Quadrupole Order in Clathrate Compound
Pr$_3$Pd$_{20}$Si$_6$

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Abstract. In order to investigate ordered phases revealed at low temperatures in clathrate compound Pr$_3$Pd$_{20}$Si$_6$, we have performed ultrasonic measurements using a single crystal in magnetic fields at low temperatures. Temperature dependence of elastic constant $C_{11}$ and $C_L[1\bar{1}0]= (C_{11} + C_{12} + 2C_{44})/2$ shows the anomalies at about 150 mK in zero field. Magnetic phase diagrams are determined by measuring $C_{11}$ in $H \parallel [001]$ and $C_L[1\bar{1}0]$ in $H \parallel [111]$. The magnetic phase diagrams along the three principal axes indicate a closed loop and a strong magnetic anisotropy. This result suggests that antiferroquadrupole ordering appears at low temperatures in Pr$_3$Pd$_{20}$Si$_6$.

1. Introduction

The ternary rare earth compounds $R_3$Pd$_{20}$X$_6$ ($R$ = rare earth, $X$ = Si or Ge) have received a lot of interest because of a rich variety of phenomena relating to rattling motions of an off-center guest atom in an oversized cage and multipole orderings caused by the spin and orbital degrees of freedom of 4$f$ electron. $R_3$Pd$_{20}$X$_6$ has a cubic Cr$_{23}$C$_6$-type structure with a space group $Fm\bar{3}m$ and 116 atoms consisting of 12 $R$ atoms, 80 Pd atoms and 24 $X$ atoms in a unit cell [1]. The $R$ atoms occupy two non-equivalent crystallographic sites, which are 4a site with $O_h$ symmetry and 8c site with $T_d$ symmetry. The $R$ atoms at 4a sites located in a cage of 12 Pd atoms and 6 Ge atoms form a face-centered cubic lattice. The $R$ atoms at 8c sites located in a cage of 16 Pd atoms form a simple cubic lattice.

The Ce-based compound Ce$_3$Pd$_{20}$Ge$_6$ reveals a $\Gamma_3$-type ferroquadrupole order accompanied by a tetragonal distortion below $T_Q = 1.3$ K at 8c site and successively an antiferromagnetic order below $T_N = 0.8$ K at 4a site [2, 3, 4]. Crystalline electric field ground states are $\Gamma_8$ quartets for both 4a and 8c sites and excited $\Gamma_7$ doublets are located at 5.2 meV for 4a site and 4.0 meV for 8c site in Ce$_3$Pd$_{20}$Ge$_6$ [5]. Elastic constant $C_{44}$ of Ce$_3$Pd$_{20}$Ge$_6$ shows a shoulder-like anomaly accompanied by frequency dependence and ultrasonic attenuation around 10 K. This is caused by a rattling motion of the $R$ ion at 4a site in the oversized cage [4]. This behavior is commonly observed in a series of $R_3$Pd$_{20}$Ge$_6$ for $R$ = La, Ce, Pr, and Nd [4, 6, 7].
Ce$_3$Pd$_{20}$Si$_6$ known as a heavy fermion compound with a very large specific heat coefficient $\gamma = 8 J/mol \cdot K^2$ exhibits field-induced antiferroquadrupole (AFQ) ordered phase II and phase III characterized by either magnetic dipole or magnetic octupole [8, 9]. The AFQ order occurs for 8c site because the Ce ion for 8c site has a $\Gamma_8$ characterized by either magnetic dipole or magnetic octupole [8, 9]. The AFQ order occurs for 8c site because the Ce ion for 8c site has a $\Gamma_8$ quartet ground state and for 4a site has a $\Gamma_7$ doublet ground state [9, 10]. The AFQ phase II shows a large magnetic anisotropy of critical fields $H_{C[001]} = 4 T$ in $H \parallel [001]$, $H_{C[110]} = 10.3 T$ in $H \parallel [110]$, and $H_{C[111]} \sim 14 T$ in $H \parallel [111]$. This anisotropic behavior is similar to that of $\Gamma_5$-type AFQ phase II of CeB$_6$ and Ce$_{0.5}$La$_{0.5}$B$_6$ [11, 12]. No elastic anomaly of $C_{44}$ due to the rattling motion has been observed in Ce$_3$Pd$_{20}$Si$_6$ [9].

In this paper we study the Pr-based compound Pr$_3$Pd$_{20}$Si$_6$ at low temperatures. In Pr$_3$Pd$_{20}$Si$_6$ ultrasonic and neutron scattering experiments have suggested that the ground state of Pr ion at 8c site is a $\Gamma_3$ doublet and one for 4a site is $\Gamma_5$ triplet [13, 14]. As is the case with Ce$_3$Pd$_{20}$Si$_6$, no anomaly caused by the rattling motion has been observed in the $C_{44}$ of Pr$_3$Pd$_{20}$Si$_6$. Magnetic susceptibility of polycrystalline sample of Pr$_3$Pd$_{20}$Si$_6$ has shown a kink around 50 mK [1]. Magnetic phase diagram in fields along the [110] direction has been determined by the ultrasonic measurements using a single crystal [13]. The elastic constant $(C_{11} - C_{12})/2$ showed an anomaly at about 100 mK, which is associated with the kink of magnetic susceptibility. Furthermore, minimum points of $(C_{11} - C_{12})/2$, which are probably brought about by the AFQ phase transition, were found at about 150 mK in zero field and below 6 T. We show the results of low-temperature ultrasonic measurements and the magnetic phase diagrams in fields along the [001] and [111] direction in order to examine the ordered phases in Pr$_3$Pd$_{20}$Si$_6$.

2. Experiment

We prepared a single crystal of Pr$_3$Pd$_{20}$Si$_6$ for the present ultrasonic measurements. The crystal was grown by a floating zone method using an image furnace equipped with double elliptical mirrors. The ultrasonic velocity $v$ of the sample was measured by an ultrasonic pulse-echo method. The elastic constants $C$ of the sample were estimated by $C = \rho v^2$ with the mass density $\rho = 9.81$ g/cm$^3$. In the present experiments, the ultrasonic wave was generated and detected by the piezoelectric LiNbO$_3$ plates. For the low-temperature ultrasonic measurements, we used a $^3$He-$^4$He dilution refrigerator down to 20 mK with a superconducting magnet (Oxford Instruments) in fields up to 14 T.

3. Results and discussion

In Fig. 1 we show the temperature dependence of the elastic constant $C_{11}$ of Pr$_3$Pd$_{20}$Si$_6$ below 500 mK in fields along the [001] direction. The $C_{11}$ shows a minimum point indicating the phase transition at about 140 mK in zero field. With increasing field, the minimum point shifts to lower temperatures up to 8 T after shifting higher temperatures up to 3 T. No sign of the phase transition has been observed above 10 T.

Figure 2 shows the temperature dependence of the elastic constant $C_{L[110]}$ of Pr$_3$Pd$_{20}$Si$_6$ below 600 mK in fields along the [111] direction. We have successfully observed two elastic anomalies indicated by down arrows in zero field. The temperature dependence of $C_{L[110]}$ in each field up to 2 T, however, shows an anomaly only. The anomaly at about 110 mK in zero field is related to the kink of magnetic susceptibility [1, 13]. A minimum of $C_{L[110]}$ is found in 4 T, while there is no elastic anomaly in 3 T.

Figure 3 shows the magnetic phase diagrams of Pr$_3$Pd$_{20}$Si$_6$ in applied fields parallel to the [001], [110], and [111] directions. The magnetic phase diagram in fields along the [110] direction has been determined from the previous ultrasonic experiments in Ref. 13. The solid lines indicate the phase boundary. The phase boundaries in each field show closed loops and a strong magnetic anisotropy of critical fields $H_{C'[001]} \sim 8 T$ in $H \parallel [001]$, $H_{C'[110]} \sim 5 T$ in $H \parallel [110]$. 


Figure 1. Temperature dependence of the elastic constant $C_{11}$ of Pr$_3$Pd$_{20}$Si$_6$ in applied magnetic fields along the [001] direction parallel to the propagation direction of the longitudinal ultrasonic wave.

Figure 2. Temperature dependence of the elastic constant $C_{L[1\bar{1}0]} = (C_{11} + C_{12} + 2C_{44})/2$ of Pr$_3$Pd$_{20}$Si$_6$ measured by the longitudinal ultrasonic wave propagating along the [110] direction in applied magnetic fields along the [111] direction.

and $H_C[111] \sim 3$ T in $H \parallel [111]$. This anisotropic behavior in magnetic phase diagrams of Pr$_3$Pd$_{20}$Si$_6$ indicates the AFQ ordering. The quadrupole order occurs at 8c site in Ce$_3$Pd$_{20}$Ge$_6$ and Ce$_3$Pd$_{20}$Si$_6$ [3, 4, 9]. Therefore, this ordered phase in Pr$_3$Pd$_{20}$Si$_6$ is probably the $\Gamma_3$-type AFQ phase due to the $\Gamma_3$ doublet ground state at 8c site. It should be noted that the $\Gamma_3$ doublet has two $\Gamma_3$-type quadrupoles $O_u$, $O_v$, and $\Gamma_2$-type octupole $T_{xyz}$. The elastic anomalies at about 100 mK and the kink of magnetic susceptibility of Pr$_3$Pd$_{20}$Si$_6$ may be caused by a magnetic phase transition at 4a site because of the $\Gamma_5$ triplet ground state at 4a site, which possesses three magnetic dipole and five quadrupole.

4. Conclusion
We have successfully observed the elastic anomalies of $C_{11}$ and $C_{L[1\bar{1}0]}$ in Pr$_3$Pd$_{20}$Si$_6$ below 300 mK in fields along the [001] and [111] axes up to 10 T, which arise from two kinds of phase transitions. The magnetic phase diagrams of Pr$_3$Pd$_{20}$Si$_6$ in $H \parallel [001]$, [111] were determined by these results. The phase exhibiting the strong magnetic anisotropy $H_C[001] > H_C[1\bar{1}0] > H_C[111]$ is presumably the $\Gamma_3$-type AFQ ordered phase appearing at 8c site. In another phase existing below 100 mK, the magnetic order occurs perhaps at 4a site. To elucidate the order parameters and further properties of these phases in Pr$_3$Pd$_{20}$Si$_6$, magnetization, specific heat, neutron scattering measurements using single crystals at low temperatures are required.
Figure 3. Magnetic phase diagrams of $\text{Pr}_3\text{Pd}_{20}\text{Si}_6$ in applied magnetic fields along the [001], [110], and [111] directions. The data in fields along the [110] direction are cited from Ref. 13.

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