EVIDENCE OF NON-KRAMERS DOUBLET GROUND STATE IN $PrFe_4P_{12}$*

Y. Nakanishi, M. Yoshizawa

Department of Materials Science and Engineering, Iwate University
Morioka 020-8551, Japan

T. Yamaguchi, H. Hazama, Y. Nemoto, T. Goto

Graduate School of Science and Technology, Niigata University
Niigata 950-2181, Japan

T.D. Matsuda, H. Sugawara and H. Sato

Department of Physics, Tokyo Metropolitan University
Hachioji 192-0397, Japan

(Received July 10, 2002)

The elastic constant $(C_{11} - C_{12})/2$ of skutterudite compound $PrFe_4P_{12}$ has been studied in a magnetic field. A remarkable softening towards low temperatures appeared only in applied magnetic field. Its magnitude reaches a value of about 10 % in magnetic field of 8 T. The results confirm that the non-Kramers doublet ground state of the Pr ion is realized in $PrFe_4P_{12}$ and indicate that the magnetic field helps to stabilize the non-Kramers doublet state.

PACS numbers: 71.27.+a, 71.70.Ch, 75.30.Mb

Since the discovery of the extraordinary heavy fermion (HF) state in skutterudite compound $PrFe_4P_{12}$, a mechanism of its formation is one of the most intriguing problems [1]. Recent experimental results of $PrFe_4P_{12}$ indicate that a value of the effective mass ratio reaches about 80. Different from the conventional magnetic Kondo effect seen in Ce- and Yb-based compounds, non-Krammers doublet (magnetic singlet ground state) is realized in Pr and U-based compounds, and it leads to form the heavy quasiparticles, so-called two channel Kondo-effect [2]. So far, $U_xTh_{1-x}Ru_2Si_2$, UBe_{13}, $Y_{1-x}U_xPd_3$ and $PrInAg_2$ are considered to be the candidate com-

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

pound [3-6]. Two channel Kondo-effect was predicted theoretically by Cox *et al.*, and Koga *et al.*, in which Γ_3 non-Krammers doublet plays a crucial role, and Γ_3 should be a ground state of the multiplet split by crystalline electric field (CEF) for the formation of the HF state [2,7]. However, the origin of the HF behavior with non-Krammers doublet has not been clarified yet. Recently, $PrFe_4P_{12}$ has been ascribed to this group. Several interesting physical properties are reported in $PrFe_4P_{12}$ [8-9]. The de Haas–van Alphen effect, specific heat, thermal conductivity and electric resistivity measurements indicate the heavy fermion behavior marked by a large γ-value with logarithmic temperature (T) dependence. The Γ_3 non-Krammers doublet realized as the CEF-ground state of the Pr ion in $PrFe_4P_{12}$ was also proposed by our group [10]. However, observed elastic softening in $(C_{11} - C_{12})/2$ in zero field was much smaller than that seen in conventional rare-earth compounds in which the Γ_3 non-Krammers doublet is realized. The magnetic entropy of $PrFe_4P_{12}$ reaches $R\ln 2$ at 5.2 K and Rln3 at 6.4 K. This is inconsistent with our result; about the Γ_3 non-Krammers doublet ground state. Another feature of $PrFe_4P_{12}$ is a remarkable phase transition occurring at 6.4 K where a clear anomaly is observed in specific heat, electric resistivity, magnetic susceptibility, elastic constant and so on [8-10]. However, a magnetic transition was excluded because no magnetic Bragg peak was observed below 6.4 K [11]. There are some scenarios to explain this transition such as quadrupolar ordering, nesting and so on until now [12]. However, the decisive interpretation has not been found yet. This is still an open problem. In this paper we focus our interest on the nature of the $4f$-ground state of the Pr ion in $PrFe_4P_{12}$ and report the magnetic-field dependence. The phase transition at 6.4 K is not discussed here. We will report on it in a separate paper. We point out that the elastic softening is enhanced and its behavior returns to the conventional one only in applied magnetic field. Specifically, we concentrate on clarifying the physical interpretation of this phenomenon and establish the magnetic phase diagram.

The single crystal of $PrFe_4P_{12}$ was grown by the tin-flux method. The sample with rectangular shape of $2.2 \times 2.3 \times 2.8\,\mathrm{mm}^3$ for the ultrasonic measurement was prepared. In order to observe the ultrasonic pulse echoes with an exponential decay, we polished carefully the surfaces of sample to be parallel. The $LiNbO_3$ transducers for the generation and detection of the sound waves with frequencies 5∼10 MHz were bonded on the surfaces of the sample by an elastic polymer Thiokol. The sound-wave velocity v was detected by an ultrasonic apparatus based on the phase-comparison method. The magnetic field up to 8 T was generated by a superconducting magnet. In the estimation of the elastic constant $C = dv^2$, the mass density $d = 5.14\,\mathrm{g/cm}^3$ derived from the lattice constant $a = 7.80\,\mathrm{\AA}$ of the present sample of $PrFe_4P_{12}$ is used.

Fig. 1(a) shows the temperature dependence of the elastic constant $(C_{11} - C_{12})/2$ in zero field and the magnetic field of 8 T along the $\langle 110 \rangle$ axis. This crystallographic axis is perpendicular to the face where the transducer is bonded. In the magnetic fields, the elastic softening of $(C_{11} - C_{12})/2$ becomes larger and the conventional softening towards low temperatures appears. With the applied magnetic fields, the transition temperature disappears. A magnitude of the softening reaches almost 10 % in the magnetic field of 8 T. Fig. 1(b) shows the magnetic field dependence of $(C_{11} - C_{12})/2$ at the

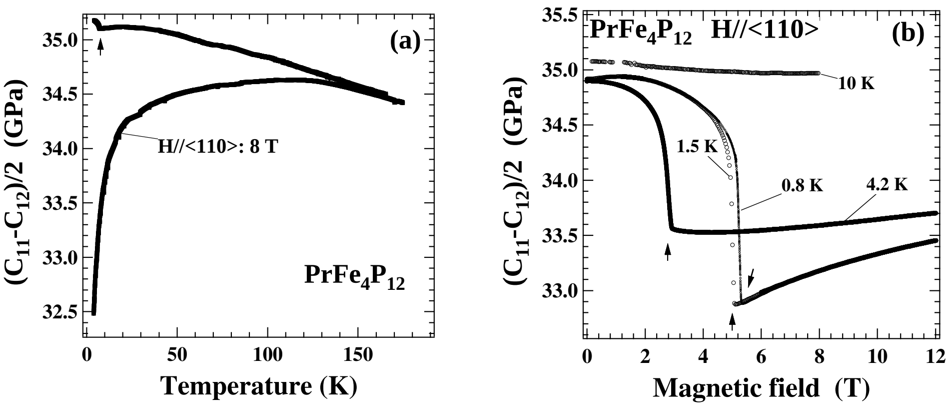

Fig. 1. (a) Temperature dependence of the elastic constant $(C_{11} - C_{12})/2$ in the magnetic fields of 0 T and 8 T along the $\langle 110 \rangle$ axis. (b) the magnetic field dependence of the elastic constant $(C_{11} - C_{12})/2$ at the selected temperatures along the $\langle 110 \rangle$ axis. The transition points are indicated by arrows.

selected temperature. An abrupt decrease is observed on the boundary of the obtained ordered phase. This transition field shifts to lower fields with the increasing temperature. From these results, combined with the previous magnetization measurement [13], the (H-T) phase diagram is derived as shown in Fig. 2. As suggested in the previous papers [10, 14], non-Kramers doublet Γ_3 is most favorable to explain the obtained behavior although the result of the entropy is inconsistent with it. If the non-Kramers doublet Γ_3 is realized as the CEF-ground state of the Pr ion, the elastic softening is expected in $(C_{11} - C_{12})/2$, but not in C_{44}. It is because $(C_{11} - C_{12})/2$ has a Curie term in its strain-susceptibility, while C_{44} does not have it. There is not any other possibility (*i.e.*, only non-Kramers doublet Γ_3) to form the $4f$-level scheme to satisfy the obtained results in a framework of the point charge model.

Next, we comment on a difference of the behavior between the elastic constant C_{11} and $(C_{11} - C_{12})/2$. As we reported in the previous paper [10], their temperature dependences are somewhat different. Under magnetic

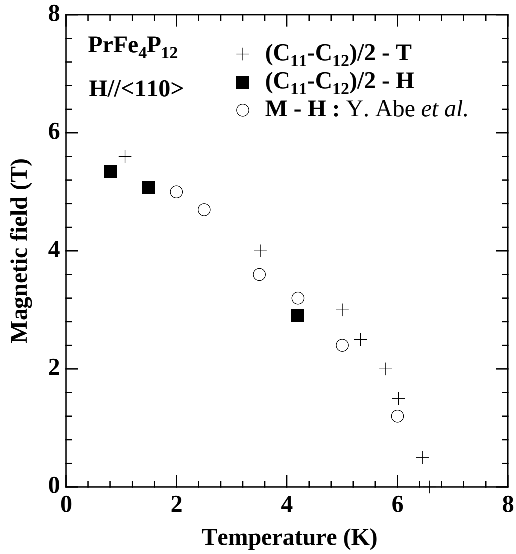

Fig. 2. The $(H–T)$ phase diagram obtained from $(C_{11} - C_{12})/2$ in magnetic fields along the $\langle 110 \rangle$ direction, combined with the magnetization measurement (Ref. [13]).

fields below 2 T, C_{11} shows a dip structure around the transition temperature. It becomes larger by applying magnetic fields similarly to that of $(C_{11} - C_{12})/2$. However, the dip of C_{11} becomes smaller above 2 T. No transition and softening were observed above 3 T in C_{11}. This is likely to be assigned to the difference of the elastic constant. The longitudinal elastic constant C_{11} consists of $(C_{11} - C_{12})/2$ and the bulk modulus C_{B}. In most cases, C_{B} increases monotonically with decreasing temperatures, unless a valence of rare-earth ions changes. The value of C_{11} is much larger than that of $(C_{11} - C_{12})/2$. Thus, we believe that the temperature dependence of C_{11} has a minimum at a certain magnetic field. Furthermore, the different direction of the applying magnetic field affects the transition field and temperature, *i.e.*, the magnetic phase diagram. Actually, the boundary between phase III and IV seen in C_{11} for $H||\langle 100 \rangle$ was not found in $(C_{11} - C_{12})/2$ for $H||\langle 110 \rangle$.

Summarizing, we measured the elastic constant $(C_{11} - C_{12})/2$ of skutterudite compound $PrFe_4P_{12}$ in magnetic field and, on this basis, have constracted its magnetic phase diagram. From experiments we obtain the following conclusions:

(1) A pronounced elastic softening with lowering temperatures was found in $(C_{11} - C_{12})/2$ under the magnetic fields of 5 T. It seems that with applying magnetic fields the non-Kramers doublet Γ_3 became more stable as $4f$-ground state of the Pr ion.

(2) The behavior of $(C_{11} - C_{12})/2$ around the transition temperature in magnetic fields was somewhat different from that of C_{11}. A field-induced phase in C_{11} was not found in $(C_{11} - C_{12})/2$.

The measurements have been carried out in the Cryogenic Division of the Center for Instrumental Analysis, Iwate University. This work was supported in part by the Grant-in-Aid for Scientific Research from the Ministry of Education, Sport, Science and Culture of Japan.

REFERENCES

[1] H. Sugawara *et al.*, *J. Magn. Magn. Matter.* **226-230**, 48 (2001).
[2] D.L. Cox, *Phys. Rev. Lett.* **59**, 1240 (1987).
[3] H. Amitsuka *et al.*, *Physica B* **186**, 337 (1993).
[4] F.G. Aliev *et al.*, *Solid State Commun.* **91**, 775 (1994).
[5] M.B. Maple *et al.*, *J. Low Temp. Phys.* **95**, 225 (1994).
[6] H. Mitamura *et al.*, *Physica B* **281**, 150 (2000).
[7] M. Koga *et al.*, *J. Phys. Soc. Jpn.* **64**, 4345 (1995).
[8] H. Sato *et al.*, *Phys. Rev.* **B63**, 15125 (2000).
[9] T.D. Matsuda *et al.*, *Physica B* **281**, 306 (2000).
[10] Y. Nakanishi *et al.*, *Phys. Rev.* **B63**, 184429 (2001).
[11] L. Keller *et al.*, *J. Alloy. Compd.* **323**, 516 (2001).
[12] Y. Aoki *et al.*, *Phys. Rev.* **B65**, 064446 (2002).
[13] Y. Abe *et al.*, unpublished.
[14] M.S. Torikachvili *et al.*, *Phys. Rev.* **B36**, 8660 (1987).