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LETTER TO THE EDITOR

Unconventional emergence of elastic softening induced by magnetic fields in the unusual heavy-fermion compound $PrFe_4P_{12}$

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Abstract

Ultrasonic measurement on the filled skutterudite compound $PrFe_4P_{12}$ exhibits a mysterious temperature dependence of the elastic constant $(C_{11}–C_{12})/2$. Pronounced elastic softening at low temperatures is revived by applying a magnetic field. This fact strongly suggests the 4f-multiplet ground state of the Pr ion split by the crystalline electric field (CEF) to be a Γ_3 non-Kramers doublet. The expectation value of a quadrupole moment with Γ_3 symmetry in the CEF ground state, which leads to elastic softening at low temperature, was evaluated by theoretical fitting to the present results. This may imply that suppression of the electric quadrupole Kondo effect occurs in $PrFe_4P_{12}$ and the quadrupole moment becomes steady due to the application of a magnetic field.

Heavy-electron materials have been studied intensively, both theoretically and experimentally, because of their interesting physical properties. Most of the systems have been found and investigated in Ce- and Yb- based compounds using specific heat measurement, study of the de Haas–van Alphen (dHvA) effect and so on [1–4]. These compounds are understood well in the framework of the 'Kondo effect': quenching of the magnetic moment of the lone Ce or Yb 4f electron or hole by antiferromagnetic interaction with conduction electrons [5–8]. However, recent works have indicated that a heavy-electron system can also be realized in U- and Pr-based compounds which have a $5f^2$ or $4f^2$ configuration (not $4f^1$) and these have received much attention. So far alloys such as $U_xTh_{1-x}Ru_2Si_2$ [9], UBe_{13} [10], $Y_{1-x}U_xPd_3$ [11] and $PrAg_2In_2$ [12] have been classified into this system. Actually, they exhibit a different behaviour at low temperature from the typical Fermi liquid as seen in conventional Kondo (CK) materials: the behaviour of resistivity and specific heat at low temperatures cannot be described by a T^2 and a T law respectively.

Recent theoretical work suggests that the non-Kramers doublet ground state of the f^2 configuration plays a crucial role in the formation of heavy quasiparticles—the electric quadrupole Kondo effect (QKE) [13, 14]. In the case of a cubic crystalline electric field (CEF) the multiplet with $J = 4$ (J being the total angular momentum) is split into a non-Kramers doublet and other excited states. The exchange scattering of conduction electrons due to a non-Kramers doublet ground state gives rise to the QKE system. Under this restriction, as pointed out, only a Γ_3 doublet ground state with a Γ_4 triplet excited state is retained within the $J = 4$ multiplet in a cubic CEF. This f^2 configuration is a prerequisite, and is indispensable for determining the multiplet ground state of the f state split by the CEF. However, we still do not understand the important and fundamental issues, such as the mechanism of heavy-quasiparticle formation in systems with the $5f^2$ and $4f^2$ configuration.

Recently, it was found that $PrFe_4P_{12}$ is an intriguing, key material; it is a strong candidate to be the QKE alloy [15]. This material belongs to the ternary iron phosphides with the general formula $ReFe_4P_{12}$ (Re being a rare earth) which crystallize in the unique body centred cubic filled skutterudite structure ($Im3$, #204, T_h^5) [16, 17]. $PrFe_4P_{12}$ has been discovered by dHvA study to have a very heavy effective mass of $m^* = 81\ m_0$ [18]. Such a record value for all Pr-based compounds seems to be very unusual in the framework of the CK mechanism. Kondo-like anomalies have been observed in the transport and thermal properties: an almost logarithmic increase of ρ, an unusually large thermoelectric power and large C_m/T at low temperatures where C_m and T represent the magnetic contribution to the specific heat and temperature respectively [19, 20]. Furthermore, it was suggested by our previous ultrasonic measurements that the Pr ion had a non-Kramers doublet ground state in $PrFe_4P_{12}$ [15]. However, we failed to measure the $(C_{11}–C_{12})/2$ mode in magnetic fields due to a lack of suitable equipment at the time.

In experimental investigations on heavy-electron systems the dHvA effect is a powerful tool for clarifying the electronic structure and effective mass of quasiparticles [1]. However, it can hardly suggest directly the mechanism by which the heavy quasiparticles are formed. In other words, it is difficult to obtain directly significant knowledge of the relation between a quadrupole moment and conduction electrons. If the quadrupole moment in a Γ_3 non-Kramers doublet plays a crucial role in these materials, ultrasonic measurement could be a much more powerful and straightforward tool for the investigation of QKE systems. Thus, the elastic constant as a function of temperature determined in this way is explained in terms of the quadrupolar response of the ground multiplet of the f state split by the CEF effect.

In this Letter we report the nature of the Γ_3 non-Kramers doublet ground state in $PrFe_4P_{12}$ in magnetic fields. Our results strongly suggest that the Γ_3 non-Kramers doublet ground state was realized in $PrFe_4P_{12}$, and that the quadrupole moment in the Γ_3 non-Kramers doublet became steady due to the application of a magnetic field.

Single crystals of $PrFe_4P_{12}$ were grown by the tin-flux method. A high-quality sample is ensured by the fact that a dHvA signal was observed. The sample had a rectangular shape of dimensions $2.2 \times 2.3 \times 2.8\ \text{mm}^3$ with two crystallographic axes along the $\langle 001\rangle$ and $\langle 011\rangle$ directions. The parallel planes of the sample were polished carefully with polishing paper in order to observe the ultrasonic pulse echoes. $LiNbO_3$ transducers for the generation and detection of the sound waves were bonded to the surfaces of the sample. The sound-wave velocity v was detected by ultrasonic apparatus using a phase-comparison method. In the estimation of the elastic constant $C = \rho v^2$ we used the mass density $\rho = 5.1417\ \text{g cm}^{-3}$ of the present sample of $PrFe_4P_{12}$.

The temperature dependence of $(C_{11}–C_{12})/2$ under the magnetic fields along the $\langle 011\rangle$ axis is shown in figure 1. A dip appears around the transition temperature of 6.4 K in low fields and it becomes larger with increase in the magnetic field. Furthermore, a remarkable

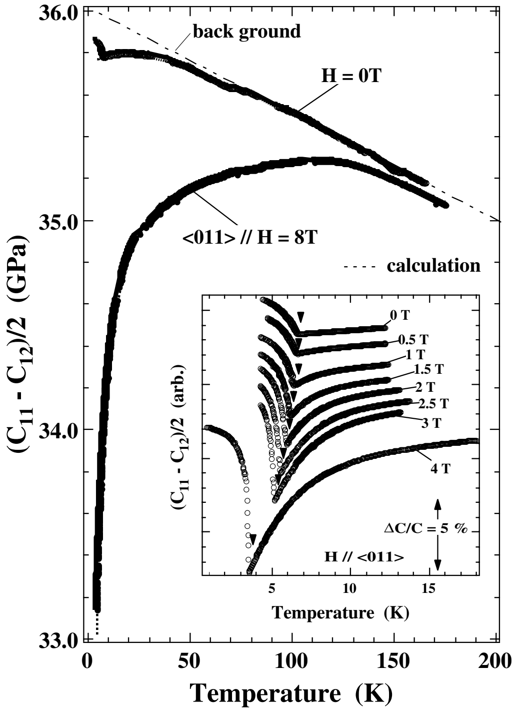

Figure 1. Temperature dependence of elastic constant $(C_{11}–C_{12})/2$ under magnetic fields of 0 and 8 T along the ⟨011⟩ axis. The dotted line represents the calculated result. The inset shows the temperature dependence of the elastic constant $(C_{11}–C_{12})/2$ under the magnetic fields along the ⟨011⟩ axis. The transition points are indicated by arrows.

softening of about 10% emerges under a field of 8 T. This field corresponds to the region outside the ordered state in the $H–T$ phase diagram. An abrupt hardening was observed below the transition temperature. This transition point shifts towards lower temperatures with increase of the magnetic field up to 4 T. No transition was observed under the field of 8 T. The elastic constant C_{44} shows no softening towards low temperature even in magnetic fields, which was reported in our previous papers [15].

Here, we analyse and discuss the obtained results. They indicate that softening emerges and develops with increasing magnetic field. This behaviour is quite different from that of normal rare-earth compounds. In cases where the ground state level is orbitally degenerate and has a magnetic moment, or the excited crystal-field levels with magnetic moment are close to that, elastic softening towards low temperatures is gradually suppressed by applying magnetic fields to gain the Zeeman energy, which lifts the orbital degeneracy, as seen in HoB_6 [21] and TmS [22]. The $Pr^{3+}(^3H_4)$ state splits in a unique skutterudite structure into the levels Γ_1 singlet, $\Gamma_4^{(1)}$ triplet, $\Gamma_4^{(2)}$ triplet and a Γ_{23} non-Kramers doublet [17]. Here, for simplicity, we neglect the additional term $B_6'(O_2^6–O_6^6)$ and use the expression for the point group O_h, where O_2^6 and O_6^6 represent the Stevens' operators. According to the anisotropy of the magnetization, this additional parameter B_6' seems to be small and has little impact on the CEF effect in this system [23]. Thus, the $Pr^{3+}(^3H_4)$ state is assumed to be split in $PrFe_4P_{12}$ into levels Γ_1 singlet, Γ_4 triplet, Γ_5 triplet and Γ_3 non-Kramers doublet [17]. As presented in a previous paper [15], at zero field the elastic constant C_{11} shows a slight softening below 30 K as well as $(C_{11}–C_{12})/2$. On the other hand, C_{44} shows no softening at low temperatures. Even when a

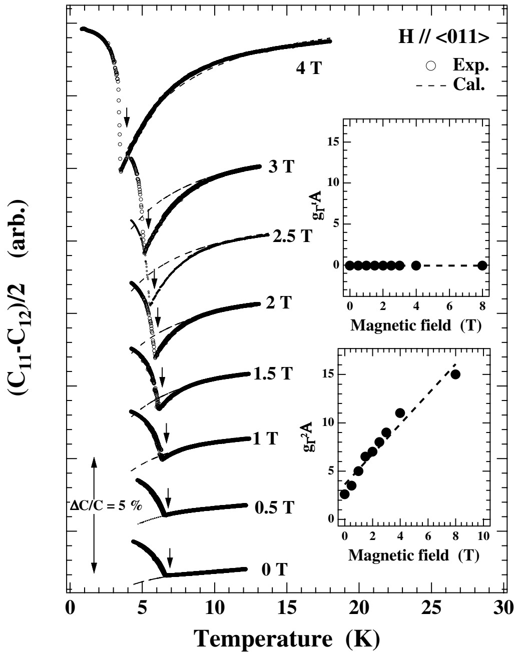

Figure 2. Calculated elastic constant curves considering CEF, quadrupole-strain, interionic quadrupolar interactions under condition (I). The inset shows the obtained magnetic field dependence of $g_\Gamma^2 A_\Gamma$ and $g'_\Gamma A_\Gamma$ under condition (I). The dotted line is a guide to the eye.

magnetic field is applied, C_{44} shows a slight increase with decreasing temperatures. An abrupt hardening on the phase boundary was also observed in C_{44}. The CEF ground state has been considered to be orbitally degenerate where the quadrupolar moment with Γ_3 symmetry exists. However, the elastic softening of $(C_{11}–C_{12})/2$ in zero field was rather weak, unlike the typical behaviour of other systems where the ground state level is orbitally degenerate. The revival of strong softening observed in the magnetic field confirmed the Γ_3 ground state in this system. The temperature dependence of elastic constants in magnetic fields was analysed by using the conventional formula including the quadrupolar-strain interaction as a perturbation [24–26]:

$$C_\Gamma(T) = C_\Gamma^0(T) - \frac{N g_\Gamma^2 A_\Gamma}{T - g'_\Gamma A_\Gamma} \qquad (1)$$

where $C_\Gamma^0(T)$ is the background without quadrupolar-strain coupling g_Γ, N is the number of Pr ions in unit volume, g'_Γ is the quadrupolar interaction between Pr^{3+} ions and A_Γ is the matrix element of the Curie term, which is proportional to the expectation value of a quadrupolar moment. Here, the suffix Γ denotes the symmetry Γ_3. The derivation of this formula was described in detail in [15]. It should be noted that the magnetic phase diagram of $\mathrm{PrFe_4P_{12}}$, reported previously by our group [15], indicates the singularity point at a temperature of around 5 K and a magnetic field of around 2 T for $H \parallel \langle 001 \rangle$. This should also be taken into account in the present analysis. Therefore, we analyse the obtained data in two ways as follows:

(I) The singular region as observed around the transition point is excluded from the fitting.
(II) The singular region is included in the fitting and assumed to be due to a quadrupolar moment. The fitting curves give us the magnetic field dependence of the parameters $g_\Gamma^2 A_\Gamma$ and $g'_\Gamma A_\Gamma$.

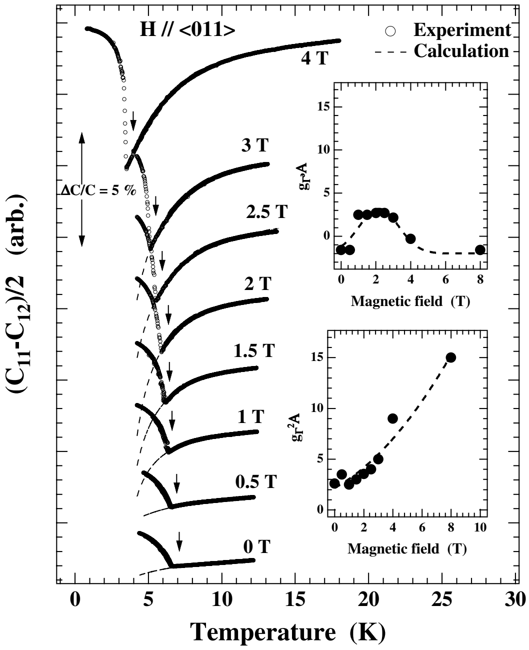

Figure 3. Calculated elastic constant curves considering CEF, quadrupole-strain and interionic quadrupolar interactions under condition (I). The inset shows the obtained magnetic field dependence of $g_\Gamma^2 A_\Gamma$ and $g'_\Gamma A_\Gamma$ under condition (II). The dotted line is a guide to the eye.

Figures 2(a) and (b) show the fitting results using condition (I). $g'_\Gamma A_\Gamma$ is almost constant, whereas $g_\Gamma^2 A_\Gamma$ increases monotonically with increasing magnetic field. Figures 3(a) and (b) show the fitting results using condition (II). $g_\Gamma^2 A_\Gamma$ increases monotonically with increasing magnetic field, similar to the case for condition (I). However, $g'_\Gamma A_\Gamma$ changes its sign around 2 T, due to the existence of a singular point in the H–T phase diagram, if the fitting is applied to experimental results explicitly. It was also found that $g_\Gamma^2 A_\Gamma$ increases monotonically with increasing magnetic field.

Usually the coupling constant g_Γ seems to be almost independent of the magnetic field. If this is so, we can deduce from our results that A_Γ, i.e. the expectation value of quadrupolar moment with Γ_3 symmetry, increases monotonically with increasing magnetic field. On the other hand, the value of $g'_\Gamma A_\Gamma$ is almost constant, although $g_\Gamma^2 A_\Gamma$ increases monotonically with increasing magnetic field. These results may be controversial because A_Γ also causes an increase in the value of $g'_\Gamma A_\Gamma$. First it should be noted that $g'_\Gamma A_\Gamma$ does not have much effect on the fitting result. Even if $g'_\Gamma A_\Gamma$ were to be set zero, the fitting result would be only slightly changed. This is clearly demonstrated by the two fitting methods. On the basis of this understanding, we would like to discuss the role and behaviour of g'_Γ in a magnetic field. It is considered that the quadrupolar interaction is caused by phonons or/and conduction electrons. In heavy-fermion systems the latter are more important. It is noteworthy that recent magnetic susceptibility measurements suggest the existence of ferromagnetic interactions in $PrFe_4P_{12}$ [27]. At present we suggest that the so-called 'conflict' between antiferroelectric quadrupolar interaction and ferromagnetic interaction may cause the magnetic field dependence of g'_Γ. This may lead to the fact that the value of $g_\Gamma^2 A_\Gamma$ increases monotonically, whereas $g'_\Gamma A_\Gamma$ is almost constant with increasing magnetic field.

$PrFe_4P_{12}$ is a strong candidate to be a quadrupole Kondo system in which a quadrupolar moment is screened by conduction electrons and quenched, i.e. the expectation value of the quadrupolar moment almost vanishes. In a previous study by our group, we reported the fact that softening observed in both C_{11} and $(C_{11}–C_{12})/2$ in zero field was slight compared with that observed in normal rare-earth compounds. The screening, however, seems to be depressed and the quadrupolar moment of the CEF ground state is revived by the application of a magnetic field in a similar manner to that seen in magnetic Kondo systems [5–8].

In conclusion, we have shown pronounced elastic softening induced by magnetic fields with a temperature dependence of $(C_{11}–C_{12})/2$ in $PrFe_4P_{12}$. The obtained results can be interpreted as a revival of the quadrupolar moment with Γ_3 symmetry in the CEF ground state of Pr ions due to the application of a magnetic field. This is the first experimental demonstration of the quadrupolar moment becoming steady due to the application of a magnetic field, implying suppression of the QKE. This study also proved that ultrasonic measurements were the most powerful strategy for elucidating the CEF ground state properties in $PrFe_4P_{12}$ as well as other rare-earth compounds in terms of quadrupolar moment.

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