Elastic properties of the filled and unfilled skutterudite compounds

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Abstract. Ultrasonic measurements were made on a single crystal of the unfilled skutterudite compounds RhSb\textsubscript{3} and IrSb\textsubscript{3} and compare with that of the filled skutterudite PrOs\textsubscript{4}Sb\textsubscript{12} to elucidate the role of the guest ions Pr. A characteristic increase was observed around 30 K in the temperature dependence of elastic constants \((C_{11}-C_{12})/2\) and \(C_{44}\) which is ascribed to unusual vibration “rattling” of Pr ions in an atomic cage formed by Sb-icosahedron. On the other hand, the elastic constants \(C_{11}\), \((C_{11}-C_{12})/2\) and \(C_{44}\) increase monotonically with decreasing temperature in the case of RhSb\textsubscript{3} and IrSb\textsubscript{3}. No such a characteristic increase was observed. These results give us a piece of evidence that the guest ions would play a crucial role for “rattling motion” in filled skutterudite compounds.

1. Introduction
In recent years attention has been focused on a role of guest ions in the filled skutterudite compounds, which are described by \(\text{RET}_{4}\text{X}_{12}\) (RE=lanthanide, alkali metal, alkaline-earth, or actinaide; Tr=transition metal, X: pnictogen).\textsuperscript{[1-5]} It is because the unusual vibration so-called “rattling” in an atomic cage formed by pnictogen-icosahedron seems to have a marked effect on the rich variety of ground-state properties. The “rattling” motion acts as excellent phonon scatterers. In fact, a marked reduction in lattice thermal conductivity was reported in the filled skutterudite compounds due to that.\textsuperscript{[6-8]} Earlier studies by means of ultrasonic measurements have shown that a characteristic increase, probably due to the “rattling” motion, is observed in elastic constants of this family, in particular, \(\text{REOs}_{4}\text{Sb}_{12}\) (RE: La, Pr, Sm, Nd).\textsuperscript{[1,5,9]} Although the experimental results have revealed unusual properties attributed to the “rattling” motion, the situation is far from reaching a consensus on the whole understanding. In the present study we investigate ultrasonic measurements on unfilled skutterudite compounds RhSb\textsubscript{3} and IrSb\textsubscript{3}, and compare with that of the filled one, PrOs\textsubscript{4}Sb\textsubscript{12} to make clear differences of their elastic properties. In particular, IrSb\textsubscript{3} is a suitable reference system for OsSb\textsubscript{3} poly-anion since they both have a similar band structure in the vicinity of Fermi level, composed mainly by 5d-derived components from Ir/Os and 5s-, 5p-derived ones from Sb. Low temperature transport properties of the unfilled skutterudite systems, RhSb\textsubscript{3} and IrSb\textsubscript{3} suggest semiconducting type...
behavior with a narrow band gap.[10-11] The aim of the present work is to evaluate the role of the guest ions RE by means of an ultrasonic measurement. Ultrasonic measurement is a powerful tool with which to study the charge fluctuation through phonons coupled with elastic strains induced by a sound wave. In valence fluctuation compounds and glass materials one can observe frequently the ultrasonic dispersion and a characteristic increase in elastic constants resulting from a thermally activated motion in a double-, or multi-well potential. Recently, the same elastic behavior was found in clathrate compounds and filled skutterudites known as cage-like compounds.[12-13] In particular, the motions of guest ions in the cage, so-called "rattling motions" have been extensively studied since then. It should be noted that one can determine symmetry of the "rattling motion" in a cage by means of a symmetry transverse ultrasonic mode. The frequency dependence of the elastic constant is described by the Debye-type dispersion as $C_\Gamma(\omega)=C_\Gamma(\infty)-(C_\Gamma(\infty)-C_\Gamma(0))/(1+\omega^2\tau^2)$. Here $C_\Gamma$ is $(C_{11} - C_{12})/2$ or $C_{44}$. $\omega$ is the angular frequency of the incident sound wave. $\tau$ is the relaxation time of the rattling motion. $C_\Gamma(0)$ and $C_\Gamma(\infty)$ are low- and high-frequency limits, respectively. A characteristic increase is expected at the temperature being satisfied with the resonant condition, where the relaxation time $\tau$ coincides with the sound angular frequency $\omega$ as $\omega\tau\approx1$.

2. Results

The single crystals of RhSb$_3$ and IrSb$_3$ were grown by the Sb-self-flux method using purity raw materials of 3N (99.9 % pure)-Rh, 4N-Ir and 6N-Sb. X-ray powder diffraction pattern shows that no impurity phase was detected, without small amounts of Rh, Ir and Sb metals of the order of ~1 % in volume. The sound wave velocity $v$ was detected by an ultrasonic apparatus based on the phase-comparison method. The piezoelectric LiNbO$_3$ transducers were used for the measurements of transverse and longitudinal ultrasonic waves with fundamental frequencies of 5 MHz and 10 MHz, respectively. The ultrasonic measurement was performed using a $^3$He-evaporation cryostat down to 400 mK.

First, the temperature dependence of elastic constants $(C_{11} - C_{12})/2$ and $C_{44}$ of the filled skutterudite compound PrOs$_4$Sb$_{12}$ is shown in figure 1. The $(C_{11} - C_{12})/2$ and $C_{44}$ were measured by the transverse sound wave with frequencies of 5 - 15 MHz propagated along the $(110)$ axis with the polarization parallel to the (1-10) axis and propagated along the (100) axis with the polarization parallel to the (010) axis, respectively. The $(C_{11} - C_{12})/2$ and $C_{44}$ modes are associated with the elastic strain, $\varepsilon_u=(2\varepsilon_{zz}\varepsilon_{xx}\varepsilon_{yy})/\sqrt{3}$, $\varepsilon_u=\varepsilon_{xx}\varepsilon_{yy}$ with $\Gamma_3$ symmetry and $\varepsilon_{yy}, \varepsilon_{zz}, \varepsilon_{xx}$ with $\Gamma_5$ symmetry, respectively. A step-like increase was observed around 30 K, followed by a characteristic elastic softening toward low temperature in the $(C_{11} - C_{12})/2$ and $C_{44}$ modes. The latter behavior is predominantly ascribed to the 4f-ground state of Pr ion split by a crystalline electric field (CEF) effect, although we do not discuss here. The details are described in Ref. [1]. On the other hand, the former behavior originated from the "rattling" motion. This can be explained by the Debye-type dispersion, where the ultrasonic wave frequency $\omega$ coincides with a relaxation time $\tau=\tau_0\exp(E/T)$ of the system as $\omega\tau\approx1$. The fit gives us the important parameters as follows: attempt time $\tau_0=9.23\times10^{-11}$ and $9.34\times10^{-11}$ s, activation energy $E=190$ K and $193$ K for $(C_{11} - C_{12})/2$ and $C_{44}$ modes, respectively. These values are good agreement with those reported by the other group, except for the presence of the characteristic increase in $C_{44}$ mode. [1] Next, the temperature dependence of the relative changes of elastic constants $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ of the "unfilled" skutterudite compound IrSb$_3$ is shown in figure 2. The $C_{11}$ was measured by the longitudinal sound wave with frequencies of 10 - 30 MHz propagated along the $(100)$ axis. The IrSb$_3$ data exhibit roughly normal behavior: a stiffening with decreasing temperature and an almost temperature independence at low temperatures. It should be noted that no characteristic increase is observed in the measured elastic constants. This point is strikingly different from that of PrOs$_4$Sb$_{12}$. Figure 3 depicts the temperature dependence of the relative changes of elastic constants $C_{11}$, $(C_{11} - C_{12})/2$ and $C_{44}$ of the
Figure 1. Temperature dependence of the elastic constants \((C_{11} - C_{12})/2\) and \(C_{44}\) of the filled skutterudite compound PrOs₄Sb₁₂. The dotted lines are a fit by the elastic constants taking account of the Debye-type dispersion.

\[ \tau = \tau_0 \exp \left( \frac{E}{T} \right) \]

\[ \tau_0 = 9.43 \times 10^{-11} \text{ (s)} \]

\[ E = 188 \text{ K} \]

\[ \tau = 9.23 \times 10^{-11} \text{ (s)} \]

\[ E = 190 \text{ K} \]

Figure 2. Temperature dependence of the relative changes of elastic constants \(C_{11}, (C_{11} - C_{12})/2\) and \(C_{44}\) of the unfilled skutterudite compound IrSb₃.

Figure 3. Temperature dependence of the relative changes of elastic constants \(C_{11}, (C_{11} - C_{12})/2\) and \(C_{44}\) of the unfilled skutterudite compound RhSb₃.

Other "unfilled" skutterudite compound RhSb₃. The RhSb₃ data also exhibits roughly normal behavior, similar to those of IrSb₃.

Here, let us discuss the obtained results. The highly contrast whether the characteristic increase appears or not in the elastic constants as a function of temperature indicates that the guest ions Pr plays an important role. However, one must consider the difference of conductivity
between the filled skutterudite compound PrOs$_4$Sb$_{12}$ and the unfilled skutterudite ones IrSb$_3$, RhSb$_3$. As mentioned in Introduction, IrSb$_3$ and RhSb$_3$ exhibit the semiconducting type behavior. On the other hand, PrOs$_4$Sb$_{12}$ exhibit metallic type one. Thus, another important issue raises, that is, how do carriers contribute to ”rattling motion”? Most of compounds in which ”rattling-motion” character has been reported so far exhibit metallic-type behavior at low temperatures. We cannot conclude at this stage whether the role of carrier is important or not to bring about ”rattling motion”. Nevertheless, absence of the characteristic increase related to the rattling motion, combined with the experimental facts of a remarkable reduction in lattice thermal conductivity in unfilled skutterudite compounds suggests strongly that the guest ions in the atomic cage formed by pnictogen-icosahedron play a fatal role. The relationship between carriers and rattling motion is still controversial issue at present. Very recently, the microscopic study of the NMR measurement proposed that the Fermi surface composed mainly d-derived components is of significant importance for the thermal rattling in the reference compound LaOs$_4$Sb$_{12}$.[2] Furthermore, no softening to Γ point of the phonon dispersion was observed in IrSb$_3$, determined by the Inelastic X-ray scattering measurement. This is strikingly different from that of REOs$_4$Sb$_{12}$. [14] These microscopically experimental facts support our above proposal.

3. Conclusion

In summary, we have investigated the elastic properties of the unfilled skutterudite compounds IrSb$_3$ and RhSb$_3$ by means of the ultrasonic measurements. The feature would reflect the absence of the ”rattling motion”. The knowledge obtained of the elastic constants of the ”unfilled” skutterudite compound IrSb$_3$, in particular, will be helpful in clarifying a role of the guest ions for ”rattling motion” in filled skutterudite compounds.

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