Quadrupole Ordering and Rattling in Clathrate Compound \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \)

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Abstract. We have studied quadrupole ordering and rattling in clathrate compound \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) using ultrasonic measurements. The softening were observed in temperature dependence of elastic constants \( C_{11} \), \( (C_{11} - C_{12})/2 \) and \( C_{44} \). The \( C_{11} \) and \( (C_{11} - C_{12})/2 \) show minimums at 250 mK indicating a transition point to an antiferroquadrupole ordered phase due to a \( \Gamma_3 \) doublet ground state at 8c site. Furthermore, the \( C_{11} \), \( (C_{11} - C_{12})/2 \) and \( C_{44} \) exhibit discontinuitive anomalies at 60 mK revealing a ferroquadrupole ordering due to a \( \Gamma_5 \) triplet ground state at 4a site. Two distinctive ultrasonic dispersions caused by thermally activated \( \Gamma_5 \)-type rattling were observed in \( C_{44} \) around 15 K and 25 K.

1. Introduction

The clathrate compounds \( \text{R}_3\text{Pd}_{20}\text{X}_6 \) (\( \text{R} = \text{rare-earth}, \ \text{X} = \text{Si or Ge} \)) have been intensively investigated because of various interesting properties consisting of quadrupole ordering caused by orbital degrees of freedom of 4f electrons and rattling motions of a guest rare-earth atom in an oversized cage. \( \text{R}_3\text{Pd}_{20}\text{X}_6 \) has a cubic \( \text{C}_{23}\text{C}_6 \)-type structure with a space group \( \text{Fm} \overline{3}m \). There are 116 atoms consisting of 12 \( \text{R} \) atoms, 80 Pd atoms and 24 \( \text{X} \) atoms in a conventional unit cell. The \( \text{R} \) atoms occupy two different crystallographic sites of 4a site with \( \text{O}_h \) symmetry and 8c site with \( \text{T}_d \) symmetry [1]. The Ce-based compound \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) with \( \Gamma_8 \) ground states at 4a and 8c sites shows a \( \text{O}_4 \)-type ferroquadrupole (FQ) ordering accompanied by a spontaneous tetragonal distortion at \( T_Q = 1.25 \) K and an antiferromagnetic ordering at \( T_N = 0.75 \) K [2, 3]. The elastic constant \( C_{44} \) of \( \text{Ce}_3\text{Pd}_{20}\text{Ge}_6 \) shows a frequency dependent shoulder-like anomaly around 10 K accompanying considerable ultrasonic attenuation, which is caused by the thermally activated rattling motion of the guest atoms of the 4a site [3, 4]. Similarly, we found ultrasonic dispersion in the series of \( \text{R}_3\text{Pd}_{20}\text{Ge}_6 \) (\( \text{R} = \text{La, Pr, Nd} \)) [4, 5]. In the isomorphic compounds of \( \text{Ce}_3\text{Pd}_{20}\text{Si}_6 \) and \( \text{Pr}_3\text{Pd}_{20}\text{Si}_6 \), however, no elastic anomaly of \( C_{44} \) associated with the rattling was observed. These compounds show antiferroquadrupole (AFQ) ordering with appreciable magnetic anisotropy at very low temperatures [6, 7].

Inelastic neutron scatterings and magnetization experiments on \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) revealed that the ground state of the \( \text{Pr}^{3+} \) ion at the 8c site is a \( \Gamma_3 \) doublet and the one at 4a site is \( \Gamma_5 \) triplet in the crystalline electric fields (CEF) [8]. Magnetic susceptibility of \( \text{Pr}_3\text{Pd}_{20}\text{Ge}_6 \) has no anomaly.
down to 80 mK. Therefore, Pr$_3$Pd$_{20}$Ge$_6$ is expected to undergo quadrupole ordering free from magnetic moments at low temperatures. In this paper, we present the study of quadrupole ordering and rattling in Pr$_3$Pd$_{20}$Ge$_6$ by using ultrasonic method down to 20 mK.

2. Experiment

We prepared single crystal of Pr$_3$Pd$_{20}$Ge$_6$ grown by a floating zone method. The specimen for the ultrasonic measurements was cut to $3.64 \times 3.05 \times 2.80$ mm$^3$ in dimension. Ultrasonic waves were generated and detected by piezoelectric LiNbO$_3$ transducers bonded on parallel surfaces of the sample. The change of ultrasound velocity $v$ was measured by using a phase difference method and the attenuation of the ultrasonic echo signals were measured by a digital storage oscilloscope. The elastic constant $C = \rho v^2$ was determined by the ultrasound velocity $v$ and the mass density $\rho = 10.29$ g/cm$^3$ for Pr$_3$Pd$_{20}$Ge$_6$ with a lattice parameter $a = 1.2445$ nm [9]. The low-temperature measurements were carried out by a homemade $^3$He refrigerator down to 0.45 K and a top-loading type dilution refrigerator equipped with a superconducting magnet down to 20 mK in magnetic fields up to 14 T.

3. Results and Discussion

Figure 1 shows the temperature dependence of the elastic constants $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ of Pr$_3$Pd$_{20}$Ge$_6$ at zero magnetic field. All of the elastic constants exhibit monotonous increase with decreasing temperature from 170 K down to 50 K. Sizable elastic softening were observed below about 10 K. The softening is described in term of quadrupole susceptibility dominated by the Curie term proportional to reciprocal temperature.

The $C_{11}$ and $(C_{11} - C_{12})/2$ show minimums at 290 mK and discontinuitive increases at $T_{Q1} = 250$ mK with decreasing temperature and further anomalies at $T_{Q2} = 60$ mK. The $C_{44}$ shows the upturn at $T_{Q2} = 60$ mK, while it shows little anomaly at $T_{Q1}$. Another notable feature is that the ultrasonic echo signals of all elastic modes are considerably attenuated below 0.1 K, not shown here. It is important to insist that the softening of $C_{44}$ below $T_{Q1}$ indicates quadrupole degeneracy remains for the $\Gamma_5$ triplet ground state at the 4a site down to $T_{Q2}$. Consequently, we suggest that the doublet $\Gamma_3$ at 8c site orders first at $T_{Q1}$, and then the triplet $\Gamma_5$ orders at the 4a site at $T_{Q2}$.

The elastic softening of $(C_{11} - C_{12})/2$ and $C_{44}$ in Pr$_3$Pd$_{20}$Ge$_6$ are described in terms of quadrupole susceptibility of 4f electrons. The solid lines for $(C_{11} - C_{12})/2$ and $C_{44}$ in Fig. 1 are calculations of quadrupole susceptibility based on the CEF level schemes at 4a and 8c sites, which were obtained from inelastic neutron scatterings and magnetization experiments [8]. The fits well reproduce the experimental results of the softening in $(C_{11} - C_{12})/2$ and $C_{44}$ below 50 K down to 0.8 K. From this analysis, we determined quadrupole-strain coupling constant $g_T$ and the intersite quadrupole coupling constant $g'_T$ to be $|g_{\Gamma_3[4a]}| = 30$ K, $|g_{\Gamma_3[8c]}| = 90$ K, $g_{\Gamma_3[4a]} = 0$ K, $g'_{\Gamma_3[8c]} = -36$ mK for the $(C_{11} - C_{12})/2$ and $|g_{\Gamma_5[4a]}| = 31$ K, $|g_{\Gamma_5[8c]}| = 13$ K, $g'_{\Gamma_5[4a]} = 13$ mK, $g'_{\Gamma_5[8c]} = -30$ mK for the $C_{44}$.

In order to elucidate the low-temperature magnetic phase diagram in Pr$_3$Pd$_{20}$Ge$_6$, we have carried out ultrasonic measurements of $(C_{11} - C_{12})/2$ down to 20 mK under magnetic fields along the [110] direction. As shown in Fig. 2, we determined the $H - T$ phase diagram of Pr$_3$Pd$_{20}$Ge$_6$. We specify the high temperature phase I to be a paramagnetic phase, the ordered phase II appearing below $T_{Q1}$ and the ordered phase III below $T_{Q2}$. The I-II phase transition point $T_{Q1}$ increases with increasing magnetic fields up to 0.5 T. Above 0.5 T, $T_{Q1}$ decreases as the field increases and crosses about 1.5 T at absolute zero. The phase II accompanied by the lifting of $\Gamma_3$ doublet ground state at the 8c site is expected to be quadrupole ordering because magnetic susceptibility has a little peak above 80 mK [8]. The magnetic fields stabilized phase II in Pr$_3$Pd$_{20}$Ge$_6$, which resembles the AFQ phase of CeB$_6$. Furthermore, the coupling constant...
of $g'_{3\text{[8c]}}$ in Pr$_3$Pd$_{20}$Ge$_6$ possesses negative sign, which indicates the antiferro-type inter-site quadrupole interaction among 8c sites. These results suggest that the phase II is AFQ ordering at the 8c site. The II-III phase transition point $T_Q2$ shifts to higher temperatures as the field increases from 1.5 T to 5 T. The phase III is probably FQ ordering state at the 4a site because the coupling constant of $g'_{3\text{[4a]}}$ possesses positive sign, which indicates the ferro-type intersite quadrupole interaction among 4a sites.

Figures 3(a) and (b) show frequency dependence of the elastic constant $C_{44}$ and the attenuation coefficient $\alpha_{44}$ in Pr$_3$Pd$_{20}$Ge$_6$. We performed ultrasonic experiments with frequencies from 15 to 151 MHz. It should be noted that we newly discover two distinctive shoulder-like anomalies in $C_{44}$ accompanying considerable ultrasonic attenuation around 15 K and 25 K. These elastic anomalies and the attenuation peaks shift to higher temperatures with increasing frequencies, which obeys thermally activated rattling processes. The $C_{11}$ and $(C_{11} - C_{12})/2$ mode in relation to $\Gamma_3$-type quadrupole fluctuation, however, exhibits no sign of ultrasonic attenuation. The results of these ultrasonic dispersions support the thermal rattling of Pr$_3^{3+}$ ion in a cage having $\Gamma_5$-type quadrupole fluctuation as similar as the ultrasonic dispersions in $C_{44}$ for Ce$_3$Pd$_{20}$Ge$_6$ [3]. These ultrasonic dispersions are well fitted by the Debye-type formula of elastic constant $C(\omega) = C_\infty - \frac{C_0 - C_\infty}{1 + \omega^2/\omega^2_T}$ and attenuation coefficient $\alpha(\omega) = \frac{C_0 - C_\infty}{2\rho\omega^2_T} \frac{\omega^2}{1 + \omega^2/\omega^2_T}$. From the fitting with Arrenius-type relaxation time $\tau = \tau_0 \exp(E/k_BT)$, we determined the activation energies of $E(L) = 102$ K, $E(H) = 198$ K and the attempt time $\tau_0(L) = 4.2 \times 10^{-11}$ s, $\tau_0(H) = 1.1 \times 10^{-11}$ s of the rattling in Pr$_3$Pd$_{20}$Ge$_6$. Here, $E(L)$ and $\tau_0(L)$ were estimated from the dispersion around 15 K, and $E(H)$ and $\tau_0(H)$ were from that around 25 K.

We carried out the low-temperature ultrasonic measurements in the clathrate compound

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**Figure 1.** Temperature dependence of the elastic constants $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ of Pr$_3$Pd$_{20}$Ge$_6$ at zero magnetic field. The insets show the expanded view of $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ below 0.6 K.

**Figure 2.** $H - T$ phase diagram of Pr$_3$Pd$_{20}$Ge$_6$ determined by low-temperature ultrasonic measurements of $(C_{11} - C_{12})/2$ under magnetic fields along [110] direction.
Pr$_3$Pd$_{20}$Ge$_6$ to investigate the quadrupole ordered phases and rattling. The elastic constants $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ shows the elastic softening associated with the $\Gamma_3$ doublet ground state at 8c site and the $\Gamma_5$ triplet ground state at 4a site. The analysis of the elastic softenings $(C_{11} - C_{12})/2$ and $C_{44}$ in terms of quadrupole susceptibility suggest that the intersite interaction among 8c site is antiferro-type and that among 4a site is ferro-type. Furthermore, the anomalies originated with phase transition at $T_{Q1} = 250$ mK and $T_{Q2} = 60$ mK have been found. Therefore, we conclude that the phase II is AFQ ordering state and the phase III is FQ ordering state. The $H - T$ phase diagram under magnetic fields along the [110] direction was determined. We found two different ultrasonic dispersions around 15 K and 25 K in $C_{44}$ due to the thermally activated $\Gamma_5$-type rattling motion in Pr$_3$Pd$_{20}$Ge$_6$.

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Figure 3. (a) The elastic constant $C_{44}$ as a function of temperature at frequencies of 19 MHz, 108 MHz and 151 MHz. (b) The lines show calculation of $C_{44}$ using the Debye type formula. (c) Temperature dependence of ultrasonic attenuation coefficient $\alpha_{44}$ at frequencies of 15 MHz, 108 MHz and 151 MHz. Solid lines are calculation of $\alpha_{44}$ using the Debye fits.