Interplay between low-energy optical phonon modes and structural transition in PrT_2Zn$_{20}$ (T=Ru and Ir)

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Interplay between low-energy optical phonon modes and structural transition in PrT_2Zn_{20} (T=Ru and Ir)

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Abstract. Atomic dynamics of PrT_2Zn_{20} for T=Ru with a structural transition at T_s=138 K and T=Ir without such a transition have been studied by inelastic X-ray scattering (IXS) measurements. The IXS spectra for T=Ru reveal an optical phonon excitation at 3 meV. We assign it to low-energy vibration of the Zn atom at the 16c site by taking account of the first principles calculation [Hasegawa *et al*. 2012 J. Phys.: Conf. Proc. **391** 012016]. For T=Ir, on the other hand, the optical excitation at 3 meV was not observed. The contrasting results indicate that the low-energy optical phonon mode has a role in the structural transition in $PrRu_2Zn_{20}$ and isostructural La counterparts.

1. Introduction

Caged compounds have attracted much attention over the last two decades. This is because these compounds show various physical phenomena arising from large amplitude vibration of guest atoms inside over-sized atomic cages. Filled-skutterudites antimonides and intermetallic-clathrate compounds are known as candidates for thermoelectric conversion materials because of the low lattice thermal conductivity. It is considered that the low thermal conductivity is partly originated from low-energy vibrations of the guest atoms which impede heat flow [1, 2]. Low-energy optical phonon modes of the guest ion in β-pyrochlore oxides and some rare earth filled skutterudites induce various electronic phenomena such as superconductivity and heavy fermion state [3, 4, 5, 6, 7].

Recently, we have focused on another class of caged compounds RT_2Zn_{20} (R: rare earth, T: transition metal) which show a variety of strongly correlated electron phenomena [8, 9, 10, 11, 12, 13, 14]. These compounds crystalize in the cubic $CeCr_2Al_{20}$-type structure with five crystallographically distinguished sites; the R atom at the 8a, T at the 16d, Zn at the 16c, 48f and 96g sites [15]. Single-crystal X-ray diffraction experiments revealed that the atomic displacement parameter of the Zn atom at the 16c site (Zn(16c)) is a few times larger than those

of others [15]. Therefore, it is expected that the Zn(16*c*) atom behaves itself as a guest in a cage formed by two *R* atoms at the 8*a* site and twelve Zn ones at the 96*g* site. Among RT_2Zn_{20} systems, LaT_2Zn_{20} (T=Ru and Ir) and $PrRu_2Zn_{20}$ undergo structural transitions at T_s=150, 200 and 138 K, respectively [16]. The first principles calculation pointed out that Zn(16*c*) is vibrating at low-energy on a two-dimensional plane, which induces the structural instability [17]. The atomic motion of Zn(16*c*) in LaT_2Zn_{20} (T=Ru and Ir) was studied by NMR for La, which is located at the second neighbor site for Zn(16*c*). The fluctuations of the electric field gradient at the La site above T_s and its slowing down below T_s were explained by the change in the atomic motion of Zn(16*c*) [18].

To gain a further insight into the low-energy optical modes of Zn(16*c*), we have performed inelastic X-ray scattering (IXS) and specific heat measurements of RT_2Zn_{20} (R=La and Pr, T=Ru and Ir). In the nonmagnetic $LaRu_2Zn_{20}$ with the structural transition at T_s=150 K, two Einstein temperatures of 35 and 82 K were estimated from the lattice specific heat [19]. As shown in Table 1, the former mode was observed by the IXS measurement as an optical phonon excitation peak at 3 meV in the [111] longitudinal mode, and the latter as that at 7 meV in the [110] transverse mode. For isostructural $PrRu_2Zn_{20}$ with the structural transition at T_s=138 K, we observed the optical phonon excitation at 7 meV in the [110] transverse mode [20]. However, the optical phonon mode at 3 meV has not been confirmed because the IXS spectra for the [111] longitudinal mode have not been measured yet.

In the present work, we have measured IXS spectra of $PrRu_2Zn_{20}$ along the [111] direction to detect the low-energy optical phonon mode at 3 meV. To understand the mechanism of the structural transitions in RT_2Zn_{20}, it is important to clarify whether 3 meV mode exist or not in $PrRu_2Zn_{20}$. Furthermore, the phonon dispersion of $PrIr_2Zn_{20}$ with no structural transition has been derived from the IXS spectra in the [110] transverse and [111] longitudinal modes. Comparing the phonon dispersions of the two compounds, we will discuss the interplay between the low-energy optical phonon modes and the structural transitions.

Table 1. Lattice parameters, structural transition temperatures, Einstein temperatures of optical phonon modes determined by the specific heat and/or inelastic X-ray scattering (IXS) measurements of RT_2Zn_{20} (R = La and Pr, T = Ru and Ir).

Compound	lattice parameter (Å) [16]	structural transition temperature T_s (K) [16]	Einstein temperature (K)
$LaRu_2Zn_{20}$	14.4263(2)	150	35, 82 (specific heat [19]) 35, 80 (IXS [19])
$PrRu_2Zn_{20}$	14.3467(4)	138	35*, 80 (IXS [20])
$PrIr_2Zn_{20}$	14.2729(2)	none	70* (IXS)

* Present work.

2. Experiments

Single crystalline samples of PrT_2Zn_{20} (T=Ru and Ir) were synthesized by the melt growth method. The detail of sample preparation was reported in previous paper [8, 9, 10]. The IXS measurements were performed at BL35XU in SPring-8, Japan [21]. We chose the Si (11 11 11) backscattering setup. The energy resolution is about 1.5 meV, which slightly depends on the quality of analyzer crystals for measuring different $\boldsymbol{Q}$ at the same time. The resolution $\Delta\boldsymbol{Q}$ was estimated to be (0.12 0.12 0.04) near the (7 7 7) and (12 12 0) reflections where the IXS spectra were measured.

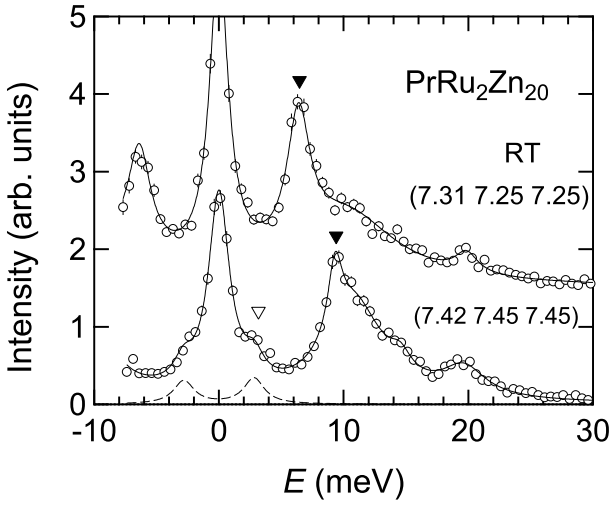

Figure 1. Inelastic X-ray scattering spectra of $PrRu_2Zn_{20}$ in the longitudinal [111] direction at room temperature. The solid lines are fits using Lorentzian functions. Black and white arrows indicate the acoustic and the lowest-energy optical phonon excitations at 3 meV, respectively. The dashed line is the contribution of the optical phonon excitation at 3 meV.

3. Results and discussion

The IXS spectra of the [110] transverse mode of $PrRu_2Zn_{20}$ showed the optical phonon excitation at 7 meV as mentioned above [20]. Figures 1 shows the IXS spectra along the [111] longitudinal direction at $\boldsymbol{Q}$=(7+ξ 7+ξ 7+ξ) for ξ=0.25 and 0.45 (near the zone boundary), respectively. At ξ=0.25, there is a peak at 6 meV which is attributed to the acoustic phonon excitation. With increasing ξ to 0.45, the energy rises to 9 meV. The broad structure above 10 meV could be deconvoluted to two or three peaks. Because the number of atoms per primitive unit cell of RT_2Zn_{20} is as large as 46, the excitation peaks consist of several optical phonon branches. The low-energy excitation at 3 meV is observed only near the zone boundary as a shoulder of the elastic peak. This contribution is shown by the dashed line in Fig. 1. We note that the energy value agrees well with the value estimated from the specific heat and the IXS measurements of the La counter-part $LaRu_2Zn_{20}$ [20]. Furthermore, it is moderately consistent with that of the low-energy optical phonon mode of the Zn(16*c*) predicted by the first principle calculation [17]. They suggest that the optical phonon mode at 3 meV results from the vibration of the Zn(16*c*).

Figure 2 shows the IXS spectra of $PrIr_2Zn_{20}$ at $\boldsymbol{Q}$ =(12+ξ 12−ξ 0) (ξ=0.4, 0.5, 0.7 and 0.9) at room temperature. These spectra give dispersion relation for the transverse phonon modes along the [110] direction. At ξ=0.4, an acoustic peak marked by the black arrow is observed at 4 meV. The energy gradually rises with increasing ξ and reaches 7 meV at ξ=0.9. The low-energy optical phonon mode is detected at 6 meV as a shoulder of the acoustic peak in the spectra for ξ=0.4 and 0.5.

Figure 3 shows the IXS spectra of PrT_2Zn_{20} (T=Ru and Ir) near their zone boundaries in the [111] direction. The acoustic modes appear at about 10 meV for both compounds. The optical modes at 3 meV observed in $PrRu_2Zn_{20}$ is absent for $PrIr_2Zn_{20}$ with no structural transition, indicating that the optical mode of Zn(16*c*) of $PrIr_2Zn_{20}$ exists at higher energy. In caged compounds, the atomic free space is often an important factor to determine the phonon energy of atoms encapsulated into the cages [2, 7, 22, 23]. Since the lattice constant of $PrIr_2Zn_{20}$ is smaller than that of $PrRu_2Zn_{20}$ as shown in Table 1, the smaller cage surrounding Zn(16*c*) in

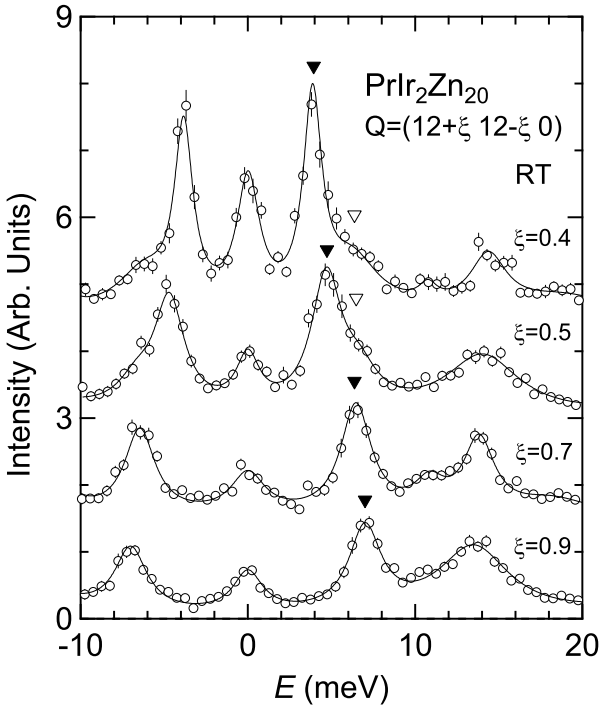

Figure 2. Inelastic X-ray scattering spectra of $PrIr_2Zn_{20}$ at $\boldsymbol{Q}$ =(12+ξ 12−ξ 0) for ξ=0.4, 0.5, 0.7 and 0.9 at room temperature. The solid lines are fits using Lorentzian functions. Black and white arrows indicate the acoustic and the low-energy optical phonon excitations at around 6 meV, respectively.

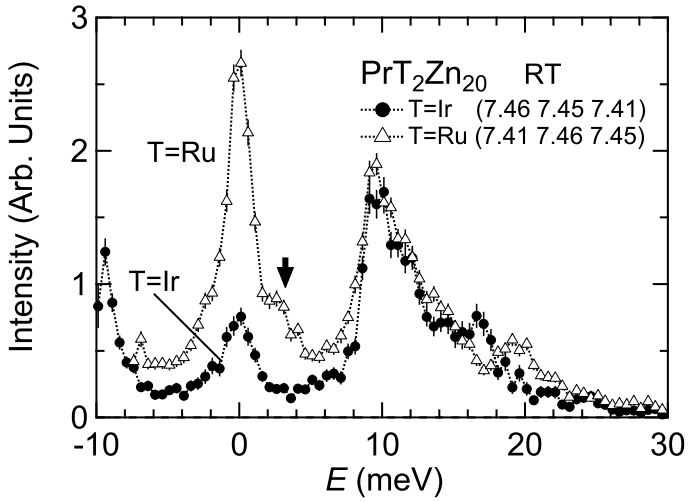

Figure 3. Inelastic X-ray scattering spectra of PrT_2Zn_{20} (T=Ru and Ir) near the zone boundary of the [111] direction at room temperature. The arrow indicates the optical phonon mode at 3 meV in $PrRu_2Zn_{20}$, which is absent in $PrIr_2Zn_{20}$.

$PrIr_2Zn_{20}$ should increase the optical phonon energy. The increase of the phonon energy could stabilize the crystal structure. The present results imply that the low-energy optical mode at 3 meV plays a role in the structural transitions in $R Ru_2Zn_{20}$. To confirm this implication, a detailed analyses of the IXS spectra and the specific heat for related compounds are in progress.

4. Conclusions

We have performed the IXS measurements of PrT_2Zn_{20} (T=Ru and Ir) to study the phonon dispersions. The IXS spectra along the [111] longitudinal direction of $PrRu_2Zn_{20}$ with the structural transition have revealed an optical phonon mode at around 3 meV in addition to that at 7 meV previously reported. On the other hand, in $PrIr_2Zn_{20}$ with no structural transition, the corresponding optical phonon mode was not found at 3 meV. The smaller cage surrounding Zn(16c) in $PrIr_2Zn_{20}$ probably leads the optical phonon to higher energy, which should hinder the structural transition. We therefore conclude that the optical phonon mode at 3 meV plays a role in the structural transition in $PrRu_2Zn_{20}$.

Acknowledgments

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