First-principles calculations of lattice vibrations on LaT₂Zn₂₀ (T = Ru and Ir)

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Abstract. Lattice vibrations of LaRu₂Zn₂₀ and LaIr₂Zn₂₀ have been investigated by the local density approximation. Although these compounds have a cage structure in which a La atom is surrounded by Zn, the calculated results show that La vibrations have large dispersion and relatively high frequencies. In both compounds, it is found that the vibrations of Zn at 16c site in the plane perpendicular to the three-fold axis have very low frequencies and can be unstable. This result suggests that the transitions in LaRu₂Zn₂₀ at 150 K and in LaIr₂Zn₂₀ at 200 K are caused by these unstable modes.

1. Introduction
We have calculated lattice dynamical properties for LaRu₂Zn₂₀ and LaIr₂Zn₂₀ with the CeCr₂Zn₂₀ structure[1]. In this structure, the La atoms are well separated from the nearest La and are surrounded by Zn. The cage structural feature has also been found in skutterudite compounds, where large amplitude vibrations of rare-earth ions have attracted much attention, because such vibrations could participate in exotic phenomena[2, 3, 4]. Therefore, it is worth to examine the possibility of such large amplitude vibrations of La in these compounds, and such modes might be one of the possible keys to understand the anomalous behavior observed in PrIr₂Zn₂₀[1, 5].

In general, frequencies of atomic vibrations depend on wavevector, but all frequencies become low when atoms vibrate with large amplitude. This can be judged by a partial density of states (partial DOS) of lattice vibrations with a narrow peak at low frequency. Thus, we have calculated the partial DOS in these compounds. On the other hand, LaRu₂Zn₂₀ and LaIr₂Zn₂₀ show a transition at 150 K and 200 K, respectively, which have been suggested as a structural transition[1]. Therefore, it is important to understand the lattice dynamical properties in these compounds.

2. Procedures
All calculations were made using ABINIT package[6, 7, 8], which is able to obtain lattice dynamical properties of crystals under the density functional theory with plane-wave basis set. We performed firstly the ground-state calculation for each compounds and obtained their optimized structures, minimizing pressures and forces on atoms until stresses are less than
0.01 GPa's and forces are less than 3 meV/Å, respectively. Then, inter-atomic force constants (IFCs) were calculated in the framework of the density functional perturbation theory [9] and the Fourier interpolation method [10]. Using the IFCs, phonon dispersion curve were obtained. DOS of phonon modes were calculated by the tetrahedron method with $8 \times 8 \times 8$ grid.

For all calculations, local density approximation (LDA) was applied with the exchange-correlation energy parameterized by Perdew and Wang [11]. The norm-conserved pseudo-potential (PP) method was used and the potentials were generated by FHI98PP [12] due to the Troullier-Martins method [13]. The plane-wave cut-off energy was 56 Ry, where 1 Ry = 13.6 eV. The integrations in the reciprocal space were replaced by summation on the $2 \times 2 \times 2$ Monkhost-Pack grid [14]. Since these compounds are metallic, smeared occupation [15] is useful to decrease the grid in the reciprocal space. The smearing parameter, which works like temperature, was set to 0.02 Ry. The IFCs have been determined by the Fourier interpolation method based on $1 \times 1 \times 1$ grid (LaT$_2$Zn$_{20}$) of the cubic cell in the reciprocal space. All these parameters were determined until the accuracy of phonon frequencies to be less than 10 cm$^{-1}$, except for low-energy modes below 40 cm$^{-1}$. The convergence of the phonon frequencies at $\mathbf{q} = 0$ was examined up to 60 Ry for plane-wave cut-off, down to 0.01 Ry for the smearing parameter, and up to $4 \times 4 \times 4$ Monkhost-Pack grid.

3. Result and discussion
The crystal structure of LaT$_2$Zn$_{20}$ has the space group Fd$\bar{3}$m. La locates at 8a position (0, 0, 0), Ru at 16d (0.625, 0.625, 0.625), Zn(1) at 16c (0.125, 0.125, 0.125), Zn(2) at 48f (x, 0.25, 0.25), and Zn(3) at 96g (y, y, z). In the optimized structure, $a = 14.159$ Å, $x = 0.6134$, $y = 0.1839$, and $z = 0.4514$ for LaRu$_2$Zn$_{20}$ and $a = 14.143$ Å, $x = 0.6110$, $y = 0.1847$, and $z = 0.4490$ for LaIr$_2$Zn$_{20}$, where $a$ is a lattice constant.

The phonon frequencies of LaRu$_2$Zn$_{20}$ are sensitive to the lattice constants. The optimized lattice constant $a$ is 14.159 Å, while the experimental value [1] is 14.426 Å. We also calculated phonon frequencies using the experimental $a$, where atomic positions were also optimized. The calculated phonon frequencies are quite different between these two lattice constants. The maximum value of the differences is more than 30 cm$^{-1}$, while the maximum frequency of phonon is about 300 cm$^{-1}$. The result with the experimental lattice shows better agreement with the Raman scattering result [16]. From now on, we discuss using the experimental one. The calculated parameters of the atomic positions become $x = 0.6139$, $y = 0.1836$, and $z = 0.4524$ for LaRu$_2$Zn$_{20}$ with $a = 14.426$ Å, and $x = 0.6111$, $y = 0.1845$, and $z = 0.4494$ for LaIr$_2$Zn$_{20}$ with $a = 14.354$ Å [1].

The calculated partial DOS in LaRu$_2$Zn$_{20}$ is shown in Figs. 1. Some phonon modes have imaginary frequencies, i.e. $\omega^2 < 0$. These modes are plotted at the negative frequency with the same absolute value. The imaginary frequency mode is unstable, that is, this unstable mode decreases the electronic energy. Therefore, some structural transition is expected. As shown in Fig. 1, the low-frequency modes are vibrations of Zn(1). Zn(1) site has two nearest-neighbor La atoms on a straight line (see Fig. 2). The La-Zn(1)-La line coincides with one of the three-fold axes. The modes above 30 cm$^{-1}$ are vibrations of Zn(1) along this three-fold axis, while the modes below 30 cm$^{-1}$ are vibrations of Zn(1) perpendicular to the axis. Therefore, the unstable modes are vibrations of Zn(1) perpendicular to the axis.

The La vibrations are distributed in wide frequency range, which is almost the same as the distribution range of the vibrations of Zn(1) along the three-fold axis. Namely, the La-Zn(1) network is tight and the La vibrations show large dispersion in LaRu$_2$Zn$_{20}$. Therefore, La atoms in LaRu$_2$Zn$_{20}$ are unlikely to vibrate with large amplitude.

The calculated frequencies of the Raman active phonons and their experimental result [16] are listed in Table 1. The agreement is not good, since the maximum difference is 18 cm$^{-1}$. As described above, the small change of the lattice constant by about 2 % makes large change.
Fig. 1. Partial density of states of lattice vibrations in LaRu$_2$Zn$_{20}$. Some modes have imaginary frequencies and those modes are shown at negative frequencies in Zn(1) DOS.

Table 1. Calculated frequencies of the Raman active phonons and their experimental values at room temperature[16] in LaRu$_2$Zn$_{20}$.

|     | A$_{1g}$ (exp.) | A$_{1g}$ (calc.) | E$_g$ (exp.) | E$_g$ (calc.) | T$_{2g}$ (exp.) | T$_{2g}$ (calc.) |
|-----|-----------------|------------------|--------------|--------------|----------------|------------------|
|     | -               | 159.1            | 201.6        | 63.3         | 81.3           | 113.1            |
|     | 138.7           | 152.1            | 183.9        | 71.5         | 81.3           | 90.5             |
|     | 141.6           | 124.2            | 165.5        | 133.8        | 141.7          | 161.4            |
|     | 165.5           | 149.5            |              | 141.7        | 157.1          | 238.0            |

of phonon frequencies by about 10%. Since the calculated lattice constants in LDA usually shows smaller values by a few % than experimental ones, this large difference might be a systematic difference in LDA. As another possibility, the structure at room temperature may not be described by the averaged structure with the space group Fd3m, because the structure will be deformed at low temperatures.

We discuss the vibration modes of Zn(1) perpendicular to the three-fold axis. If we consider the arrangement of atoms around Zn(1), as shown in Fig. 2, it is found that Zn(1) is surrounded by two La atoms and 12 Zn(2) atoms. Along the three-fold axis, Zn(1) is tightly bonded to two La atoms. However, the atomic distance between Zn(1) and Zn(2) is very long compared with the other nearest-neighbor Zn-Zn distances. This means that there is a free space for Zn(1) toward perpendicular to the axis. As the result, the vibrations of Zn(1) perpendicular to the axis have low frequencies. In this case, this atomic displacements of Zn(1) may decrease the electronic energy. Therefore, some modes become unstable. The most unstable mode is triply degenerated T$_{2u}$ mode at $\mathbf{q} = \mathbf{0}$ in the present result. If the structural transition at 150 K is driven by this mode, Landau theory predicts that the space group of deformed structures is

Figure 2. Zn(1) atom and its ligand atoms. Zn(1) atom is tightly bonded with two La atoms. Zn(1) atom can easily move toward Zn(2), since the distance to Zn(2) atom is very long.
I43d or R32. However, the calculated frequencies of these low-frequency modes are sensitive to the lattice constant and parameters of the calculation, because their frequencies are too low. We cannot conclude which mode is the most unstable at this stage. The calculated result of LaIr$_2$Zn$_{20}$ also shows low-frequency modes around 20 cm$^{-1}$ for Zn(1) vibrations, but they are not the unstable modes, that is, they have the positive energies. The origin of the transition at 200 K in LaIr$_2$Zn$_{20}$ is likely to be the Zn(1) vibrations, since the other optical modes have much higher frequencies.

4. Conclusion
The phonon frequencies of LaRu$_2$Zn$_{20}$ and LaIr$_2$Zn$_{20}$ have been calculated. Both compounds have cage-like structures, where a La atom is surrounded by Zn. In such structures, the guest mode due to La might have small dispersion and low frequencies. However, the calculated results show that La vibrations have large dispersion and high frequencies. Therefore, large amplitude vibrations of La atoms will not be found. On the other hand, it is found that the vibrations of Zn(1) perpendicular to the three-fold axis have very low frequencies and that some of them are unstable. Therefore, the structural transition reported in LaRu$_2$Zn$_{20}$ and LaIr$_2$Zn$_{20}$ can be caused by these modes, and the Zn(1) modes have large amplitude in the plane perpendicular to the axis above the transition temperature.

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