Interplay between low-energy optical phonon modes and structural transition in Pr\(T_2\)Zn\(_{20}\) (\(T=\)Ru and Ir)

K Wakiya\(^1\), T Onimaru\(^1\), S Tsutsui\(^2,3\), K T Matsumoto\(^1\), N Nagasawa\(^1\), A Q R Baron\(^2,4\), T Hasegawa\(^5\), N Ogita\(^5\), M Udagawa\(^3,5\) and T Takabatake\(^1,3\)

\(^1\)Department of Quantum Matter, Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima, 739-8530, Japan
\(^2\)Japan Synchrotron Radiation Research Institute, SPring-8, Sayo, Hyogo 679-5198, Japan
\(^3\)Institute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima, 739-8530, Japan
\(^4\)Materials Dynamics Laboratory, RIKEN SPring-8 Center, Sayo, Hyogo 679-5148, Japan
\(^5\)Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima, 739-8521, Japan

E-mail: D145957@hiroshima-u.ac.jp

Abstract. Atomic dynamics of Pr\(T_2\)Zn\(_{20}\) 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 16\(c\) 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 Pr\(Ru_2\)Zn\(_{20}\) and isostructual 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 \(\beta\)-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 \(RT_2\)Zn\(_{20}\) (\(R=\)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 Ce\(Cr_2\)Al\(_{20}\) -type structure with five crystallographically distinguished sites: the \(R\) atom at the 8\(a\), \(T\) at the 16\(d\), Zn at the 16\(c\), 48\(f\) and 96\(g\) sites [15]. Single-crystal X-ray diffraction experiments revealed that the atomic displacement parameter of the Zn atom at the 16\(c\) site (Zn(16\(c\))) is a few times larger than those...
of others [15]. Therefore, it is expected that the Zn(16c) atom behaves itself as a guest in a cage formed by two R atoms at the 8a site and twelve Zn ones at the 96g site. Among $RT_2\text{Zn}_{20}$ systems, La$T_2\text{Zn}_{20}$ ($T=$Ru and Ir) and PrRu$_2\text{Zn}_{20}$ undergo structural transitions at $T_s=150$, 200 and 138 K, respectively [16]. The first principles calculation pointed out that Zn(16c) is vibrating at low-energy on a two-dimensional plane, which induces the structural instability [17].

The atomic motion of Zn(16c) in La$T_2\text{Zn}_{20}$ ($T=$Ru and Ir) was studied by NMR for La, which is located at the second neighbor site for Zn(16c). 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(16c) [18].

To gain a further insight into the low-energy optical modes of Zn(16c), we have performed inelastic X-ray scattering (IXS) and specific heat measurements of $RT_2\text{Zn}_{20}$ ($R=$La and Pr, $T=$Ru and Ir). In the nonmagnetic LaRu$_2\text{Zn}_{20}$ 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$_2\text{Zn}_{20}$ 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$_2\text{Zn}_{20}$ along the [111] direction to detect the low-energy optical phonon mode at 3 meV. To understand the mechanism of the structural transitions in $RT_2\text{Zn}_{20}$, it is important to clarify whether 3 meV mode exist or not in PrRu$_2\text{Zn}_{20}$. Furthermore, the phonon dispersion of PrIr$_2\text{Zn}_{20}$ 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.

| Compound   | Lattice parameter (Å) | Structural transition temperature $T_s$ (K) | Einstein temperature (K) |
|------------|------------------------|---------------------------------|------------------------|
| LaRu$_2\text{Zn}_{20}$ | 14.4263(2) | 150 | 35, 82 (specific heat [19]) |
| PrRu$_2\text{Zn}_{20}$ | 14.3467(4) | 138 | 35*, 80 (IXS [19]) |
| PrIr$_2\text{Zn}_{20}$ | 14.2729(2) | none | 70* (IXS) |

* Present work.

2. Experiments

Single crystalline samples of Pr$T_2\text{Zn}_{20}$ ($T=$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 $Q$ at the same time. The resolution $\Delta Q$ 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.
3. Results and discussion

The IXS spectra of the [110] transverse mode of PrRu$_2$Zn$_{20}$ showed the optical phonon excitation at 7 meV as mentioned above [20]. Figures 1 shows the IXS spectra along the [111] longitudinal direction at $Q=(7+\xi 7+\xi 7+\xi)$ for $\xi=0.25$ and 0.45 (near the zone boundary), respectively. At $\xi=0.25$, there is a peak at 6 meV which is attributed to the acoustic phonon excitation. With increasing $\xi$ 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$_2$Zn$_{20}$ 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$_2$Zn$_{20}$ [20]. Moreover, it is moderately consistent with that of the low-energy optical phonon mode of the Zn(16c) predicted by the first principle calculation [17]. They suggest that the optical phonon mode at 3 meV results from the vibration of the Zn(16c).

Figure 2 shows the IXS spectra of PrIr$_2$Zn$_{20}$ at $Q=(12+\xi 12-\xi 0)$ ($\xi=0.4, 0.5, 0.7$ and 0.9) at room temperature. These spectra give dispersion relation for the transverse phonon modes along the [110] direction. At $\xi=0.4$, an acoustic peak marked by the black arrow is observed at 4 meV. The energy gradually rises with increasing $\xi$ and reaches 7 meV at $\xi=0.9$. The low-energy optical phonon mode is detected at 6 meV as a shoulder of the acoustic peak in the spectra for $\xi=0.4$ and 0.5.

Figure 3 shows the IXS spectra of PrT$_2$Zn$_{20}$ ($T=$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$_2$Zn$_{20}$ is absent for PrIr$_2$Zn$_{20}$ with no structural transition, indicating that the optical mode of Zn(16c) of PrIr$_2$Zn$_{20}$ 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$_2$Zn$_{20}$ is smaller than that of PrRu$_2$Zn$_{20}$ as shown in Table 1, the smaller cage surrounding Zn(16c) in
Figure 2. Inelastic X-ray scattering spectra of PrIr$_2$Zn$_{20}$ at $Q=(12+\xi, 12-\xi, 0)$ for $\xi=0.4$, 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 Pr$T_2$Zn$_{20}$ ($T=$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$_2$Zn$_{20}$, which is absent in PrIr$_2$Zn$_{20}$. 
PrIr$_2$Zn$_{20}$ 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 RRu$_2$Zn$_{20}$. 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$_2$Zn$_{20}$ (T=Ru and Ir) to study the phonon dispersions. The IXS spectra along the [111] longitudinal direction of PrRu$_2$Zn$_{20}$ 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$_2$Zn$_{20}$ with no structural transition, the corresponding optical phonon mode was not found at 3 meV. The smaller cage surrounding Zn(16c) in PrIr$_2$Zn$_{20}$ 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$_2$Zn$_{20}$.

### Acknowledgments

The IXS experiments were carried out under the approval of JASRI (Proposal Nos. 2012A1506, 2012B1596, 2014A1678). A part of the IXS experiments (Proposal No. 2014A1678) was performed under the SPring-8 Budding Researchers Support Program. This work was financially supported by MEXT/JSPS KAKENHI Grant Numbers 20102004, 20102005, 21102516, 22540345, 23740275, 23102718, and 26707017. K. W. and K. T. M were supported by JSPS Research Fellowships for Young Scientists.

### References

[1] Sales B C, Mandrus D and Williams R K 1996 Science 272 1325.
[2] Takabatake T, Suekuni K, Nakayama T and Kaneshita E 2014 Rev. Mod. Phys. 86 669.
[3] Hiroi Z, Yamaura J and Hattori K 2012 J. Phys. Soc. Jpn. 81 011012.
[4] Sanada S, Aoki Y, Aoki H, Tsuchiya A, Kikuchi D, Sugawara H and Sato H 2005 J. Phys. Soc. Jpn. 74 246.
[5] Hattori K, Hirayama Y and Miyake K 2005 J. Phys. Soc. Jpn. 74 3306.
[6] Goto T, Nemoto Y, Sakai K, Yamaguchi T, Akatsu M, Yanagisawa T, Hazama H and Omuki K 2004 Phys. Rev. B 69 180511.
[7] Tsutsui S, Uchiyama H, Sutter J P, Baron A Q R, Mizunuki M, Kawamura N, Uruga T, Sugawara H, Yamaura J, Ochiai A, Hasegawa T, Ogita N, Udagawa M and Sato H 2012 Phys. Rev. B. 86 195115.
[8] Jia S, Bud’ko S L, Samolyuk G D and Canfield P C 2007 Nat. Phys. 3 334.
[9] Torikachvili M S, Jia S, Mun E D, Hansnah S T, Black R C, Neils W K, Martien D, Bud’ko S L and Canfield P C 2007 Proc. Natl. Acad. Sci. U.S.A. 104 9960.
[10] Jia S, Ni N, Samolyuk G D, Safa-Sefat A, Dennis K, Ko H, Miller G J, Bud’ko S L and Canfield P C 2008 Phys. Rev. B. 77 104408.
[11] Onimaru T, Matsumoto K T, Inoue Y F, Umesawa K, Sakakibara T, Karaki Y, Kubota M and Takabatake T 2011 Phys. Rev. Lett. 106 177001.
[12] Onimaru T, Nagasawa N, Matsumoto K T, Wakiya K, Umesawa K, Kitakado S, Sakakibara T, Matsushita Y and Takabatake T 2012 Phys. Rev. B. 86 184426.
[13] Matsubayashi K, Tanaka T, Sakai A, Nakatsuji S, Kubo Y and Uwatoko Y 2012 Phys. Rev. Lett. 109 170004.
[14] Tsujimoto M, Matsumoto Y, Tomita T, Sakai A and Nakatsuji S 2014 Phys. Rev. Lett. 113 267001.
[15] Nasch T, Jeitschko W and Rodewald U C 1997 Z. Naturforsch. B 52 1023.
[16] Onimaru T, Matsumoto K T, Inoue Y F, Umesawa K, Saiga Y, Matsushita Y, Tamura R, Nishimoto K, Ishii I, Suzuki T and Takabatake T 2010 J. Phys. Soc. Jpn. 79 033704.
[17] Hasegawa T, Ogita N and Udagawa M 2012 J. Phys.: Conf. Ser. 391 012016.
[18] Asaki K, Kotehawa H, Tou H, Onimaru T, Matsumoto K T, Inoue Y F and Takabatake T 2012 J. Phys. Soc. Jpn. 81 023711.
[19] Wakiya K, Onimaru T, Tsutsui S, Matsumoto K T, Nagasawa N, Baron A Q R, Hasegawa T, Ogita N, Udagawa M and Takabatake T Preprint cond-mat/1410.7916.
[20] Wakiya K, Onimaru T, Tsutsui S, Matsumoto K T, Nagasawa N, Baron A Q R, Hasegawa T, Ogita N, Udagawa M and Takabatake T 2014 JPS Conf. Proc. 3 011068.
[21] Baron A Q R, Tanaka Y, Goto S, Takeshita K, Matsushita T and Ishikawa T 2000 J. Phys. Chem. Solids 61 461.

[22] Matsuhira K, Sekine C, Wakeshima M, Hinatsu Y, Namiki T, Takeda K, Shirotani I, Sugawara H, Kikuchi D and Sato H 2009 J. Phys. Soc. Jpn. 78 124601.

[23] Suekuni K, Avila M A, Umeo K, Fukuoka H, Yamanaka S, Nakagawa T and Takabatake T 2008 Phys. Rev. B. 77 235119.