Elastic modulus of cage compound PrRu$_2$Zn$_{20}$

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Abstract. Elastic properties of the cage compound PrRu$_2$Zn$_{20}$ have been investigated by means of ultrasonic measurement. The transverse modulus $(C_{11} - C_{12})/2$ shows elastic softening below 250 K and exhibits a discontinuous change in the slope at 150 K. An abrupt elastic hardening is observed below $T_s = 138$ K which is a non-magnetic phase transition temperature. The phase transition at $T_s$ is accompanied by hysteresis indicating that the transition is of first-order. The softening above 150 K is well reproduced by Curie-Weiss-like formula for the co-operative Jahn-Teller effect with a negative quadrupole-quadrupole coupling constant. The phase transition at $T_s$ is not caused by 4$f$-electrons of Pr ions. There is a possibility that the elastic hardening below 3 K originates from the rattling motion.

1. Introduction

Cage compounds have attracted much attention in recent years because these compounds show various physical properties affected by the ionic degrees of freedom of the rattling motion, which is a large amplitude atomic motion. In ultrasonic measurements, cage compounds, such as the filled skutterudite RO$_3$Sb$_{12}$ [1, 2] and RFe$_3$Sb$_{12}$ [3, 4], show the ultrasonic frequency dependences of elastic modulus and ultrasonic attenuation, which is so-called ultrasonic dispersion. Furthermore, elastic softening due to the rattling motion is observed at very low temperatures in these compounds [1, 2, 3, 4].

The cage compound RT$_2$Zn$_{20}$ (R: rare earth, T = Ru, Ir, etc.) has the cubic CeCr$_2$Al$_{20}$-type structure (space group Fd$ar{3}$m) with the lattice parameter of $a = 14.336$ Å at room temperature [5]. R atoms are accommodated at a single 8a site in the Frank-Kasper cages which consist of 16 Zn atoms. Onimaru et al. reported that PrRu$_2$Zn$_{20}$ shows a first-order phase transition at $T_s = 138$ K accompanied by structural modulation by their specific heat, electrical resistivity and magnetization experiments [6]. Temperature $T$ dependence of the magnetic susceptibility shows no anomaly at $T_s$ suggesting a non-magnetic phase transition. To investigate the origin of phase transition and the rattling motion in the cage compound PrRu$_2$Zn$_{20}$, we have measured $T$ dependence of elastic modulus on a single crystalline sample.
2. Experimental
Single crystal of PrRu$_2$Zn$_{20}$ was grown by the Zn self-flux method. Details of the sample preparation were reported in ref. 7. The sample was shaped in a rectangular parallelepiped of $2.470 \times 2.182 \times 1.865 \text{ mm}^3$. The elastic modulus $(C_{11} - C_{12})/2$, which is the transverse mode with the sound propagation direction $k // [110]$ and the displacement direction $u // [1\overline{1}0]$, was measured as a function of $T$ from 0.4 to 310 K using the phase comparison-type pulse echo method [8]. Detailed experimental technique was described in ref. 9. The elastic modulus $C$ was calculated using $C = \rho v^2$ with a room-temperature mass density $\rho = 7.443 \text{ g/cm}^3$, where $v$ is the sound velocity in a sample. The frequency range was from 18 to 27MHz.

3. Results and discussion
Figure 1 shows $T$ dependence of the transverse elastic modulus $(C_{11} - C_{12})/2$ in PrRu$_2$Zn$_{20}$. The modulus $(C_{11} - C_{12})/2$ increases monotonically with decreasing $T$ above 250 K. It turns into decrease gradually below 250 K and exhibits a discontinuous change in the slope at 150 K. With further decreasing $T$, an abrupt elastic hardening is observed below $T_s$. The phase transition at $T_s$ is accompanied by hysteresis as shown in the upper inset in Fig. 1. It suggests the first-order phase transition, being consistent with the results reported by Onimaru et al. Huge ultrasonic attenuation is observed at around $T_s$. At low temperatures, it should be noted that $(C_{11} - C_{12})/2$ shows elastic hardening below 3 K and leveling off below 1 K as shown in the lower inset in Fig. 1. The origin of hardening below 3 K will be discussed in detail later. No elastic softening at very low temperatures is observed down to 0.4 K.

We discuss the origin of phase transition at $T_s$ in PrRu$_2$Zn$_{20}$. The modulus $(C_{11} - C_{12})/2$ shows abrupt elastic hardening below $T_s$. On the other hand, a similar phase transition is reported at 150 K in LaRu$_2$Zn$_{20}$ [6]. In our preliminary ultrasonic measurements, elastic modulus in LaRu$_2$Zn$_{20}$ also shows the hardening below $T_s$ without softening. These suggest that the phase transition at $T_s$ in PrRu$_2$Zn$_{20}$ is not caused by 4$f$-electrons of Pr ions. Onimaru et al. reported that the phase transition at $T_s$ is accompanied by structural modulation. A possible candidate of the origin of phase transition is the band Jahn-Teller effect. To clarify the origin of the phase transition in PrRu$_2$Zn$_{20}$ and LaRu$_2$Zn$_{20}$, a band calculation to examine the existence of degenerated band structure at the Fermi energy is necessary.

As for the softening below 250 K, it would be caused by a strain-quadrupole and quadrupole-quadrupole interaction. We carried out the theoretical fitting based on the Curie-Weiss-like

![Figure 1. $T$ dependence of transverse elastic modulus $(C_{11} - C_{12})/2$. The upper inset represents the same data in an expanded scale between 110 and 150 K. The lower inset also shows the same data between 0.4 and 10 K.](image-url)
Table 1. Fitting parameters of \((C_{11} - C_{12})/2\).

| \(\Theta\) (K) | \(T_c - \Theta\) (K) | \(a\) (GPa) | \(b \times 10^{-2}\) GPa/K |
|----------------|----------------------|-------------|--------------------------|
| -1.5           | 41.2                 | 74.6        | -4.5                     |

formula for the co-operative Jahn-Teller effect [10]:

\[
C(T) = C_0 \frac{T - T_c}{T - \Theta},
\]

where \(\Theta\) is proportional to the quadrupole-quadrupole coupling constant, \(T_c - \Theta\) is a measure of Jahn-Teller energy including the strain-quadrupole coupling constant and \(C_0\) is a background stiffness assumed as linear \(T\) dependence:

\[
C_0 = a + bT.
\]

As shown in Fig. 2, \((C_{11} - C_{12})/2\) is well reproduced above 150 K with fitting parameters listed in Table 1. The negative value of \(\Theta\) suggests that there are the antiferro-quadrupolar interaction among quadrupole moments at 8\(a\) sites. Since \((C_{11} - C_{12})/2\) shows a discontinuous change in the slope at 150 K, the theoretical curve deviates from the data. In PrRu\(_2\)Zn\(_{20}\), however, no anomaly at 150 K is reported in other measurements [6]. It would be necessary to carry out further detailed measurements of physical properties, such as specific heat, because there is a possibility to be a phase transition at 150 K.

Hereafter, we discuss the elastic behaviors at low temperatures. The modulus \((C_{11} - C_{12})/2\) shows elastic hardening below 3 K and leveling off below 1 K as shown in the lower inset in Fig. 1. No anomaly has been reported around these temperatures in other measurements [6]. In cage compounds, the filled skutterudite compounds \(RO_{5}Sb_{12}\) [1, 2] and \(RFe_{5}Sb_{12}\) [3, 4] show elastic hardening at low temperatures, and the temperature where the hardening occurs depends on ultrasonic frequency. This ultrasonic frequency dependence of elastic modulus in cage compounds is due to the rattling motion. The modulus \((C_{11} - C_{12})/2\) in PrRu\(_2\)Zn\(_{20}\) shows the characteristic hardening below 3 K. There is a possibility that it originates from the rattling...
motion of Pr ions. To examine whether the hardening below 3 K is ultrasonic dispersion, ultrasonic attenuation and elastic modulus measurements using the overtone of the fundamental resonance frequencies of transducers are requisite.

4. Conclusion

We have performed ultrasonic experiments on the cage compound PrRu$_2$Zn$_{20}$. The elastic softening is observed below 250 K in $(C_{11} - C_{12})/2$, and it exhibits a discontinuous change in the slope at 150 K. The modulus $(C_{11} - C_{12})/2$ turns into increase suddenly below $T_s$ accompanied by hysteresis, suggesting the first-order phase transition. The softening below 250 K is caused by the strain-quadrupole and quadrupole-quadrupole interaction. The theoretical curve using the Curie-Weiss-like formula for the co-operative Jahn-Teller effect deviates from the data below 150 K, suggesting a possibility to be a phase transition at 150 K. The elastic hardening below 3 K could be ultrasonic dispersion due to the rattling motion.

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