

## Elastic constants of $\text{PrFe}_4\text{P}_{12}$ in magnetic fields

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Elastic properties of  $\text{PrFe}_4\text{P}_{12}$  have been investigated by means of the ultrasonic measurement. A softening has been observed in the elastic constants  $C_{11}$ , and  $(C_{11} - C_{12})/2$ . This indicates that the ground-state multiplet  $^3H_4$  of  $4f^2$  configuration in  $\text{Pr}^{3+}$  has  $\Gamma_3$  symmetry. Temperature dependence of  $C_{11}$  shows that the pronounced dip appears around  $T_N$  in magnetic fields and it becomes larger with increasing magnetic fields up to 2 T, then it is suppressed gradually by applying higher magnetic field. This dip disappears completely in the magnetic field above 3 T. Furthermore, a transition has been observed in the magnetic field dependence of  $C_{11}$  at constant temperatures. A  $(H-T)$  phase diagram has been proposed by the obtained results. Experimental results suggest that antiferroquadrupolar interaction plays an important role.

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### I. INTRODUCTION

A system of ternary iron phosphide  $R\text{Fe}_4\text{P}_{12}$  compounds ( $R$  is rare earth) have attracted much attention in recent years because of their mysterious magnetic and transport properties.<sup>1-6</sup> Depending on the rare-earth element in  $R\text{Fe}_4\text{P}_{12}$  compounds, they exhibit various interesting phenomena, such as superconducting below  $T_s = 4.2$  K in  $\text{LaFe}_4\text{P}_{12}$ , semiconducting in  $\text{CeFe}_4\text{P}_{12}$ , “antiferromagnetic” below  $T_N = 6.4$  K in  $\text{PrFe}_4\text{P}_{12}$ , and ferromagnetic below  $T_c = 1.9$  K in  $\text{NdFe}_4\text{P}_{12}$ . Also when replacing Fe and P sites by other elements, they exhibit many anomalous phenomena.<sup>7-14</sup>

$R\text{Fe}_4\text{P}_{12}$  compounds crystallize in the filled skutterudite structure, which has the isostructural cubic structure belonging to the space group  $Im\bar{3}$ .<sup>15,16</sup> Within the bcc network of Pr atoms, the eight-corner-sharing Fe-P<sub>6</sub> octahedra are distorted along triad axes into trigonal antiprisms. The crystal structure is shown in Fig. 1. The rare-earth atoms in  $R\text{Fe}_4\text{P}_{12}$  locate at the positions with the site symmetry of  $T_h^5$ .

The magnetic properties reported before would indicate that Pr ion in  $\text{PrFe}_4\text{P}_{12}$  is trivalent.<sup>1</sup> The inverse susceptibility gives the effective moment of  $\text{PrFe}_4\text{P}_{12}$  to be  $3.62\mu_B$  in the temperature range from 80 K to 300 K. This value is close to that of  $\text{Pr}^{3+}$  free ion value of  $3.58\mu_B$ . Likewise, the effective moment is estimated to be  $3.18\mu_B$  below 40 K. This difference would be caused by crystalline electric field (CEF) effects.

$\text{PrFe}_4\text{P}_{12}$  undergoes a phase transition at  $T_N = 6.4$  K. The resistivity shows a steep increase below  $T_N$ . A cusp is observed in its inverse susceptibility at  $T_N$ , and a remarkable peak is observed in the specific heat.<sup>1,17</sup> No crystallographic phase transformation has been found in x-ray powder diffraction experiment at temperatures down to 4 K.<sup>1</sup> There is the magnetic-field-induced transition in the magnetization process below  $T_N$ . This transition has been considered to be either a spin-flop or metamagnetic transition.<sup>1</sup> Specific heat in ordered state shows  $T^3$  temperature dependence and sug-

gested antiferromagnetic spin wave. From these experimental results, the phase below  $T_N$  has been considered to be an antiferromagnetic ordering, so far.<sup>1</sup> To our knowledge, no magnetic Bragg peak has been found in neutron diffraction measurement.

Pr ion in compounds is so stable that Pr-based compounds have been considered to be more rigid against attempts to drive them into instability than Ce- or Yb-based compounds.  $\text{PrFe}_4\text{P}_{12}$  exhibits metallic conduction at high temperatures and shows a Kondo-like logarithmic temperature dependence below 130 K.<sup>17</sup> According to the recent de Haas-van Alphen (dHvA) measurements, extremely heavy electron mass has been observed.<sup>18</sup> These results may indicate the instability of the electronic state in  $\text{PrFe}_4\text{P}_{12}$ .

In this way,  $\text{PrFe}_4\text{P}_{12}$  exhibits various magnetic and transport properties. Especially, the character and the origin of such behaviors are not still clear. Thus, we have performed ultrasonic measurements to elucidate the magnetic properties due to  $4f$  electron nature around  $T_N$  including CEF effect

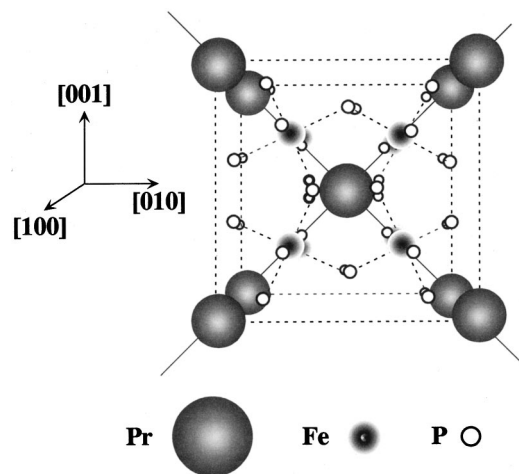


FIG. 1. Crystal structure of  $\text{PrFe}_4\text{P}_{12}$  which has the isostructural cubic belonging to the space group  $T_h^5 - Im\bar{3}$ , which is characterized by the lack of fourfold symmetry along  $\langle 100 \rangle$  direction.

and the elastic properties accompanying them. In this paper, we will report the anomalous behavior in the elastic constants on  $\text{PrFe}_4\text{P}_{12}$  in magnetic fields.

## II. EXPERIMENT

Single crystals of  $\text{PrFe}_4\text{P}_{12}$  were grown by the tin-flux method. The evaluation of sample quality by residual resistivity ratio (RRR) was difficult in this system due to a large jump in its resistivity at  $T_N$ . However, high quality of the sample is assured by the fact that dHvA signal was observed. Each specimen used for the present ultrasonic measurement was cut into a rectangular shape with two axes along the  $\langle 001 \rangle$  and  $\langle 110 \rangle$  directions. The specimen used in our study has a size of  $2.2 \times 2.3 \times 2.8 \text{ mm}^3$  with the crystallographic  $\langle 100 \rangle$  axis directed along the largest dimension. This specimen was cut from the same ingot used in Refs. 3 and 17. The sample was polished by polishing papers.

The sound velocity was measured by an ultrasonic apparatus based on a phase comparison method at the temperatures down to 1.5 K in the magnetic field up to 8 T. Plates of quartz and  $\text{LiNbO}_3$  were used for the piezoelectric transducers. The fundamental resonance frequency of quartz and  $\text{LiNbO}_3$  transducers is 10–30 MHz. The transducers were glued on the parallel planes of the sample by an elastic polymer Thiokol. The absolute value of the sound velocity was obtained by measuring the delay time between the ultrasonic echo signals with an accuracy of a few percent. The elastic constant was calculated as  $C = \rho v^2$  by using the sound velocity  $v$  and the density  $\rho$  of the crystal. The lattice constants of  $\text{PrFe}_4\text{P}_{12}$  at room temperature ( $a = 7.8053 \text{ \AA}$ ) (Ref. 17) were used for the estimation of its density ( $\rho = 5.1417 \text{ g/cm}^3$ ).

## III. EXPERIMENTAL RESULTS

We have measured the longitudinal as well as transverse ultrasonic velocity. Figure 2 shows the temperature dependence of the elastic constants  $C_{11}$ ,  $(C_{11} - C_{12})/2$ , and  $C_{44}$  in  $\text{PrFe}_4\text{P}_{12}$ . We used 10 MHz for the measurement of  $C_{11}$ , and 18 MHz for  $(C_{11} - C_{12})/2$  and  $C_{44}$ . They increase monotonously with decreasing temperature. The constants  $C_{11}$ ,  $(C_{11} - C_{12})/2$  show maximum around 20 and 30 K, respectively, and then a slight softening is found in  $C_{11}$  and  $(C_{11} - C_{12})/2$  below these temperatures. They show an abrupt increase below  $T_N = 6.4 \text{ K}$ . On the other hand,  $C_{44}$  increases monotonously with decreasing temperature above  $T_N$ . No softening has been observed in zero fields. The absolute values of each elastic constants and calculated bulk modulus  $C_B = (C_{11} + 2C_{12})/3$  and Poisson ratio  $\gamma = C_{12}/(C_{11} + C_{12})$  from  $C_{11}$  and  $(C_{11} - C_{12})/2$  at both 77 and 4.2 K are listed in Table I.

At first, we look at temperature dependence of  $C_{11}$  around  $T_N$  under the magnetic fields along  $\langle 001 \rangle$  axis, as shown in Fig. 3. In the magnetic fields below 2 T,  $C_{11}$  shows a dip structure at a certain temperature, which corresponds to the transition. It becomes larger with the increase of magnetic field. Then the dip becomes smaller as the increasing magnetic field crosses 2 T. Simultaneously, the transition tem-

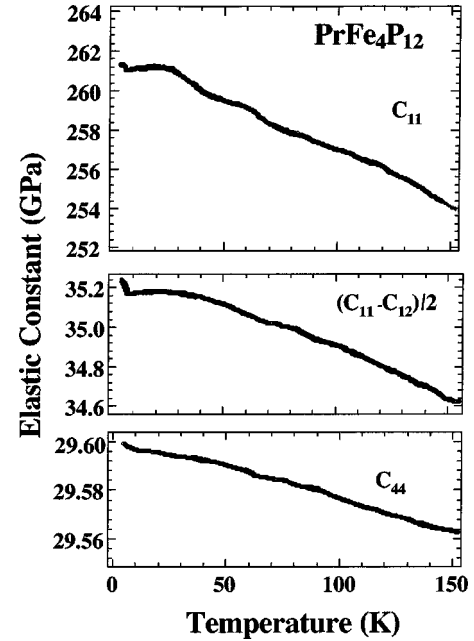


FIG. 2. Temperature dependence of the elastic constants  $C_{11}$ ,  $(C_{11} - C_{12})/2$ , and  $C_{44}$  in  $\text{PrFe}_4\text{P}_{12}$  in zero field.

perature decreases with increasing fields. Above 3 T, the transition is a low-temperature one, below 4.2 K, and the dip disappears. The largest anomaly was observed in the fields of 2 T at 5 K. A minimum structure appears above 4 T, as indicated by arrows in Fig. 3. It shifts to higher temperature with increasing magnetic fields. Figure 4 shows the temperature dependence of  $C_{44}$  around  $T_N$  under the magnetic fields along  $\langle 001 \rangle$  axis. At zero fields  $C_{44}$  increases slightly with decreasing temperature and increases abruptly below  $T_N$ . A small dip was observed above 1 T. In contrast to  $C_{11}$ , however, a huge dip was not observed in  $C_{44}$ . Two distinct anomalies can be observed at 2 T. At this moment, it is not clear whether this is intrinsic or not.

Figure 5 shows the field dependence of  $C_{11}$  at several temperatures around  $T_N$ . At 10 K the elastic constant shows no remarkable magnetic field dependence. With a decreasing temperature, however, a clear dip appears gradually and shifts to low magnetic fields, as indicated by arrows in Fig. 5. This dip corresponds to the observed one in the temperature scan in Fig. 3. The dip grows toward 2 T at 5 K. This experimental result accords with the fact observed in the

TABLE I. The absolute values of each elastic constants and estimated bulk modulus  $C_B$ , Poisson ratio  $\gamma$  at 4.2 and 77 K.

Mode	Elastic constants	
	at 4.2 K	at 77 K
$C_{11}$	261 GPa	258 GPa
$(C_{11} - C_{12})/2$	35.16 GPa	34.98 GPa
$C_{44}$	29.60 GPa	29.58 GPa
$C_B = (C_{11} + 2C_{12})/3$	214.12 GPa	211.36 GPa
$\gamma = C_{12}/(C_{11} + C_{12})$	0.4222	0.4216

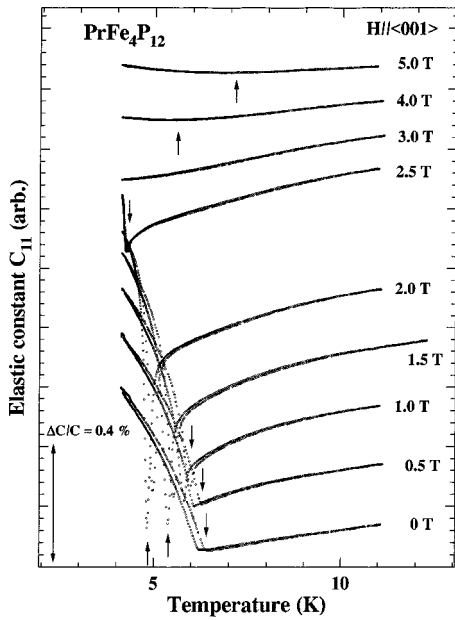


FIG. 3. Temperature dependence of  $C_{11}$  in  $\text{PrFe}_4\text{P}_{12}$  around  $T_N$  under the magnetic fields along  $\langle 001 \rangle$  axis in arbitrary units. Arrows indicate the magnetic transition temperature  $T_N$ .

temperature dependence. In lower temperature below 4.1 K, this dip splits into two and an additional elastic anomaly appears. The lower transition field shifts to lower side, while the higher one shifts to higher side. The higher field transition is consistent with the former results of the magnetization measurement. The lower field transition is observed in this study.

From these experimental results one can draw the phase

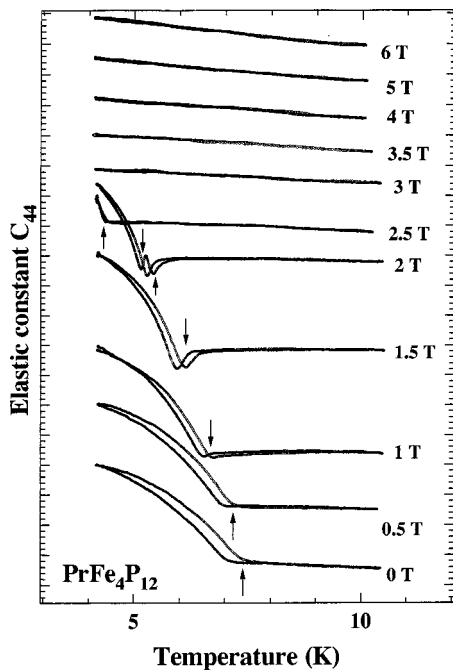


FIG. 4. Temperature dependence of  $C_{44}$  in  $\text{PrFe}_4\text{P}_{12}$  around  $T_N$  under the magnetic fields along  $\langle 001 \rangle$  axis in arbitrary units. Arrows indicate the magnetic transition temperature  $T_N$ .

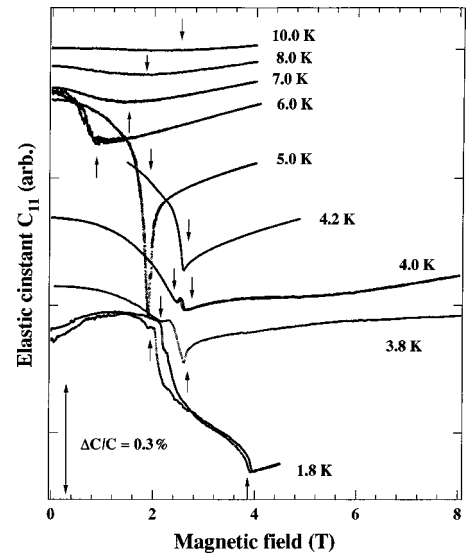


FIG. 5. Magnetic field dependence of  $C_{11}$  in  $\text{PrFe}_4\text{P}_{12}$  at constant temperatures in arbitrary units. Arrows indicate the phase transition points.

diagram as shown in Fig. 6. The darkness of the marks represents the largeness of the elastic constant anomalies. The boundary indicated by a solid line is consistent with the results obtained from magnetization and specific heat.<sup>1,3</sup> It is suggested that this boundary comes from the magnetic origin.<sup>25</sup> The new boundary observed as an elastic anomaly in Fig. 5 goes up to the higher field side with a positive

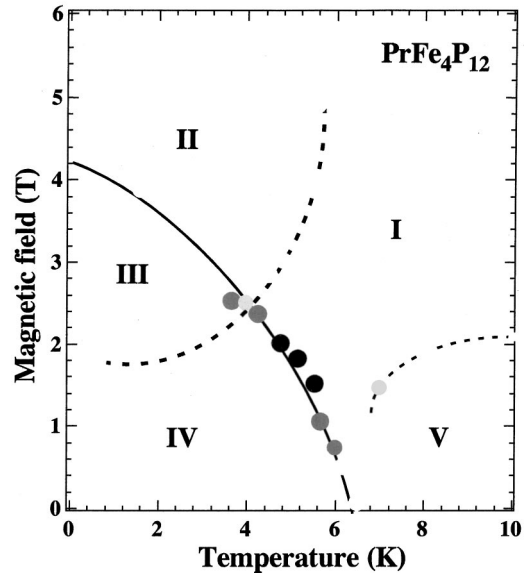


FIG. 6. Phase diagram of  $\text{PrFe}_4\text{P}_{12}$  under the magnetic fields along  $\langle 001 \rangle$  axis. Closed circles are the phase transition points obtained from  $C_{11}$ . The darkness of the marks represent the sharpness of the elastic constant dips. Under the assumption that the transition at 6.4 K would be due to the magnetic ordering, our proposed model is following: I is the paramagnetic phase ( $\Gamma_3$ ), II is the induced ferromagnetic+antiferro quadrupolar phase, III is the antiferromagnetic phase+antiferro quadrupolar phase, IV is the antiferromagnetic phase, and V is considered to be the paramagnetic phase ( $\Gamma_3+\Gamma_4$ ).

curvature in higher temperature. This boundary is obvious below 5 K. It becomes gradually smaller and obscure above 5 K. It should be noted that the points around 2 T and 5 K have huge dips. This area is considered to be a kind of critical point in this phase diagram. Furthermore, one could draw a boundary above  $T_N$ , from the shallow anomaly in  $C_{11}$ . This lies around 2 T and is mostly independent of temperature. This boundary is also obscure.

#### IV. ANALYSIS AND DISCUSSION

First, we discuss the CEF splitting of the  $4f$  level of  $\text{Pr}^{3+}$  in  $\text{PrFe}_4\text{P}_{12}$ . The Hund's ground state of multiplet  $^3H_4$  in  $4f^2$  configuration of  $\text{Pr}^{3+}$  ion is  $J=4$ , which splits into  $\Gamma_1$  singlet,  $\Gamma_4$  triplet,  $\Gamma_3$  doublet, and  $\Gamma_5$  triplet under the cubic CEF.<sup>19,20</sup> There are two terms in the CEF Hamiltonian as  $O_4^0 + 5O_4^4$  and  $O_6^0 - 21O_6^4$  for the site symmetry  $O_h$  and  $T_d$ . Because  $\text{Pr}^{3+}$  ion in  $\text{PrFe}_4\text{P}_{12}$  is in the site symmetry  $T_b$ , the CEF Hamiltonian has the additional terms of  $B'_6(O_2^6 - O_6^6)$ , where  $B'_6$  is the proportional coefficient. This causes the slight change in the  $4f$  level splitting. The degeneracy of the above state multiplets is not affected by introducing the additional term. Especially, the relative energy scheme of  $\Gamma_1$  and  $\Gamma_3$  is the same, but those of  $\Gamma_4$  and  $\Gamma_5$  are dominated by the value of  $B'_6$ . This may bring a new feature in the CEF splitting that has not been expected for  $O_h$  and  $T_d$  systems.<sup>41</sup>

Previous reports on specific-heat measurement of  $\text{PrFe}_4\text{P}_{12}$  stated that the magnetic entropy reaches  $R \ln 2$  at nearly 5.5 K and  $R \ln 3$  at nearly 7 K.<sup>1</sup> This implies the ground state to be  $\Gamma_3$  doublet,  $\Gamma_4$  or  $\Gamma_5$  triplets.

The ordered state below 6.4 K in  $\text{PrFe}_4\text{P}_{12}$  has been considered to be antiferromagnetic so far, although the magnetic structure has not been determined. It is supported by the magnetic susceptibility and specific heat measurements.  $T^3$  temperature dependence of the specific heat was reported in the ordered state, which has been considered to be due to antiferromagnetic spin wave.<sup>1</sup> Magnetic susceptibility exhibits antiferromagneticlike cusp anomaly at 6.4 K.<sup>1</sup>

The softening of  $C_{11}$  and  $(C_{11} - C_{12})/2$  strongly suggests the ground state of Pr ion to be  $\Gamma_3$  symmetry. If  $\Gamma_3$  is the ground state,  $\Gamma_4$  or  $\Gamma_5$  as an excited state will be needed, since  $\Gamma_3$  has no magnetic moment. Very recently, magnetic structure has been investigated by neutron scattering. However, no Bragg peak has been found at zero fields.<sup>21</sup> It is considered that the kind of the ordered state is still not clear.

Nevertheless, the energy scheme that  $\Gamma_3$  is the ground state and  $\Gamma_4$  the first excited state would be preferable to explain the elastic and magnetic properties of this system. Susceptibility and magnetization measurements imply the existence of the level having the magnetic moment to be the ground state or located near the ground state. Because of no softening in  $C_{44}$ , this work suggests that  $\Gamma_5$  is a state with a large excitation energy, for  $\Gamma_5$  triplet causes the softening in  $C_{44}$ . Otherwise, according to the Lea, Leask, and Wolf (LLW) calculation,  $\Gamma_5$  must locate at a much higher energy than the  $\Gamma_4$  in the cubic symmetry case.<sup>20</sup>

If the ordered state really comes from the magnetic origin,  $\Gamma_3$ - $\Gamma_4$  scheme brings the magnetic ordering by the same

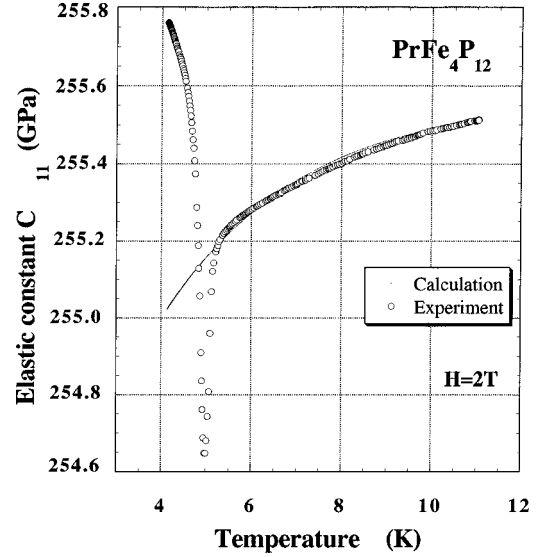


FIG. 7. Temperature dependence of the elastic constant of  $C_{11}$  in  $\text{PrFe}_4\text{P}_{12}$  around  $T_N$  under the magnetic fields of 2 T along  $\langle 001 \rangle$  axis. Dotted line means a theoretical fit in terms of Eq. (4.2) in text. Here, we obtain the parameter  $g'_{T_3} = -5.2$  K < 0.

story as a singlet-ground-state problem,<sup>22</sup> where the interaction between thermally induced magnetic moments brings about the magnetic order. If this is so, the first excitation energy must be of the same order in magnitude as the ordering temperature and the magnetic interaction.

$\Gamma_3$  ground state may bring a quadrupolar ordering or a charge ordering transition. Actually, there is antiferro quadrupolar interaction as mentioned below. We analyze the temperature dependence of  $C_{11}$  at 2 T with the following formula (5.1):<sup>23-26</sup>

$$C_{\Gamma}(T) = C_{\Gamma}^0(T) - \frac{Ng_{\Gamma}^2\chi_{\Gamma}^S(T)}{1 - g'_{\Gamma}\chi_{\Gamma}^S(T)}. \quad (4.1)$$

Here  $N$  is the number of Pr ions in unit volume and  $C_{\Gamma}^0(T)$  is the lattice part without quadrupolar-strain coupling  $g_{\Gamma}$ .  $\chi_{\Gamma}^S(T)$  denotes the quadrupolar susceptibility for the  $4f$  electronic state in the CEF potential.  $g'_{\Gamma}$  is the quadrupolar interaction between  $\text{Pr}^{3+}$  ions. For  $\text{PrFe}_4\text{P}_{12}$ ,  $\Gamma_3$  doublet is the ground state. Therefore, the Curie term of the  $\Gamma_3$  doublet is dominant in the quadrupolar susceptibility at low temperatures. If  $T_3$  doublet is dominant, and then the formula (5.1) is rewritten by using  $\chi_{\Gamma} = A_{\Gamma}/T$ , where  $A_{\Gamma}$  is the Curie constant of the quadrupolar susceptibility:

$$C_{\Gamma}(T) = C_{\Gamma}^0(T) - \frac{Ng^2A_{\Gamma}}{T - g'A_{\Gamma}}. \quad (4.2)$$

As shown in Fig. 7, the fitting curve gives us the parameter of  $T_0 = g'A_{\Gamma} = -5.2$  K. This result implies that the antiferro quadrupolar interaction among quadrupolar moments with  $\Gamma_3$  symmetry develops at low temperatures in magnetic fields.

The obtained value of  $T_0$  is so similar to  $T_N$ , that it would be interesting to see whether the antiferromagnetic quadrupolar interaction plays a relevant role in this system. It is



difficult to conclude at this moment that the transition at 6.4 K originates from a quadrupolar ordering, because the softening is not large enough compared to typical materials in which those orderings occur. Many other systems that undergo quadrupolar ordering, such as TmTe (Ref. 27) or TmAu<sub>2</sub>,<sup>28</sup> show no remarkable anomaly in the susceptibility and a large elastic softening at the transition temperature. In this sense, the transition of PrFe<sub>4</sub>P<sub>12</sub> would be most likely of magnetic origin.

The effect of quadrupole appears in the magnetization process. It is mostly isotropic in the ordered state. This is due to lack of uniaxial or biaxial anisotropy, which is mainly coming from  $\Gamma_5$  level in case of PrFe<sub>4</sub>P<sub>12</sub>. Therefore, the isotropic behavior in the magnetization process is consistent with our conclusion that  $\Gamma_5$  has a high excitation energy, which is deduced from our elastic measurement. But it shows the pronounced anisotropy above  $H_t$  of nearly 3 T in the induced ferromagnetic state.  $H_t$  is itself anisotropic. Similar behavior is seen in NdB<sub>6</sub>.<sup>30</sup> Generally speaking, these phenomena are inconsistent with each other and can be explained by taking the role of quadrupolar interaction into account. If a quadrupole moment is induced by the magnetic field and the quadrupolar ordering occurs, it would introduce the anisotropy. This consideration leads the phase IV to be due to an antiferro quadrupolar ordering. The fact that the magnetization shows no remarkable anomaly at this field is consistent with our consideration.<sup>13</sup>

PrFe<sub>4</sub>P<sub>12</sub> shows a huge value of  $C_m/T$ , where  $C_m$  means the magnetic contribution to the specific heat.<sup>3</sup> Especially at 6 T, in which the ordering has already been destroyed by magnetic field<sup>31,32</sup> it reaches nearly 1.4 J/K<sup>2</sup> mol. Furthermore, in the recent dHvA measurement of PrFe<sub>4</sub>P<sub>12</sub>, very heavy electron masses of about eighty times compared to a free electron have been reported by Sugawara *et al.*<sup>18</sup> The resistivity also shows a Kondo-like logarithmic temperature dependence, with a minimum near 200 K, with decreasing temperatures.<sup>17</sup> The origin of this typical heavy-fermion-like behavior is not clear. But these results let us imagine Kondo effect to have some responsibility for the observed phenomena in PrFe<sub>4</sub>P<sub>12</sub>. Cox and Zawadowski discussed the quadrupolar Kondo effect to explain the phenomena observed in the U compounds.<sup>33-37</sup> The wave function of  $5f$  state in U compound has the more extended wave function than  $4f$  one in Pr compound. However, this model can be applied to the case of Pr compounds, because they both have the same configuration of  $f$  electrons. Heavy effective mass of conduction band would be caused by this mechanism.

Let us come back to the magnetic phase diagram determined by this study. The solid line in Fig. 6, which is determined by  $C_{11}$ , is the boundary due to the magnetic order reported before.<sup>1,3,29</sup> Another boundary was found in this

study, which goes up to higher-field side with a curvature in higher temperature. In addition, the boundary lies at fields of 2 T, which is mostly independent of temperature above  $T_N$ . As experimental facts, the field of  $\Delta = 2$  T has a particular meaning in this system. The value of this field corresponds to 1 K. If the logarithmic temperature dependence in the resistivity comes from Kondo effect, the Kondo temperature is evaluated to be nearly 30 K from the resistivity midpoint reported before.<sup>17</sup> There is some relation between the characteristic temperature in PrFe<sub>4</sub>P<sub>12</sub>:

$$T_K \gg T_N > \Delta/k_B. \quad (4.3)$$

As already mentioned, this system is a possible candidate for the system showing the quadrupolar Kondo effect. If it is really so, both magnetic and quadrupolar moments will be shrunk by the Kondo screening.<sup>38-40</sup> This effect makes the elastic softening of  $C_{11}$  and  $(C_{11} - C_{12})/2$  weaker. The origin of  $\Delta$  is an open problem.

## V. CONCLUSIONS

In this paper we have presented the elastic properties of PrFe<sub>4</sub>P<sub>12</sub>. We have measured the temperature and field dependence of elastic constants  $C_{11}$ ,  $(C_{11} - C_{12})/2$ , and  $C_{44}$  and determined the phase diagram. From our experiments we obtain the following conclusions. The orbital freedom of the  $\Gamma_3$  doublet ground state is responsible for the elastic softening of  $C_{11}$  and  $(C_{11} - C_{12})/2$  above  $T_N$ . The first excited state is considered to be  $\Gamma_4$ . In this scheme, magnetic ordering can occur in the frame of singlet ground-state story. However, the properties of the phase below 6.4 K are not clear. We found an anomaly in the elastic constant, which would indicate the existence of unknown phase. By analyzing the temperature dependence of  $C_{11}$ , we proposed that the antiferro quadrupolar ordering with  $\Gamma_3$  symmetry would occur induced by magnetic fields. It is indicated, from this work, that PrFe<sub>4</sub>P<sub>12</sub> is a possible candidate for a two-channel quadrupolar Kondo effect. For a further and quantitative discussion, it is necessary to make clear the magnetic structure and the explicit total level scheme of multiplets of Pr ion in PrFe<sub>4</sub>P<sub>12</sub>.

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