Thermal expansion and magnetostriction of clathrate compound Pr$_3$Pd$_{20}$Ge$_6$

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Abstract. In Pr$_3$Pd$_{20}$Ge$_6$, the Pr ions are located at two different crystallographic sites, 4a and 8c site. Antiferro-quadrupole ordering (AFQ) of the 8c site occurs at 250 mK. Ac susceptibility measurement indicated that antiferromagnetic ordering (AFM) of the 4a site and Hyperfine-enhanced Pr nuclear magnetic ordering of the 8c site occur at 77 and 9 mK, respectively. To clarify the magnetic and quadrupole properties of Pr$_3$Pd$_{20}$Ge$_6$, thermal expansion and magnetostriction measurements on single crystal sample were carried out along the [001] direction up to 8 T down to 500 K using a capacitive dilatometer. In zero field, relative length change $\Delta L/L$ in [001] direction had a dip at AFQ and abrupt decrease at AFM ordering. From thermal expansion and isothermal magnetostriction measurements, magnetic phase diagram of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction was obtained.

1. Introduction

The clathrate compounds R$_3$Pd$_{20}$X$_6$ where R = rare earth and X = Si or Ge show either rattling motions of R atoms, quadrupole order of 4f electrons, or both [1, 2]. Especially, Pr$_3$Pd$_{20}$X$_6$ have attracted attention because of hyperfine-coupled magnetic properties at very low temperatures. Hyperfine interaction through the 4f-electrons and nuclei plays an important role in understanding magnetic ground states of Pr$_3$Pd$_{20}$X$_6$ [3, 4].

Pr$_3$Pd$_{20}$X$_6$ have a $\text{Cr}_2\text{C}_6$-type cubic structure with a space group $Fm\bar{3}m$. The R ions are located at two different crystallographic sites, where 4a and 8c site have a $O_h$ symmetry and a $T_d$ symmetry, respectively. In cubic Pr compounds, crystalline electric field (CEF) effects split the ninefold degenerate $J = 4$ multiplet of Pr$^{3+}$ ions into a $\Gamma_1$ singlet, non-Kramers $\Gamma_3$ doublet, $\Gamma_4$, and $\Gamma_5$ triplets. Interestingly, the ground states in Pr$_3$Pd$_{20}$Ge$_6$ are different for each sites [5, 6]. The ground state at the 4a site is a magnetic $\Gamma_5$ triplet which has three magnetic dipoles and five quadrupoles, while that at the 8c site is a non-magnetic $\Gamma_3$ doublet which has two quadrupoles and an octupole. The 4a and 8c site in the series of $R_3$Pd$_{20}$X$_6$ systems show quadrupole or magnetic ordering independently at different temperatures. Quadrupole and magnetic ordering in Pr$_3$Pd$_{20}$Ge$_6$ have been studied by ultrasound and ac susceptibility measurements [4, 7]. According to the analysis of the elastic constants, antiferro-quadrupole
ordering of the 8c site occurs at $T_{\text{AFQ}} = 250$ mK and ferro-quadrupole ordering occurs at 60 mK. It has been reported that quadrupole ordered phase closes in the critical field of $H_{\text{AFQ}} = 2.5$ T along [001] direction. The ac susceptibility measurements indicated that magnetic ordering of the 4a site occurs at $T_{\text{AFM}} = 77$ mK. Furthermore, the hyperfine-enhanced Pr nuclear magnetic ordering of the 8c site was observed at $T_{\text{NMO}} = 9$ mK. However, the origin of the dissipation phenomenon observed in ac susceptibility measurements and the interplay between different sites are still unsolved.

Thermal expansion and magnetostriction are important to clarify the magnetic and quadrupole properties of Pr$_3$Pd$_{20}$Ge$_6$. In this paper, we report thermal expansion and magnetostriction measurements on single crystal of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction and discuss phase diagram.

2. Experimental procedures

Single crystal Pr$_3$Pd$_{20}$Ge$_6$ used in our study was obtained from the same batch of high quality samples, grown by a floating zone method, for ultrasound and ac susceptibility experiments. Thermal expansion and magnetostriction $\Delta L/L$ were measured along [001] direction of the cubic structure and magnetic field was applied along the same direction ($L \parallel H$). The sample length $L$ was 3.84 mm. Thermal expansion measurements on single crystal La$_3$Pd$_{20}$Ge$_6$ along [001] direction were also carried out to compare with Pr$_3$Pd$_{20}$Ge$_6$. The sample length was 3.5 mm along [001].

$\Delta L/L$ was measured by the capacitance method. The capacitive dilatometer was constructed in similar way to our previous studies [8, 9, 10]. We used a capacitance bridge based on ratio-transformer comparing the sample capacitance with a reference one. Thermal expansion and magnetostriction coefficients were obtained by differentiating the change rate of sample length $\Delta L/L$ with respect to temperature and magnetic field as $\alpha = \partial(\Delta L(T)/L)/\partial T$ and $\lambda = \partial(\Delta L(B)/L)/\partial B$, respectively.

Thermal expansion in zero magnetic field was measured using a copper nuclear demagnetization refrigerator and a $^3$He-$^4$He dilution refrigerator down to 500 $\mu$K. The temperature was measured by a Pt-NMR thermometer, a $^3$He melting curve thermometer, and a RuO$_2$ resistance thermometer. For measuring $\Delta L/L$ up to 8 T, the dilatometer was attached to an annealed copper thermal link which connected between the mixing chamber of $^3$He-$^4$He dilution refrigerator and the bore of a NbTi superconducting magnet. The sample was cooled down to 10 mK and the temperature of the sample was measured by a $^3$He melting curve thermometer and a carbon resistance thermometer.

3. Results and Discussion

3.1. Thermal expansion

Relative length changes $\Delta L/L$ of Pr$_3$Pd$_{20}$Ge$_6$ and La$_3$Pd$_{20}$Ge$_6$ in zero magnetic field are shown in the lower panel of Fig. 1. Ac susceptibility of Pr$_3$Pd$_{20}$Ge$_6$ in zero static magnetic field is represented in the upper panel. It is shown that La$_3$Pd$_{20}$Ge$_6$ shows almost no change in $\Delta L/L$ below 1 K. Then, temperature dependent $\Delta L/L$ of Pr$_3$Pd$_{20}$Ge$_6$ is attributed to magnetic contribution of Pr atoms. At AFQ transition of 8c site ($T_{\text{AFQ}} = 250$ mK), no magnetic anomaly was observed. The dip of $\Delta L/L$ along [001] direction at AFQ transition had magnitude of $10^{-8}$ order so that lattice distortion is very small. These behaviors are expected from the nature of AFQ transition. In decreasing temperature, $\Delta L/L$ rapidly decreased near the antiferromagnetic (AFM) ordering of the 4a site and $\alpha$ had a sharp peak at 77 mK ($T_{\text{AFM}}$), where susceptibility represented a peak. Below 15 mK, $\Delta L/L$ shows negative thermal expansion. However, there was no significant anomalous change at the Pr nuclear magnetic ordering of the 8c site ($T_{\text{NMO}} = 9$ mK). Nuclear spin order possibly has only small effect on electron wave functions that cause lattice distortion.
Figure 1. (Upper Panel) Ac susceptibility of single crystalline Pr$_3$Pd$_{20}$Ge$_6$ along the [001] axis in zero static magnetic field. (Lower Panel) Thermal expansion $\Delta L/L$ of single crystalline Pr$_3$Pd$_{20}$Ge$_6$ and that of La$_3$Pd$_{20}$Ge$_6$ both along the [001] axis in zero field.

Figure 2 shows thermal expansion $\Delta L/L$ of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction when magnetic field was applied to the same direction. $\Delta L/L$ is plotted as relative change from 300 mK and shifted vertically for clarity. A dip in $\Delta L/L$ was observed at the AFQ transition in $B < 0.05$ T. In contrast to low field, AFQ transition was recognized as a peak in $\Delta L/L$ from 0.1 to 0.75 T and $T_{AFQ}$ were represented as arrows. When $B \geq 1$ T, $\Delta L/L$ shows large temperature variation because of CEF effect. Then, AFQ transition was recognized as a peak in $\alpha$ as shown in the right inset of Fig. 2. AFQ transition was hardly recognized above 2 T in thermal expansion experiments because the phase boundary line became almost temperature independent. AFQ transition in low temperatures was identified by magnetostriction measurements explained in the next subsection.

At $T_{AFM}$, $\alpha$ had a clear peak associated with magnetic ordering in magnetic field smaller than 0.2 T, but no peak could be observed above 0.2 T. $\Delta L/L$ showed negative thermal expansion below 50 mK in magnetic fields lower than 2.5 T and changed positive one above 2.5 T.

3.2. magnetostriction

Figure 3 shows magnetostriction $\Delta L/L$ of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction when magnetic field was applied to the same direction. Magnetostriction was small in high temperatures such as 10 K and increased with decreasing temperature. Eventually, $\Delta L/L$ had maximum at around 7 T in 2 K. The magnetic field at the maximum decreased with decreasing temperature and became 3.8 T at 283 mK where Pr$_3$Pd$_{20}$Ge$_6$ was in paramagnetic phase. The sign change in magnetostriction coefficient so called “reversed magnetostriction” was observed in other rare earth materials [11]. CEF and symmetric strain play an important role in reversed magnetostriction.

Below $T_{AFQ}$, AFQ transition at $H_{AFQ}$ was identified as inflection point of $\Delta L/L$ in Fig. 3. Below 200 mK, abrupt increase of $\Delta L/L$ was observed at about 1.4 T. This implies that structure of ordered quadrupole largely varied at this critical field $H^*$. 

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Figure 2. Thermal expansion $\Delta L/L$ of single crystalline Pr$_3$Pd$_{20}$Ge$_6$ along the [001] axis in 0, 0.5, 1, 1.5, 2, 2.5, and 3 T. $\Delta L/L$ is plotted as relative change from 300 mK and shifted for clarity. AFQ and AFM ordering of 4f electron are represented as solid arrows $T_{AFQ}$ and open arrow $T_{AFM}$, respectively. Right and left inset respectively show the expanded plot of $\Delta L$ in 1, 1.5 T and $\Delta L/L$ in 0, 0.5 T around AFQ transition.

3.3. Magnetic phase diagram

Figure 5 shows the magnetic phase diagram of Pr$_3$Pd$_{20}$Ge$_6$ for magnetic fields applied along the [001] direction. Open circles are AFQ transition points observed by thermal expansion measurements in constant fields. Closed circles represent AFQ transition points obtained from the magnetostriction measurements at constant temperatures. The phase boundary of AFQ ordered phase obtained by this work is in reasonable agreement with that by ultrasound measurement[7]. $T_{AFQ}$ increased with increasing field and then started decreasing above 0.75 T. This field dependence of $T_{AFQ}$ is often observed in AFQ transitions for example PrPb$_3$, CeB$_6$, TmTe, and DyB$_2$C$_2$[12, 13, 14, 15]. The quadrupole ordered phase closes in critical field of about 2.4 T. There is an almost temperature independent phase boundary with critical field $H^*$ of 1.4 T as shown by squares. AFM transition of 4a site shown by solid triangles was observed by thermal expansion in magnetic field smaller than 0.2 T. This transition temperature appears to be almost field independent.

We observed hysteresis in thermal expansion measurements between 30 and 90 mK in low magnetic fields. In similar regions, dispersion was observed in magnetic susceptibility measurements[4] and hysteresis of elastic constant during magnetic field ramping was observed in ultrasonic experiments[7]. Interplay between magnetic dipole and electric quadrupole is considered as an open question and important issue.

It has been reported that magnetic phase diagram of Pr$_3$Pd$_{20}$Ge$_6$ has large anisotropy for field directions by ultrasound experiments[7]. Anisotropy for field directions has also been reported in
Figure 3. Magnetostriction $\Delta L/L$ of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction in paramagnetic and quadrupole ordered phase. $\Delta L/L$ is shifted vertically for clarity. Critical field of AFQ transition $H_{AFQ}$ at 70 mK is shown as an arrow. $\Delta L/L$ shows abrupt change at $H^*$. 

Figure 4. Magnetostriction coefficient $\lambda$ of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction in paramagnetic and quadrupole ordered phase. $\lambda$ is shifted vertically for clarity. Critical field of AFQ transition $H_{AFQ}$ are shown as arrows. Inset shows overall view of $\lambda$ at 38 mK.

CeB$_6$[16], but the relative strength of critical fields along three directions are different from each other. Thermal expansion and magnetostriction study of Pr$_3$Pd$_{20}$Ge$_6$ along other directions are important for characterizing the order parameter of quadrupole ordered phase because relative length change $\Delta L/L$ along [001], [110], and [111] directions of the cubic symmetry are corresponding to symmetric strain $\epsilon_i$ as

$$\frac{\Delta L}{L}|_{[001]} = \frac{1}{2}\epsilon_B + \frac{1}{\sqrt{3}}\epsilon_u,$$

$$\frac{\Delta L}{L}|_{[110]} = \frac{1}{3}\epsilon_B - \frac{1}{2\sqrt{3}}\epsilon_u + \epsilon_{xy},$$

and

$$\frac{\Delta L}{L}|_{[111]} = \frac{1}{3}\epsilon_B + \frac{2}{3}(\epsilon_{xy} + \epsilon_{yz} + \epsilon_{xz})$$

respectively. Here, $\epsilon_B$ and $\epsilon_u$ are the volume and tetragonal strain, respectively. $\epsilon_{xy}, \epsilon_{yz}, \epsilon_{xz}$ are the shear strains.

4. Summary
We studied thermal expansion and magnetostriction of Pr$_3$Pd$_{20}$Ge$_6$ using a capacitive dilatometer in order to clarify the magnetic and quadrupole properties. Thermal expansion and magnetostriction measurements on single crystal sample were carried out along the [001] in applied external fields up to 8 T and down to 500 $\mu$K. From these measurements, magnetic phase diagram was obtained. The quadrupole ordered phase closes in critical field of about 2.4 T that agreed with ultrasonic experiments. In magnetostriction measurements, an almost temperature independent phase boundary was observed and the critical field $H^*$ was 1.4 T.

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Figure 5. Magnetic Phase diagram of Pr$_3$Pd$_{20}$Ge$_6$ along [001] direction. AFQ transitions observed by thermal expansion and magnetostriction are plotted as open circles and closed circles. AFM transition of 4$f$ electron in 4a site is shown as solid triangle. Critical points of abrupt change in $\Delta L/L$ observed by magnetostriction measurements are plotted as squares. Lines are guide to the eye.

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