Low-Energy Optical Phonon Modes in the Caged Compound

LaRu$_2$Zn$_{20}$

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Abstract

We have investigated atomic dynamics in the caged compound LaRu$_2$Zn$_{20}$ which has a structural transition at $T_S = 150$ K by the measurements of specific heat $C$ and inelastic X-ray scattering (IXS). The lattice part of the specific heat $C_{\text{lat}}$ divided by $T^3$, $C_{\text{lat}}/T^3$, exhibits a broad peak at around 15 K, which is reproduced by two Einstein modes with characteristic temperatures of $\theta_E = 35$ and 82 K, respectively. IXS measurements along the [111] and [110] directions of LaRu$_2$Zn$_{20}$ reveal optical phonon modes at 3 meV (35 K) and 7 meV (80 K) whose values agree with the estimate of $\theta_E$'s. The optical phonon excitation at 3 meV is identified as a low-energy vibration of Zn atoms at the 16c site, which is surrounded by 12 Zn atoms and 2 La atoms. This vibration is probably responsible for the structural transition in this compound.
Caged compounds such as intermetallic-clathrates, filled-skutterudites, and β-pyrochlore oxides have attracted much attention in recent years, since a variety of interesting physical phenomena arise from large-amplitude and anharmonic vibration of guest atoms inside the cages\cite{1, 2}. The low-energy optical phonons in the intermetallic-clathrates and filled-skutterudites are thought to reduce the thermal conductivity and thus enhance the thermoelectric figure of merit\cite{3, 4}. In rare-earth filled-skutterudites, strongly correlated electronic phenomena such as heavy fermion state, superconductivity, and quadrupolar fluctuations have been discussed by taking the low-energy optical phonon modes of guest atoms into consideration. \cite{5, 6, 7, 8}.

The family of $RT_2X_{20}$ ($R$: Rare earth, $T$: Transition metal, $X$=Al and Zn) is another class of the caged compounds \cite{9}. They show various physical properties such as structural transition, superconductivity, heavy fermion state, and multipolar ordering. YbCo$_2$Zn$_{20}$ has the largest electronic specific heat coefficient of 8 J/K$^2$ mol among the intermetallic rare-earth compounds \cite{11}. La$T_2$Zn$_{20}$ ($T$=Ru and Ir) and PrRu$_2$Zn$_{20}$ undergo the structural phase transitions at $T_s$=150, 200 and 138 K, respectively \cite{12, 13}. PrIr$_2$Zn$_{20}$ with no structural transition has a non-Kramers $\Gamma_3$ doublet ground state of $4f^2$ configuration, in which a superconducting transition manifests itself in the presence of antiferroquadrupole ordering \cite{12, 14}. The coexistence of the superconductivity and quadrupole order has been also observed in the isostructural Pr compounds PrRh$_2$Zn$_{20}$ and Pr$T_2$Al$_{20}$ ($T$=Ti and V) \cite{15, 16, 17}. On the other hand, the symmetry of the Pr site in PrRu$_2$Zn$_{20}$ is lowered by the structural transition, and the ground state falls into a non-magnetic singlet.

The compounds $RT_2Zn_{20}$ crystalize in the cubic CeCr$_2$Al$_{20}$-type structure with the space group of Fd$\overline{3}$m. The total number of atoms per formula unit is 23 and the number of the formula units per unit cell is 8 \cite{10}. There are five crystallographically different sites; the $R$ atom at the 8$a$, $T$ at the 16$d$, Zn at the 16$c$, 48$f$ and 96$g$ sites. One of the crystallographic characteristics is that the atomic displacement parameter of the Zn atom at the 16$c$ site, Zn (16$c$), is approximately twice or three times larger than those of other atoms \cite{10}. Recently, a first principles calculation of La$T_2$Zn$_{20}$ ($T$=Ru and Ir) has pointed out that the Zn (16$c$) vibrates at low frequencies in a two-dimensional plane, which probably induces the structural transition \cite{19}. The Zn (16$c$) is encapsulated in a cage consisting of two $R$ atoms and twelve Zn atoms at the 96$g$ site as is shown in the inset of Fig. 1. In analogy of intermetallic-clathrates and rare-earth filled-skutterudites $RT_4$Sb$_{12}$, low-energy vibrations of the Zn atoms
may play a crucial role not only in the structural property but also in the electronic one. Experimentally, ultrasonic measurements of PrRu$_2$Zn$_{20}$ revealed elastic hardening due to the structural transition\[20\]. The elastic moduli in PrT$_2$Zn$_{20}$ ($T=$Rh and Ir) depend on the ultrasonic frequency at around 2 K \[21, 22\], as found in some of filled skutterudites\[9\]. Furthermore, $^{139}$La-NMR measurements of LaT$_2$Zn$_{20}$ ($T=$Ru and Ir) have indicated that Zn (16c) moves from the 16c site to off-center positions below $T_s$. This fact suggests that the low-energy Zn vibration plays a role in the structural transition \[23\]. Here, it is noted that not the $R$ atom but the Zn atom is vibrating with a large amplitude in $RT_2Zn_{20}$, whereas the $R$ atom is rattling in $RT_4Sb_{12}$\[2\].

Inelastic X-ray scattering (IXS) and specific heat measurements are powerful techniques to observe low-energy optical phonon modes in solids. The specific heat gives information on the phonon density of states, while the IXS measurements on single-crystalline samples provide us with the phonon dispersion relations. Combining them, lattice specific heat can be reproduced with phonon dispersion microscopically measured by inelastic scattering techniques\[21\]. In fact, the specific heat, IXS and inelastic neutron scattering measurements were used to study the anharmonic vibration of the guest atoms in intermetallic-clathrates, filled-skutterudites, and the β-pyrochlore oxides\[25–33\].

In the present work, we have measured the specific heat and the IXS spectra for LaRu$_2$Zn$_{20}$ to study the low-energy Zn vibration. The study has directly revealed the optical phonon excitation of Zn (16c) at around 3 meV. The specific heat data of LaRu$_2$Zn$_{20}$ was already reported in ref. 34, which is reanalyzed in this paper.

Single-crystalline samples of LaRu$_2$Zn$_{20}$ were prepared by the melt-growth method as was described in the previous report \[12\]. The specific heat was measured by a thermal-relaxation method from 2 to 300 K using a Quantum Design physical property measurement system. The high resolution IXS measurements were carried out at BL35XU of SPring-8 \[35\]. We have chosen the set up of Si (11 11 11) backscattering whose energy resolution is about 1.5 meV. The typical $Q$ resolution in the present condition was $\Delta Q = (0.12 0.12 0.04)$ in the reciprocal lattice unit for LaRu$_2$Zn$_{20}$ with the lattice parameter of 14.4263(2) Å \[12\]. By using the sample of about 3 mm$^3$ in volume, we have measured transverse modes along the [110] direction and longitudinal modes along the [111] direction.

We first show the data of specific heat $C$ of LaRu$_2$Zn$_{20}$ in Fig. 1. The lattice specific heat $C_{\text{lat}} = C - \gamma T$ is plotted as $C_{\text{lat}}/T^3$ versus $T$, where $\gamma$ is the Sommerfeld coefficient, 11.9
FIG. 1. (Collar online) The specific heat depicted as $C_{\text{lat}} / T^3$ vs $T$ for LaRu$_2$Zn$_{20}$ [34]. The solid lines indicate fits using the Debye and Einstein models. The dashed, dotted and dashed-dotted curves are individual contributions from the Debye and Einstein models with the fitting procedure of the Model 2 as is described in the text.

TABLE I. Fitting parameters for the lattice specific heat of LaRu$_2$Zn$_{20}$. The labels of D and E denote the Debye and Einstein models to fit the specific heat data, respectively.

| Mode | Energy (K) | Oscillator number /f.u. |
|------|------------|-------------------------|
| Model 1 | D 246 | 21+2/3 |
| | E 67 | 4/3 |
| Model 2 | D 259 | 21.10 |
| | E1 35 | 0.13 |
| | E2 82 | 1.77 |

mJ/K$^2$ mol [34]. In the plot of $C_{\text{lat}} / T^3$, the Debye specific heat approaches a constant value on cooling to the lowest temperature, since it obeys the $T^3$ law. The Einstein specific heat, on the other hand, manifests itself as a peak with a maximum at $T \approx \theta_E/5$, where $\theta_E$ is the Einstein temperature. It is represented as

$$C_E(T) = 3n_ER\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E/T)}{[\exp(\theta_E/T) - 1]^2},$$

(1)

where $n_E$ is the number of the Einstein oscillators per formula unit. As shown in Fig. 1, $C_{\text{lat}} / T^3$ of LaRu$_2$Zn$_{20}$ exhibits a broad peak at around 15 K, which must result from weak
dispersive optical phonon modes. Similar broad peaks in $C_{\text{lat}}/T^3$ were observed in other caged compounds such as intermetallic-clathrates, filled-skutterudites, and $\beta$-pyrochlore oxides [27, 30, 31, 33]. The specific heat data of these compounds were fit by the sum of the Einstein specific heat for the guest atom and the Debye one for the framework atoms. To extract the contribution from the low-energy optical modes to the specific heat data, we used two different procedures for least-squares fitting with the Debye and Einstein models, as shown in Table I.

In the Model 1, we assumed that oscillations of Zn (16c) are approximated by the Einstein model and the others by the Debye model. Because two Zn (16c) atoms per formula unit are vibrating with a large amplitude on the plane (see the inset of Fig. 1), the number of the Einstein oscillators is set as $n_E=(2/3) \times 2=4/3$ per formula unit. Thereby, the total number of the Debye oscillators including the framework oscillations is evaluated to be $n_D=23-4/3=65/3$. In this case, fitting parameters are only the Debye temperature $\theta_D$ and Einstein one $\theta_E$. The fitting result is shown with the (blue) solid curve in Fig. 1, and the parameters are listed in Table I. Although the peak position is well fit, the wide profile below 20 K is not reproduced.

As a better fit to the $C_{\text{lat}}/T^3$ data, we used the Model 2 assuming that the specific heat would be composed of one Debye and two Einstein modes. The parameters are the oscillators number per formula unit ($n_D$, $n_{E1}$, and $n_{E2}$) and characteristic temperatures ($\theta_D$, $\theta_{E1}$, and $\theta_{E2}$) of the Debye and Einstein models, respectively. Here, we assume that the total number of atoms per formula unit is 23; $n_D+n_{E1}+n_{E2}=23$. The analysis has yielded $\theta_D=259$ K, $\theta_{E1}=35$ K, and $\theta_{E2}=82$ K as summarized in Table I. The fit drawn by the (red) solid curve in Fig. 1 well reproduces the broad peak profile. The total number of the Einstein oscillators in Model 2, $n_{E1}+n_{E2}=1.9$, is larger than $n_E=4/3$ in the Model 1 whose value is expected from the two-dimensional vibration of Zn (16c) as described above. According to the first principles calculation, the optical phonon modes of the Zn atoms at the 96g site are distributed at around 7 meV [19]. Therefore, these modes may partly contribute to the broad peak in the specific heat. On the other hand, the number of $n_{E1}=0.13$ for $\theta_{E1}=35$ K in Model 2 is smaller than $n_E=4/3$ for Model 1. This discrepancy indicates that some of the low-energy optical phonon modes of Zn (16c) are distributed at around 3 meV. Another possibility is that the energy of some optical phonon branches at 3 meV is increased on cooling below $T_s$ in the stabilized structure.
FIG. 2. Inelastic X-ray scattering spectra of LaRu$_2$Zn$_{20}$ at $Q=(12+\xi, 12-\xi, 0)$ for $\xi=0.2$, 0.4 and 0.6 at room temperature. The solid lines are fits using the Lorentzian function. Black and white arrows indicate the acoustic and optical phonon excitations, respectively. The dashed lines are contributions of the elastic scattering at $E=0$, the acoustic phonon excitation and the optical excitation at 7 meV.

Next, we present the results of the IXS measurements of LaRu$_2$Zn$_{20}$. Figure 2 shows the room-temperature IXS spectra of LaRu$_2$Zn$_{20}$ at $Q=(12+\xi, 12-\xi, 0)$ for $\xi=0.2$, 0.4 and 0.6, which correspond to the transverse phonon modes along the [110] direction. In addition to the elastic peaks at $E=0$, there are Stokes and anti-Stokes components of phonon excitations due to phonon creation and annihilation processes, respectively. In the spectrum at $\xi=0.2$, a well-defined shoulder exists at around 2 meV which is owing to the acoustic phonon excitation (closed triangle). With increasing $\xi$, this peak shifts to higher energy and reaches 7 meV at $\xi=0.6$. A few broad peaks due to weakly dispersive optical phonon modes exist at 7, 11, and 18 meV (open triangle). Because the primitive unit cell of LaRu$_2$Zn$_{20}$ contains 46 atoms, each broad peak probably consists of several phonon branches.

The phonon dispersion relation of LaRu$_2$Zn$_{20}$ along the [110] direction derived from the IXS spectra is shown in Fig. 3 (a). The closed circles represent the peak positions in the IXS spectra. The accuracy of the energy determination is comparable to the symbol size. The
FIG. 3. Phonon dispersion curves of LaRu$_2$Zn$_{20}$ measured along (a) $Q=(12+\xi \ 12-\xi \ 0)$ and (b) $Q=(7+\xi \ 7+\xi \ 7+\xi)$ at room temperature. The solid and dashed lines are guides to the eyes. The closed circles represent the phonon peak positions in the inelastic X-ray scattering spectra. The accuracy of the energy determination is comparable to the symbol size. The bold lines near the zone center indicate the sound velocity of LaRu$_2$Zn$_{20}$ measured by the ultrasonic measurement\cite{36}. The solid and dotted lines are guides to the eyes. The sound velocities can be evaluated from the initial slope of the dispersion curve of the acoustic modes. The value of $(2.4 \pm 1.1) \times 10^3$ m/s is in good agreement with $2.05 \times 10^3$ m/s measured by the ultrasound technique, which is shown by the bold line\cite{36}. Another notable feature in Fig. 3(a) is the low-energy optical phonon branch at 7 meV. This energy agrees with the Einstein temperature $\theta_{E2}=82$ K estimated from the lattice specific heat.

Figure 4 shows the IXS spectra along the $Q=(7+\xi \ 7+\xi \ 7+\xi)$ for $\xi=0.2$ and 0.45 which correspond to the longitudinal phonon modes along the [111] direction. In the upper panel for $\xi=0.2$, there are an acoustic phonon excitation peak at 5 meV (closed triangle) and two optical phonon peaks at around 10 and 20 meV (open triangle). In the lower panel for $\xi=0.45$, the acoustic one shifts to 9 meV, and a shoulder appears at around 3 meV. To confirm whether this shoulder comes from a phonon excitation or not, we have measured the IXS spectrum at 50 K. As shown in the inset of Fig. 4, a peak is observed at 3 meV in the Stokes part, while it is hardly observed in the anti-Stokes part as is expected by the Bose thermal excitation factor. Therefore, the peak at 3 meV is identified as the optical phonon mode. The dispersion along the [111] direction is shown in Fig. 3(b). The optical phonon mode at 3 meV is weakly dispersive near the zone boundary. We note that the
optical phonon mode was detected by Raman spectroscopy, indicating the existence of the low-energy mode at the zone center [37]. The low-energy optical excitation at 3 meV was detected as the peak only in the IXS spectra for the [111] longitudinal mode as shown in Fig. 4. It is probably because the contribution of the acoustic peak and the optical peak at 7 meV does not conceal the peak at 3 meV.

Let us recall the specific heat of LaRu$_2$Zn$_{20}$ shown in Fig. 1. The energy of the phonon excitation at 3 meV is almost the same as the Einstein temperature $\theta_{E1} = 35$ K evaluated from the lattice specific heat. According to the first principles calculation, the optical phonon modes arising from the low-energy vibration of Zn (16c) should be distributed below 3 meV. Therefore, we assign the optical phonon modes at 3 meV to the vibration of Zn (16c) [19].

In summary, we have observed low-energy optical phonon excitations in LaRu$_2$Zn$_{20}$ by specific heat and IXS measurements. The temperature dependence of $C_{lat}/T^3$ showed the
The presence of two Einstein modes with characteristic temperatures of 35 and 83 K, respectively. The IXS measurements revealed the phonon dispersion relation of the transverse modes along the [110] direction and the longitudinal ones along the [111] direction. Along the [111] and [110] directions, optical phonon excitations were found at around 3 and 7 meV, where the energy values agree with the Einstein temperatures, respectively. Taking the first principles calculation into consideration, the optical phonon mode at 3 meV is identified as the low-energy vibration of Zn (16c), which probably induces the structural transition at $T_s=150$ K.

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