f electronic state.

Figure 3 shows the magnetization curves of $PrOs_4Sb_{12}$ for two field directions ($H \parallel [100]$ and [110]), obtained at 0.06 K. At low fields, the magnetization shows small hysteresis due to flux pinning in the superconducting mixed state. The irreversible magnetization exhibits a peak effect at around 1.6 T, just below the upper critical field $H_{\mathrm{c2}} = 1.8$ T. It should be noticed

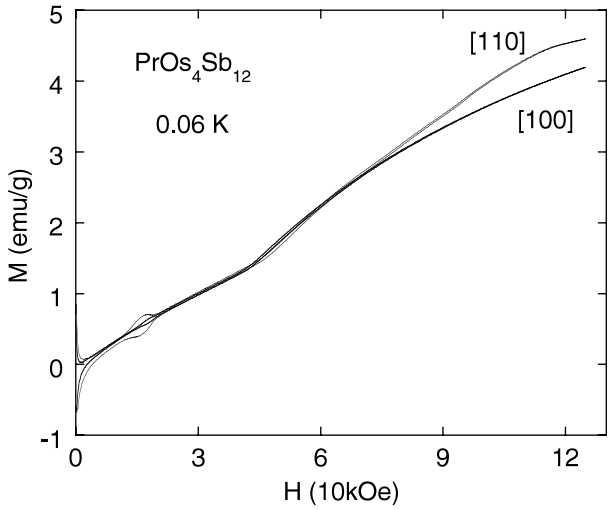

Figure 3. Magnetization curves of $PrOs_4Sb_{12}$ with $H \parallel [100]$ and [110], measured at 0.06 K.

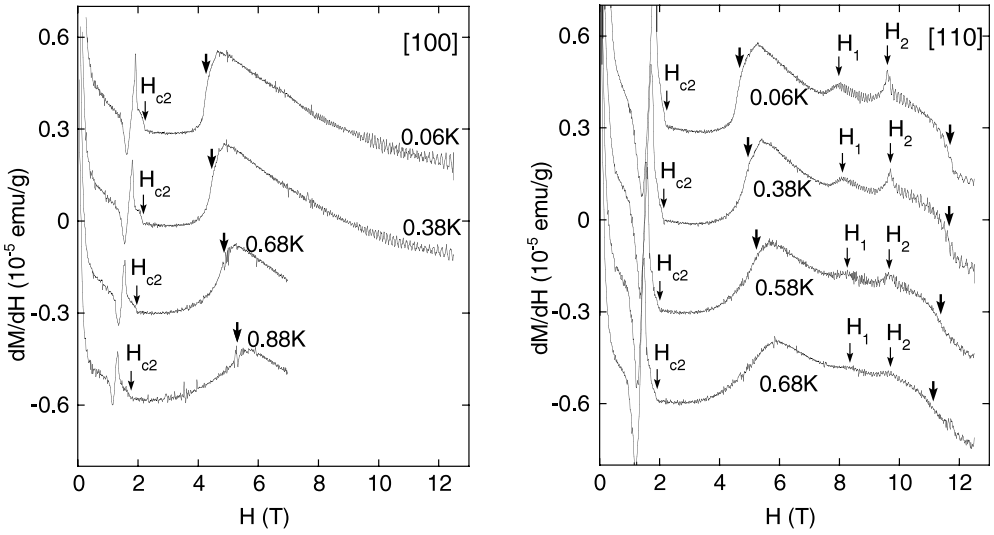

Figure 4. Differential susceptibility of $PrOs_4Sb_{12}$ with $H \parallel [100]$ and [110]. The FIO is indicated by a jump in dM/dT as shown by thick arrows. For $H \parallel [110]$, two distinct peaks are observed in dM/dT within the ordered phase, suggesting some changes in the ordered structure. The sharp structures below H_{c2} are due to the peak effect.

that $M(H)$ in the paramagnetic state above H_{c2} is nearly isotropic. For both directions, one can see an upward bending in $M(H)$ at ∼4.5 T. This indicates a transition to the field-induced ordered state, which we call the 'A-phase' in this paper.

The transition behaviour can be seen more clearly in the dM/dH plot shown in figure 4. Here the transition to the A-phase is indicated by a jump in dM/dH (thick arrows). For $H \parallel [100]$, the A-phase extends beyond the present experimental limit (12.5 T) whereas for $H \parallel [110]$ an upper boundary of the A-phase is observed at 11.5 T. For the latter direction, we observed additional peaks in dM/dH at H_1 and H_2 within the A-phase, possibly due to certain changes in the ordered structure.

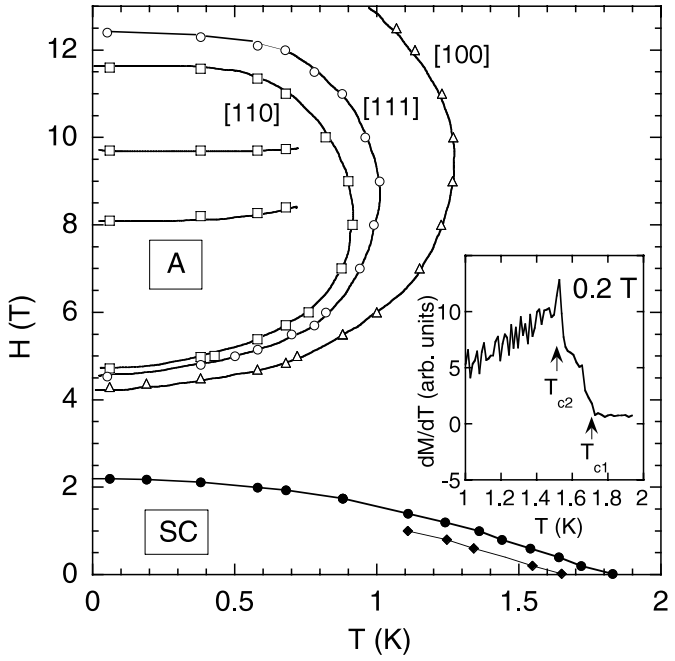

Figure 5. H–T phase diagram of $PrOs_4Sb_{12}$ with $H \parallel [100]$ (open triangles), [110] (open squares) and [111] (open circles). A field-induced ordered phase (A-phase) is observed for all the principal directions. No strong anisotropy is found for the superconducting state. The inset shows the dM/dT data near T_c, suggesting a double superconducting transition.

We also continued the measurements for $H \parallel [111]$, and obtained the field–temperature phase diagrams as shown in figure 5 [22]. For all the directions, the transition temperature $T_A(H)$ becomes highest at around 8 T. $T_A(H)$ is somewhat anisotropic, being lowest (highest) for $H \parallel [110]$ ([100]). We also confirmed that the A-phase closes at high fields except for $H \parallel [100]$ where the upper border was not observed because of the present experimental limitation. It should be emphasized that the A-phase exists for all the principal crystallographic directions. As will be discussed later, this fact would be a clue for the identification of the CEF ground state of Pr^{3+} in this compound. The inset shows an example of the temperature derivative of the magnetization dM/dT near the superconducting transition. We observed two distinct anomalies in dM/dT at T_{c1} and T_{c2}, in agreement with those reported in the specific heat measurements [16, 19]. These transition temperatures determined by the present measurements are also plotted in the phase diagram, where the low-temperature part of the transition line is obtained from the dM/dH data. Interestingly, the lower transition temperature $T_{c2}(H)$ lies almost parallel to the upper one $T_{c1}(H)$, without showing a tendency to intersect each other. More detailed results on the superconducting transition will be given in a separate paper [23].

We now briefly discuss the possible origin of the FIO. While the actual order parameter of the A-phase is unknown at present, this type of phase diagram is naturally explained by the Γ_1 ground state model within the localized electron picture [23]. In this case, it can be shown that the Zeeman effect of the low-lying CEF levels is nearly isotropic and exhibits a level crossing at $\sim$8 T for all directions. If an antiferro-quadrupolar interaction exists in the system, then an AFQ ordering can easily be induced around the crossing field since quadrupolar degrees of freedom are restored there.

For the Γ_3 ground state model, however, the situation is quite different. The Zeeman effect of the low-lying states is strongly anisotropic, with a level crossing occurring only for $H \parallel [100]$ at a rather high field ($\sim$20 T) [23]; one cannot rely on the CEF excited states in explaining the FIO. Because the CEF ground state itself has the quadrupolar moments, a quadrupolar ordering should set in at $H = 0$ in the presence of quadrupolar interactions. The phase diagram may show a re-entrant behaviour as is the case of $PrPb_3$, but it would be difficult to explain the FIO within the localized electron picture. Of course, it remains an interesting question whether a screening of the quadrupole moment due to the c–f hybridization effect in this case leads to a phase diagram like figure 5 or not; i.e., an AFQ ordering that is destroyed by the delocalization effect of 4f electrons at low field might be restored by application of a strong magnetic field. In this regard, we should recall that none of the Ce-based heavy-fermion compounds, whose CEF ground state always has the Kramers degeneracy, exhibits such a phase diagram (field-induced AF order in this case). This fact suggests that the possibility of FIO in the Γ_3 ground state model is not likely to be the case, even in the presence of the hybridization effect. Although still not conclusive at present, we believe that the existence of the FIO favours the Γ_1 CEF ground state in $PrOs_4Sb_{12}$. An obvious question that remains is why the conduction electrons become heavy in this situation. Possibly, the Γ_5 triplet excited state lying $\sim$6 K above the ground state [17, 23] might be responsible for the mass enhancement in the presence of hybridization with conduction electrons. Further careful study would be needed to clarify these points. More details of the experimental results and the analyses will be published elsewhere [23].

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