Systematic Study of Lattice Specific Heat of Filled Skutterudites

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The lattice specific heat $C_{\rm lat}$ of La-based filled skutterudites LaT_4X_{12} (T = Fe, Ru and Os; X = P, As and Sb) has been systematically studied, and both the Debye temperature $\Theta_{\rm D}$ and the Einstein temperature $\Theta_{\rm E}$ of LaT_4X_{12} were carefully estimated. We confirmed that a correlation exists between $\Theta_{\rm D}$ and the reciprocal of the square root of average atomic mass for LaT_4P$_{12}$, LaT_4As$_{12}$, and LaT_4Sb$_{12}$. The $\Theta_{\rm D}$ of filled skutterudites was found to depend mainly on the nature of the species X forming the cage. The temperature dependence of $C_{\rm lat}/T^3$ for LaT_4X$_{12}$ exhibited a large broad maximum at low temperatures (10 - 30 K), which suggests a nearly dispersionless low-energy optical mode characterized by Einstein specific heat. Since no such broad maximum exists for the *unfilled* skutterudite RhP$_3$, the low-energy optical modes are associated with vibration involving La ions in the X_{12} cage (the so-called "guest ion modes"). The $\Theta_{\rm E}$ of filled skutterudites was found to roughly correspond to the energy of low-energy guest ion optical modes. Furthermore, a good correlation was shown to exist between $\Theta_{\rm E}$ and $r_{\rm R-X} - r_{\rm R3+}$, where $r_{\rm R-X}$ is the R-X distance and $r_{\rm R3+}$ is the effective ionic radius of R^{3+}. As $r_{\rm R-X} - r_{\rm R3+}$ increased, $\Theta_{\rm E}$ was found to decrease.

KEYWORDS: skutterudite, specific heat, Debye temperature, Einstein temperature, rattling vibration, guest ion mode

1. Introduction

Recent active research on filled skutterudite compounds of the form RT_4X$_{12}$ has revealed the wide variety of physical properties resulting from the strong c-f hybridization effect, the unique band structure, and the degree of freedom of the multipole moment due to f electrons in R sites of the cubically symmetric X_{12} cage.[1–17] In addition, it is well known that filled skutterudite compounds show a low glasslike thermal conductivity.[18,19] It has been presumed

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that this suppression of thermal conductivity comes from low-energy optical modes associated with the vibration of R ions in the X_{12} cage.[20] This characteristic vibration is called "rattling vibration" or the "guest ion mode". Furthermore, recently, some interesting phenomena such as ultrasonic absorption in $Ln$$Os_4Sb_{12}$ and a novel heavy-fermion state robust against magnetic fields in $SmOs_4Sb_{12}$ have been reported.[21–23] It has been proposed that the electron-phonon coupling between conduction electrons and guest ion modes is responsible for these interesting phenomena.[24,25]

To clarify the above-mentioned interesting phenomena, more basic information on the phonon modes is required. In particular, it is important to reveal the chemical trend on low-energy guest-ion optical modes (LGOMs). From an analysis of the specific heat of La-based filled skutterudites, we can make a rough estimate of the phonon spectrum in the low-energy region because lattice specific heat is obtained by subtracting the contribution of the electronic specific heat γT from the total specific heat C, where γ is the electronic specific heat coefficient. We can obtain γ and the Debye temperature Θ_D by applying the Debye T^3 law at low temperatures. However, for filled skutterudites, since significant deviations from the Debye T^3 law are caused by LGOMs, we have to carefully estimate γ and Θ_D. LGOMs characterized by Einstein specific heat lead to a broad maximum in $(C-\gamma T)/T^3$ at $\sim \Theta_E/4.92$, where Θ_E is the Einstein temperature; the peak in $(C - \gamma T)/T^3$ cannot be described by Debye specific heat. Therefore, we can obtain Θ_E from the maximum temperature T_{max} in $(C - \gamma T)/T^3$. Θ_E roughly corresponds to the energy of LGOMs. In this paper, we report the lattice specific heat of LaT_4X_{12} and discuss the Θ_D and Θ_E of these compounds. In addition, we examine the correlations between the energy of LGOMs (Θ_E) and structural parameters in filled skutterudites.

2. Experimental Procedure

Polycrystalline samples of LaT_4P_{12}, LaT_4As_{12} (T=Fe, Ru, Os), and RhP_3 were prepared at high temperatures and high pressures. A polycrystalline sample of $LaFe_4Sb_{12}$ was prepared as reported in ref. 26. Single crystals of LaT_4Sb_{12} (T=Ru, Os) were grown by the Sb-self-flux method.[27] Specific heat measurement was carried out by a thermal-relaxation method (PPMS, Quantum Design Inc.) from 1.8 to 300 K.

3. Results and Discussion

3.1 Analysis of specific heat

Figures 1(a) and 1(b) show the specific heat divided by the temperature C/T for $LaRu_4P_{12}$ and $LaOs_4Sb_{12}$, respectively. Both compounds show a superconducting transition at T_{SC}=7 K and T_{SC}=0.74 K, respectively.[28] In Fig. 1(a), the anomaly in $C(T)$ at 7 K originates from this superconducting transition. For $LaRu_4P_{12}$, we obtained the specific heat in the normal state by applying a magnetic field with a strength above H_{c2}. In a magnetic field of 3 T, the

$C(T)$ for $LaRu_4P_{12}$ between 2.8 and 6 K can be well fitted by $C/T = \gamma + \beta T^2$ (Debye T^3 law); $\Theta_D = (12\pi^4 R_g n/5\beta)^{1/3}$, where R_g is the gas constant and n=17. In this manner we obtained γ = 28.8 mJ/K^2 mole and Θ_D=603 K, as previously reported.[29] As the temperature range in which $C(T)$ obeys the Debye T^3 law tends to be narrow in filled skutterudites, we have to carefully estimate γ and Θ_D; significant deviations from the Debye T^3 law are caused by LGOMs, as will be discussed later. As seen in Fig. 1(b), the $C(T)$ of $LaOs_4Sb_{12}$ obeys the Debye T^3 law below 4 K, and in this region we obtained γ = 54 mJ/K^2 mole and Θ_D=270 K. γ is consistent with previous reports.[30,31]

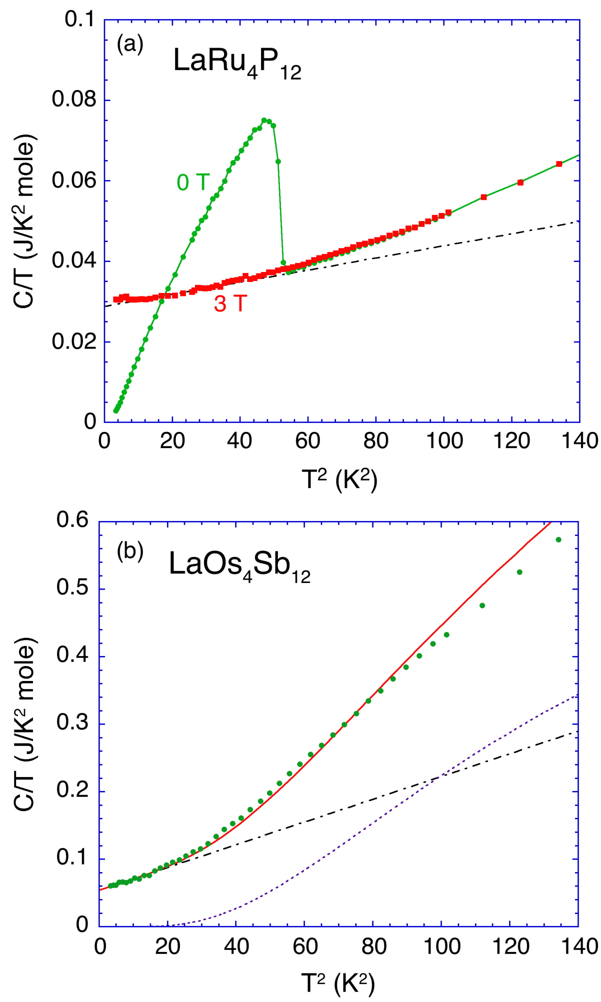

Fig. 1. (a) (Color online) Specific heat divided by temperature C/T for $LaRu_4P_{12}$ of magnetic fields of 0 and 3 T. The dash-dotted line represents a fit using the Debye T^3 law. (b) (Color online) Specific heat divided by temperature C/T for $LaOs_4Sb_{12}$. The dash-dotted line shows $C/T = \gamma + C_D(T, \Theta_D)/T$ with γ=54 mJ/K^2 mole, Θ_D=270 K. The dotted line represents $C_E(T, \Theta_E)/T$ whith Θ_E=60.5 K. The solid line shows the sum of these contributions.

Figure 2 shows the temperature dependence of $(C - \gamma T)/T^3$ for LaT_4X_{12}. Below 10 K, $(C-$

$\gamma T)/T^3$ tends to have a finite value (β). This behavior is characterized by the Debye specific heat $C_{\rm D}(T, \Theta_{\rm D})$ at low temperatures; $C_{\rm D}(T,\Theta_{\rm D} = 670$ K) is shown in Fig. 2. Furthermore, we can easily see the contribution of LGOMs in the C/T^3 plot. It should be noted that all of the compounds exhibit a large broad maximum at around 10 - 30 K, which is a commonly observed feature in filled skutterudites. The broad maximum is characterized by the Einstein specific heat $C_{\rm E}(T, \Theta_{\rm E})$; $C_{\rm D}(T, \Theta_{\rm D})$ has no maximum in the C/T^3 plot. The maximum in the $C_{\rm E}/T^3$ plot is located at $T_{\rm max} \cong \Theta_{\rm E}/4.92$; $C_{\rm E}(T,\Theta_{\rm E} = 140$ K) is also shown in Fig. 2. Therefore, we can estimate $\Theta_{\rm E}$ from $T_{\rm max}$ in $(C - \gamma T)/T^3$. Recent Raman and inelastic X-ray scattering (IXS) studies have observed LGOMs.[32–34] In light of these results, $\Theta_{\rm E}$ can be said to roughly correspond to the energy of LGOMs. The values of γ, $\Theta_{\rm D}$, and $\Theta_{\rm E}$ of LaT_4X$_{12}$ are shown in Table I. The LGOMs of LaT_4X_{12} are centered at around 60 - 140 K.

It has been reported that the specific heat of AT_4Sb$_{12}$ (A=Ca, Sr, Ba, La; T=Fe, Ru, Os) is roughly the sum of $C_{\rm E}(T, \Theta_{\rm E})$ and $C_{\rm D}(T, \Theta_{\rm D})$.[35] In the same way, we found that the specific heat of LaT_4X$_{12}$ is roughly equal to the sum of $C_{\rm E}(T, \Theta_{\rm E})$ and $C_{\rm D}(T, \Theta_{\rm D})$ (not shown). This result suggests that the dispersion of LGOMs is weak in filled skutterudites. For example, we obtained a good fit (solid line) for the specific heat of LaOs$_4$Sb$_{12}$ below 9 K (Fig. 1 (b)). The fitting curve is described by $C/T = \gamma + C_{\rm D}(T,\ \Theta_{\rm D} = 270\ {\rm K})/T + C_{\rm E}(T,\ \Theta_{\rm E} = 60.5\ {\rm K})/T$, where γ is 54 mJ/K^2 mole.

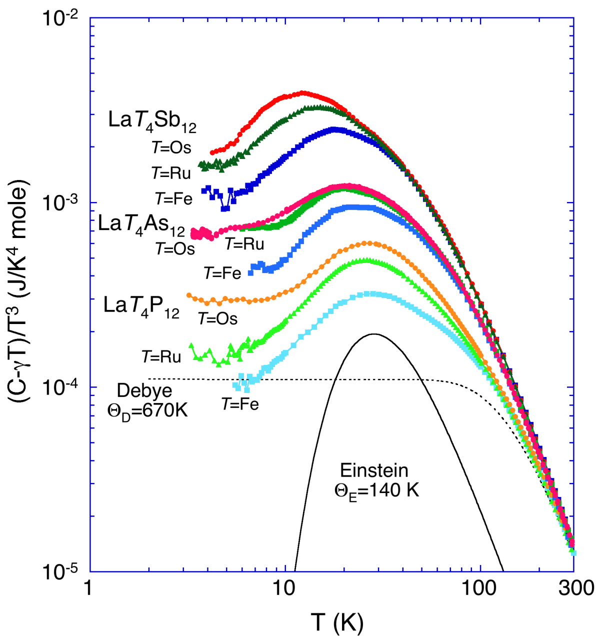

Fig. 2. (Color online) Temperature dependence of $(C - \gamma T)/T^3$ for LaT_4X_{12}.

Table I. Electronic specific heat coefficients γ, Debye temperatures Θ_D, and Einstein temperatures Θ_E for LaT_4X$_{12}$.

Compound	γ (mJ/K^2 mole)	Θ_D (K)	Θ_E (K)
$LaFe_4P_{12}$	52	670	138
$LaRu_4P_{12}$	29	603	128
$LaOs_4P_{12}$	20	482	131
$LaFe_4As_{12}$	135	421	113
$LaRu_4As_{12}$	58	355	98.4
$LaOs_4As_{12}$	49	360	99.4
$LaFe_4Sb_{12}$	122	314	87.6
$LaRu_4Sb_{12}$	47	275	72.8
$LaOs_4Sb_{12}$	54	270	60.5

3.2 Specific heat of unfilled skutterudite RhP_3

Figure 3 shows the temperature dependences of $(C-\gamma T)/T^3$ for $LaRu_4P_{12}$ and RhP_3. The skutterudite RhP_3 has no La ions in the P_{12} cage, and is therefore a good reference compound for $LaRu_4P_{12}$ to clarify the effect of LGOM. For comparison with the lattice specific heat of $LaRu_4P_{12}$, the specific heat $(C-\gamma T)/T^3$ of RhP_3 is multiplied by 4 in Fig. 3. Although RhP_3 is thought of as a semiconductor,[36] a small contribution to the specific heat from a T-linear term was observed. The $C(T)$ curve for RhP_3 between 5 and 30 K can be well fitted by $C/T = \gamma + \beta T^2$, from which we obtained $\gamma = 3.79$ mJ/K^2 mole and $\Theta_D = 498$ K using n=4; the origin of the small T-linear term is not yet clear. Although the $(C-\gamma T)/T^3$ curve for $LaRu_4P_{12}$ exhibits a large broad maximum at around 26 K, the curve for RhP_3 has no such feature. This is good evidence that LGOMs are due to optical modes related to the presence of La ions that fill in the P_{12} cage. Therefore, we may conclude that the Θ_E of filled skutterudites roughly corresponds to the energy of LGOMs in the X_{12} cage.

3.3 Debye temperature

We next discuss the Debye temperature of LaT_4X$_{12}$. According to the Debye model, Θ_D is proportional to the velocity of sound in a solid. This in turn is proportional to the reciprocal of the square root of the density of the solid. Since density roughly corresponds to the average atomic mass M_{av}, Θ_D is ultimately linearly proportional to the reciprocal of the square root of M_{av}. The gradient of this linear relationship is roughly proportional to the square root of a force constant. Figure 4 shows the dependence of Θ_D on average atomic mass for LaT_4X$_{12}$. We found correlations between Θ_D and the reciprocal of the square root of M_{av} for LaT_4P$_{12}$, LaT_4As$_{12}$, and LaT_4Sb$_{12}$. The gradient for LaT_4P$_{12}$ is 1.2 times larger than that for LaT_4As$_{12}$ and 1.4 times larger than that for LaT_4Sb$_{12}$. Therefore, LaT_4P$_{12}$ is expected to be roughly

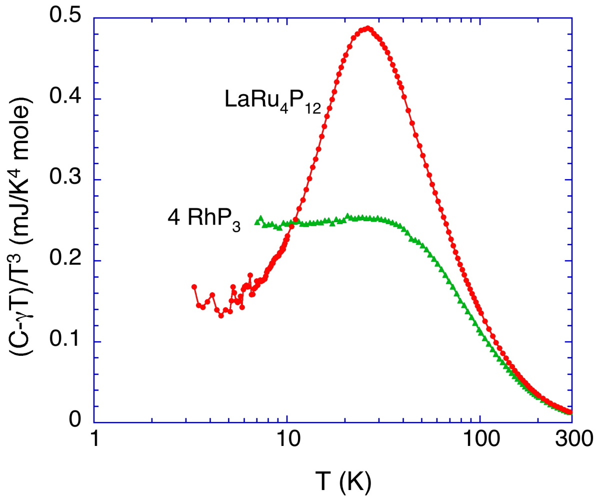

Fig. 3. (Color online) Temperature dependences of $(C - \gamma T)/T^3$ for $LaRu_4P_{12}$ and RhP_3. The $(C - \gamma T)/T^3$ curve for RhP_3 is multiplied by a factor of 4 for easier comparison.

2 times harder than LaT_4Sb_{12}. The bulk moduli of $LaRu_4P_{12}$ and $LaRu_4Sb_{12}$ are reported to be 172 and 98 GPa, respectively,[37] and the above results are consistent with these values. The X_{12} cage in filled skutterudites consists of X_4 rings formed by strong covalent bonds. The present result indicates that the Θ_D of filled skutterudites depends mainly on the nature of X.

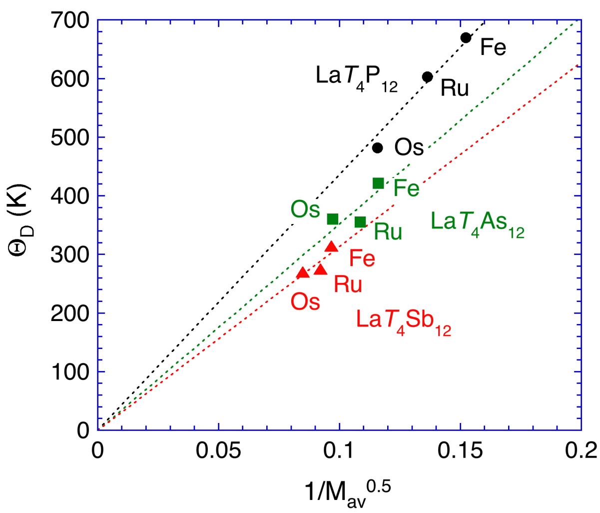

Fig. 4. (Color online) Dependence of Θ_D on average atomic mass.

3.4 Specific heats of $GdOs_4P_{12}$ and $GdRu_4P_{12}$

We next discuss the lattice specific heats of $GdOs_4P_{12}$ and $GdRu_4P_{12}$. $GdOs_4P_{12}$ exhibits a ferromagnetic transition at T_C=5 K,[38,39] whereas $GdRu_4P_{12}$ shows an antiferromagnetic transition at T_N=22 K.[7,40] Figure 5 shows the specific heats (ΔC) and entropies (ΔS) of $GdOs_4P_{12}$ and $GdRu_4P_{12}$. To obtain a $4f$ magnetic contribution, we estimated the ΔC values of $GdOs_4P_{12}$ and $GdRu_4P_{12}$ by subtracting the specific heats of $LaOs_4P_{12}$ and $LaRu_4P_{12}$, respectively, as nonmagnetic components. We now focus on the magnetic contribution of $GdOs_4P_{12}$. A broad peak in ΔC for $GdOs_4P_{12}$ appears at around 30 K in Fig. 5(a). The ΔS value of $GdOs_4P_{12}$ estimated using ΔC data is beyond Rln8 (14.9 J/K^2 mole), which is expected to be in the ground state S=7/2 multiplet of Gd^{3+}. However, in general, there is no splitting of CEF levels in the ground state of Gd^{3+}, and therefore the broad peak does not come from the Schottky anomaly.

The broad peak is best explained by a lattice contribution resulting from a significant shift of LGOMs towards a low energy. We have already reported on a similar phenomenon in $SmOs_4Sb_{12}$.[31] The effect of the energy shift of LGOMs on lattice specific heat is evaluated using Θ_E as a fitting parameter. We estimated the change in Θ_E for $GdOs_4P_{12}$ from Θ_E=131 K for $LaOs_4P_{12}$. The resulting ΔC_E curve is shown in Fig. 5(a) where $\Delta C_E(T) = C_E(T, \Theta_E) - C_E(T, \Theta_E = 131\text{ K})$. In this manner, we obtained Θ_E=87 K for $GdOs_4P_{12}$. The above-mentioned Schottky-like anomaly at 80 K is well reproduced by the curve. The *true* magnetic contribution appears below 20 K. In addition, ΔS after correcting for the contribution from ΔC_E is close to Rln8 at 80 K. In this analysis, excess entropy can also be explained by the low-energy shift of LGOMs. In a similar manner, we estimated Θ_E=98 K for $GdRu_4P_{12}$. The results for ΔC_E are shown in Fig. 5(b). The long tail in ΔC above T_N=22 K is mainly due to a significant energy shift of LGOMs towards a low energy. The *true* magnetic contribution appears below 30 K. A short-range ordering in this antiferromagnetic transition develops below this temperature.

3.5 Correlation between structure parameters and Θ_E

We will now discuss the correlations between structure parameters and Θ_E for $\mathrm{La}T_4X_{12}$, $\mathrm{Gd}T_4\mathrm{P}_{12}$, and $\mathrm{Sm}T_4X_{12}$. First, we define the guest free distance r_{GFD} as

$$r_{\mathrm{GFD}} = r_{\mathrm{R-X}} - r_{\mathrm{R3+}} - r_{\mathrm{X}}, \qquad (1)$$

where $r_{\mathrm{R-X}}$ is the distance between R and X, $r_{\mathrm{R3+}}$ is the effective ionic radius of R^{3+} for a 12-coordination-number site, and r_{X} is the covalent radius of X.[41] If the energy of LGOMs depends only on the structure parameters, we would expect to see a good correlation between r_{GFD} and Θ_E. In this estimation of r_{GFD}, we used the lattice parameters shown in Table II. In considering the effective space in the cage, we should take into account the effective ionic radius of rare-earth ions. The effective ionic radius of Sm^{3+} (1.24 Å) is smaller than

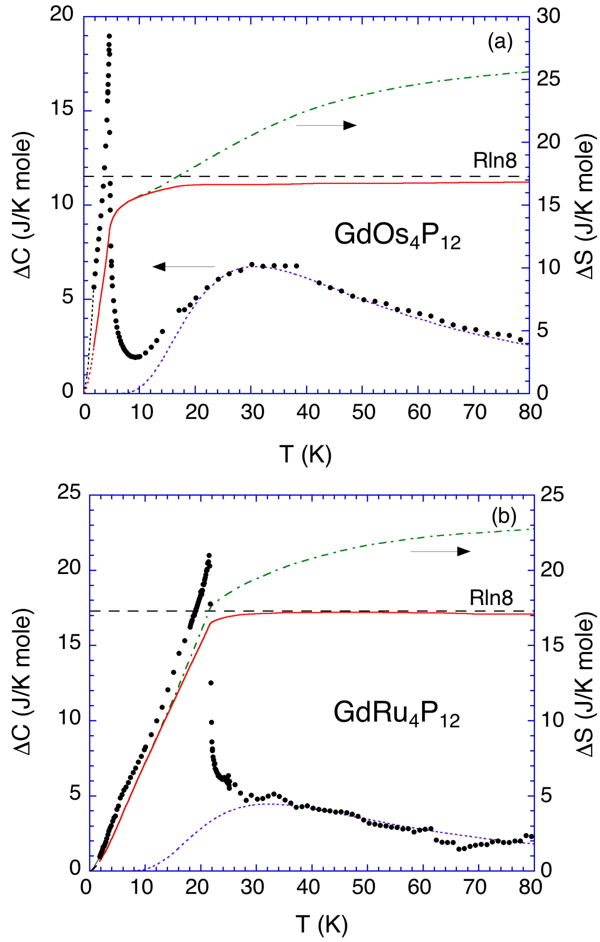

Fig. 5. (Color online) Specific heats (ΔC) and entropies (ΔS) of (a) $GdOs_4P_{12}$ and (b) $GdRu_4P_{12}$. The broken lines show $\Delta C_{\mathrm{E}}(T)$ (see text for details). The solid lines show the true magnetic entropy after correcting for the contribution of ΔC_{E}.

that of La^{3+} (1.36 Å). The effective ionic radius of Gd^{3+} for a 12-coordination-number site has not been reported so far. Therefore, we estimated it to be 1.21 Å by extrapolation from those of other rare-earth elements. To derive $r_{\mathrm{R-X}}$, we need the lattice parameters u and v. Unfortunately, these parameters, which determine the position of X atoms, have not been reported so far for $LaRu_4As_{12}$ or $LaOs_4As_{12}$. However, the relationship $u + v \sim 0.50$ is well-known for filled skutterudites. In fact, from Table II, we can see that $u + v = 0.500 \pm 0.005$ for the other compounds. Therefore, for the estimation of the $r_{\mathrm{R-X}}$ values of $LaRu_4As_{12}$ and $LaOs_4As_{12}$, we used the lattice parameters $u = 0.350 \pm 0.005$ and $v = 0.150 \mp 0.005$. Next, since the lattice parameters u and v for $\mathrm{Sm}T_4X_{12}$ and $\mathrm{Gd}T_4\mathrm{P}_{12}$ have also not been reported except in the case of the compound $SmOs_4Sb_{12}$, we substituted the parameters of the La analogue for those of $\mathrm{Sm}T_4X_{12}$ and $\mathrm{Gd}T_4\mathrm{P}_{12}$. Although ambiguities in u and v lead to an error of roughly 1% in the estimation of $r_{\mathrm{R-X}}$, this is not significant in the present discussion.

Table II. Lattice parameters (a (Å) and (u, v)) for RT_4X_{12}. nd: not determined.

Compound	a	(u, v)	Ref.
$LaFe_4P_{12}$	7.83160	(0.3539, 0.1504)	42
$SmFe_4P_{12}$	7.8029	nd	42
$LaRu_4P_{12}$	8.0610	(0.3591, 0.1428)	43
$SmRu_4P_{12}$	8.0397	nd	8
$GdRu_4P_{12}$	8.0375	nd	7
$LaOs_4P_{12}$	8.08197	(0.35700, 0.14002)	44
$GdOs_4P_{12}$	8.0657	nd	38
$LaFe_4As_{12}$	8.3252	(0.34556, 0.15474)	45
$SmFe_4As_{12}$	8.3003	nd	46
$LaRu_4As_{12}$	8.50810	nd	45
$LaOs_4As_{12}$	8.54370	nd	45
$LaFe_4Sb_{12}$	9.1395	(0.33696, 0.16042)	47
$SmFe_4Sb_{12}$	9.130	nd	48
$LaRu_4Sb_{12}$	9.2732	(0.34174, 0.1581)	49
$LaOs_4Sb_{12}$	9.30799	(0.34118, 0.1565)	49
$SmOs_4Sb_{12}$	9.3085	(0.34009, 0.15589)	50

The r_X values of P, As, and Sb are 1.06, 1.19 and 1.38 Å, respectively. Actually, the average X-X distance in the X_4 ring is close to $2r_X$ and slightly larger than $2r_X$.

Figures 6(a) and 6(b) show the dependences of Θ_E on r_{GFD} and $r_{R-X} - r_{R3+}$, respectively. For SmT_4X_{12}, the energy of LGOMs obtained by Raman scattering and IXS is shown in the figures.[32–34] We found that the correlation between r_{GFD} and Θ_E is not strong at first sight. Instead, there appears to be a better linear correlation between $r_{R-X} - r_{R3+}$ and Θ_E, which suggests that r_X does not affect Θ_E. One reason for the deviation may be the rigidity of the X_{12} cage. The X_4 ring has a strong covalency as mentioned above, and the X_{12} cage is formed by six such rings, each of which connects between two X_{12} cages. Associated with each X_{12} cage, there are two different X-X distances. The X-X distance in the X_4 ring is close to $2r_X$. However, the second X-X distance is 1.4 - 1.7 times longer than $2r_X$. Since the degree of covalency in the X_{12} cage is not so strong, the cage is not very rigid. As noted previously in the discussion on the Θ_D of LaT_4X_{12}, LaT_4P_{12} is roughly 2 times harder than LaT_4Sb_{12}; thus, we can expect that the Sb_{12} cage is less rigid. For a nonrigid cage, the concept of guest free distance collapses. Therefore, the deformation of the X_{12} cage may cause a significant deviation from the linear correlation between r_{GFD} and Θ_E. Another possibility is that, since all of these compounds are metallic, both the X_{12} cage and the simple cubic T-lattice are conductive. Since bondings in the X_{12} cage, in the simple cubic T-lattice, and between X and T sites are the most important contributions to metallicity, the covalent radius of the X_{12} cage is not important for guest ions. Therefore, Θ_{E} is unaffected by r_{X}.

Next, it should be noted that the deviation from the linear relationship between $r_{\mathrm{R-X}} - r_{\mathrm{R3+}}$ and Θ_{E} for Os skutterudites with f electrons can be seen in Fig. 6(b). This suggests that some other factors affect LGOMs. One such factor is a strong electron-lattice interaction, which can lead to anharmonic vibration.[51] When LGOM exhibits strong anharmonic vibration, the energy of LGOM decreases upon cooling.[52] In fact, the energy of LGOMs for $LaOs_4Sb_{12}$ is decreased by 5% from 300 down to 4 K; it is suggested that LGOMs for $LaOs_4Sb_{12}$ are anharmonic.[33] Although in these calculations we used Θ_{E} estimated at low temperatures, the structure parameters used were determined at room temperature. At low temperatures, these differences are expected to become larger. The present result suggests a strong anharmonic vibration of LGOMs in Os skutterudites. Another possible origin is a strong c-f hybridization effect, which may lead to a strong interaction between the R-filler with $4f$ electrons and the X_{12} cage and the T lattice with conduction electrons. Actually, novel types of behavior resulting from a strong c-f hybridization have been reported in many Os skutterudites with f electrons.[9,22,23,53–57] Further study is needed to clarify how the interaction between the guest ions and the host cage due to c-f hybridization affects LGOM.

Now, we discuss the significant deviation from the linear relationship between $r_{\mathrm{R-X}} - r_{\mathrm{R3+}}$ and Θ_{E} for $SmOs_4Sb_{12}$ in Fig. 6(b). This compound is known to be an intermediate-valence heavy-fermion compound; the average valence of Sm ions is 2.83 at room temperature.[54] From a recent result on the temperature dependence of structure parameters for $SmOs_4Sb_{12}$, the Sm-Sb distance has been found to decrease by 0.016 Å as the temperature changes from 300 to 20 K.[56] Thus, the guest free distance of $SmOs_4Sb_{12}$ decreases with a decrease in temperature. The deviation from the linear correlation between $r_{\mathrm{R-X}} - r_{\mathrm{R3+}}$ and Θ_{E} becomes much greater at low temperatures. Furthermore, the average effective ionic radius of Sm ions in $SmOs_4Sb_{12}$ is larger than $r_{\mathrm{R3+}}$ for Sm^{3+} because of the existence of Sm^{2+} with a larger effective ionic radius. Since the difference between the Sm-Sb distance and the average effective ionic radius of Sm is much smaller than $r_{\mathrm{R-X}} - r_{\mathrm{R3+}}$, the deviation seen in Fig. 6(b) becomes clear. This means that the energy of LGOMs in $SmOs_4Sb_{12}$ is not determined by only the structure parameters. The above results strongly suggest that the guest-host interaction due to c-f hybridization plays an important role in determining the LGOMs of $SmOs_4Sb_{12}$.

4. Conclusions

We have systematically studied the lattice specific heat of La-based filled skutterudites $\mathrm{La}T_4X_{12}$ (T=Fe, Ru and Os; X=P, As and Sb), and their Θ_{D} and Θ_{E} were carefully determined. The Θ_{D} of filled skutterudites was found to depend mainly on the nature of the X species forming the cage; $\mathrm{La}T_4\mathrm{P}_{12}$ was shown to be roughly 2 times harder than $\mathrm{La}T_4\mathrm{Sb}_{12}$.

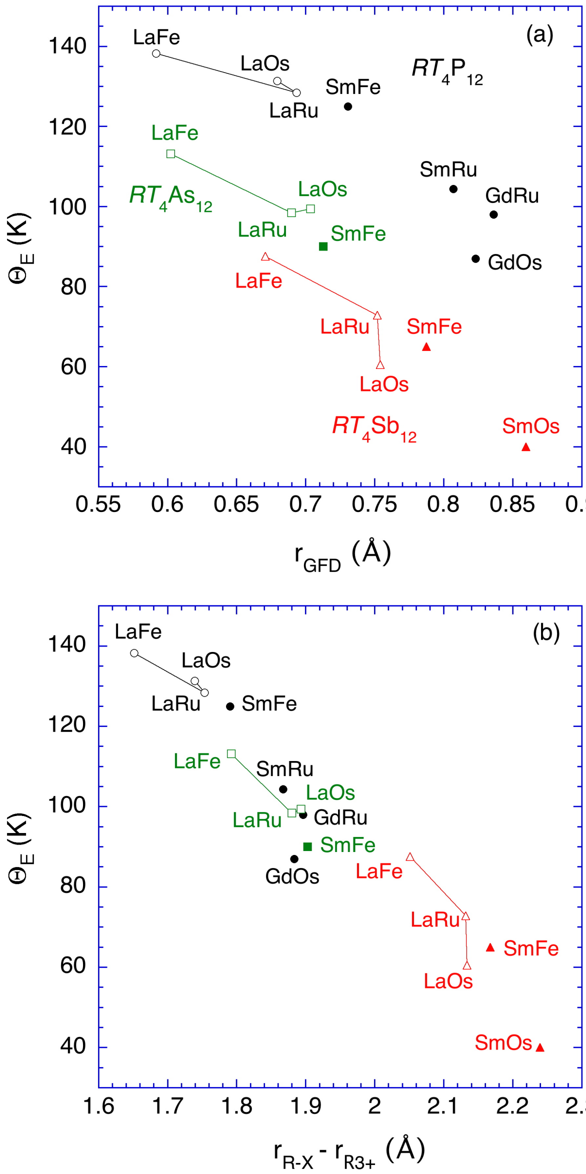

Fig. 6. (Color online) Dependences of Θ_E on (a) guest free distance r_{GFD} and (b) $r_{R-X} - r_{R3+}$ for RT_4P_{12} (open circles: R=La, closed circles: R=Sm and Gd), RT_4As_{12} (open squares: R= La, closed squares: R=Sm), and RT_4Sb_{12} (open triangles: R= La, closed triangles: R=Sm and Gd).

The Θ_E of filled skutterudites was found to correspond roughly to the energy of LGOMs. We found a good linear correlation between $r_{R-X} - r_{R3+}$ and Θ_E, with Θ_E decreasing as $r_{R-X} - r_{R3+}$ increases. However, we found a deviation from the linear relationship between $r_{R-X} - r_{R3+}$ and Θ_E for Os compounds with f electrons. This was discussed in terms of the effects of both anharmonic vibration due to a strong electron-lattice interaction and guest-host interaction due to c-f hybridization in these compounds. In particular, for $SmOs_4Sb_{12}$, the present results suggest that the guest-host interaction due to c-f hybridization has the most critical effect on LGOMs.

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References

1) G. P. Meisner: Physica B **108** (1981) 763.
2) G. P. Meisner, M. S. Torikachvili, K. N. Yang, M. B. Maple, and R. P. Guertin: J. Appl. Phys. **57** (1985) 3073.
3) I. Shirotani, T. Adachi, K. Tachi, S. Todo, K. Nozawa, T. Yagi, and M. Kinoshita: J. Chem. Solids **57** (1996) 211.
4) I. Shirotani, T. Uchiumi, K. Ohno, C. Sekine, Y. Nakazawa, K. Kanoda, S. Todo, and T. Yagi: Phys. Rev. B **56** (1997) 7866.
5) C. Sekine, T. Uchiumi, I. Shirotani, and T. Yagi: Phys. Rev. Lett. **79** (1997) 3218.
6) H. Sato, Y. Abe, H. Okada, T. D. Matsuda, K. Abe, H. Sugawara, and Y. Aoki: Phys. Rev. B **62** (2000) 15125.
7) C. Sekine, T. Uchiumi, I. Shirotani, K. Matsuhira, T. Sakakibara, T. Goto, and T. Yagi: Phys. Rev. B **62** (2000) 11581.
8) C. Sekine, T. Uchiumi, I. Shirotani and T. Yagi: in *Science and Technology of High Pressure*, ed. M. H. Manghnant and M. F. Nicol (Universities Press, Hyderabad, India, 2000) p. 826.
9) E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple: Phys. Rev. B **65** (2002) 100506.
10) H. Sugawara, T. D. Matsuda, K. Abe, Y. Aoki, H. Sato, S. Nojiri, Y. Inada, R. Settai, and Y Ōnuki: Phys. Rev. B **66** (2002) 134411.
11) K. Matsuhira, Y. Hinatsu, C. Sekine, T. Togashi, H. Maki, I. Shirotani, H. Kitazawa, T. Takamasu and G. Kido: J. Phys. Soc. Jpn. **71** (2002) Suppl. p. 237.
12) M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, H. Sugawara: J. Phys. Soc. Jpn. **72** (2003) 1002.
13) C. H. Lee, H. Matsuhata, H. Yamaguchi, C. Sekine, K. Kihou, T. Suzuki, T. Noro, and I. Shirotani: Phys. Rev. B **70** (2004) 153105.
14) M. Yoshizawa, Y. Nakanishi, M. Oikawa, C. Sekine, I. Shirotani, S. R. Saha, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **74** (2005) 2141.
15) I. Shirotani, S. Sato, C. Sekine, K. Takeda, I. Inagawa, and T. Yagi: J. Phys.: Condens. Matter **17** (2005) 7353.
16) T. Takimoto: Physica B **378-380** (2006) 252.
17) Y. Kuramoto and A. Kiss: J. Phys. Soc. Jpn. **77** (2008) Suppl. A 187.
18) B. C. Sales, D. Mandrus, and R. K. Williams: Science **272** (1996) 1325.
19) G. S. Nolas, G. A. Slack, D. T. Morelli, T. M. Tritt, and A. C. Ehrlich: J. Appl. Phys. **79** (1996) 4002.
20) V. Keppens, D. Mandrus, B. C. Sales, B. C. Chakoumakos. P. Dai, R. Coldea, M. B. Maple, D. A. Gajewski, E. J. Freeman, and S. Bennington: Nature **395** (1998) 876.
21) T. Goto, Y. Nemoto, K. Sakai, T. Yamaguchi, M. Akatsu, T. Yanagisawa, H. Hazama, K. Onuki, H. Sugawara, and H. Sato: Phys. Rev. B **69** (2004) 180511R.
22) T. Yanagisawa, W. M. Yuhasz, P.-C. Ho, M. B. Maple, H. Watanabe, Y. Yasumoto, Y. Nemoto, and T. Goto: Physica B **403** (2008) 735.
23) S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **74** (2005) 246.

24) K. Hattori and K. Miyake: J. Phys. Soc. Jpn. **76** (2007) 094603.
25) T. Hotta: J. Phys. Soc. Jpn. **77** (2008) 103711.
26) D. T. Morelli and G. P. Meisner: J. Appl. Phys. **77** (1995) 3777.
27) H. Sugawara, S. Osaki, S. R. Saha, Y. Aoki, H. Sato, Y. Inada, H. Shishido, R. Settai, Y. Onuki, H. Harima, and K. Oikawa: Phys. Rev. B **66** (2002) 220504.
28) L. E. DeLong and G. P. Meisner: Soild State Commun. **53** (1985) 119.
29) K. Matsuhira, Y. Doi, M. Wakeshima, Y. Hinatsu, H. Amitsuka, Y. Shimaya, R. Giri, C.Sekine, and I. Shirotani: J. Phys. Soc. Jpn. **74** (2005) 1030.
30) Y. Aoki, W. Higemoto, S. Sanada, K. Ohishi, S.R. Saha, A. Koda, K. Nishiyama, R. Kadono, H. Sugawara, and H. Sato: Physica B **359-361** (2005) 895.
31) K. Matsuhira, M. Wakeshima, Y. Hinatsu, C. Sekine, I. Shirotani, D. Kikuchi, H. Sugawara, and H. Sato: J. Magn. Magn. Mater. **310** (2007) 226.
32) N. Ogita, T. Kondo, T. Hasegawa, Y. Takasu, M. Udagawa, N. Takeda, K. Ishikawa, H. Sugawara, D. Kukuchi, H. Sato, C. Sekine, I. Shirotani: Physica B **383** (2006) 128.
33) S. Tsutsui, H. Kobayashi, J. P. Sutter, H. Uchiyama, A. Q. R. Baron, Y. Yoda, D. Kikuchi, H. Sugawara, C. Sekine, I. Shirotani, A. Ochiai, and H. Sato: J. Phys. Soc. Jpn. **77** (2008) Suppl. A 257.
34) S. Tsutsui, Y. Yoda, and H. Kobayashi: J. Phys. Soc. Jpn. **76** (2007) 065003.
35) T. Takabatake, E. Matsuoka, S. Narazu, K. Hayashi, S. Morimoto, T. Sasakawa, K. Umeo, and M. Sera: Physica B **383** (2006) 93.
36) A. Watcharapasorn, R. C. DeMattei, R.S . Feigelson, T. Caillat, A. Borshchevsky, G. J. Snyder, and J.-P. Fleurial: J. Appl. Phys. **86** (1999) 6213.
37) I. Shirotani, T. Noro, J. Hayashi, C. Sekine, R. Giri, and T. Kikegawa: J. Phys.: Condens. Matter **16** (2004) 7853.
38) K. Kihou, I. Shirotani, C. Sekine, and T. Yagi: Mater. Res. Bull. **39** (2004) 317.
39) C. Sekine, H. Ando, Y. Sugiuchi, I. Shirotani, K. Matsuhira, and M. Wakeshima: J. Phys. Soc. Jpn. **77** (2008) Suppl. A 135.
40) K. Matsuhira, C. Sekine, K. Kihou, I. Shirotani, M. Wakeshima, Y. Hinatsu, Y. Sei, A. Nakamura, and S. Takagi: Physica B **378-380** (2006) 235.
41) R. Shannon: Acta Cryst. **A32** (1976) 751.
42) W. Jeitschko and D. Braun: Acta Crystallogr., Sect. B **33** (1977) 3401.
43) I. Shirotani, T. Uchiumi, C. Sekine, M. Hori, S. Kimura, and N. Hamaya: J. Solid State Chem. **142** (1999) 146.
44) C. Sekine and K. Takeda: private communication.
45) D. J. Braun and W. Jeitschko: J. Solid State Chem. **32** (1980) 357.
46) T. Namiki and C. Sekine: private communication.
47) D. J. Braun and W. Jeitschko: J. Less-Common Metals **72** (1980) 147.
48) C. B. H. Evers, W. Jeitschko, L. Boonk, D. J. Braun, T. Ebel, and U. D. Scholz: J. Alloys and Compounds **224** (1995) 184.
49) K. Oikawa: in *Skutterudite News Letter*, ed. H. Sato and H. Harima, (2004) No. 2, p. 8 [in Japanese].
50) W. M. Yuhasz, N. A. Frederick, P.-C. Ho, N. P. Butch, B. J. Taylor, T. A. Sayles, M. B. Maple, J. B. Betts, A. H. Lacerda, P. Rogl, and G. Giester: Phys. Rev. B **71** (2005) 104402.

51) C. C. Yu and P. W. Anderson: Phys. Rev. B **29** (1984) 6165.

52) M. Udagawa, T. Hasegawa, Y. Takasu, N. Ogita, K. Suekuni, M. A. Avila, T. Takabatake, Y. Ishikawa, N. Takeda, Y. Nemoto, T. Goto, H. Sugawara, D. Kikuchi, H. Sato, C. Sekine, I. Shirotani, J. Yamaura, Y. Nagao, and Z. Hiroi: J. Phys. Soc. Jpn. **77** (2008) Suppl. A 142.

53) H. Sugawara, S. Osaki, M. Kobayashi, T. Namiki, S. R. Saha, Y. Aoki, and H. Sato: Phys. Rev. B **71** (2005) 125127.

54) M. Mizumaki, S. Tsutsui, H. Tanida, T. Uruga, D. Kikuchi, H. Sugawara, and H. Sato: J. Phys. Soc. Jpn. **76** (2007) 053706.

55) A. Yamasaki, S. Imada, H. Higashimichi, H. Fujiwara, T. Saita, T. Miyamachi, A. Sekiyama, H. Sugawara, H. Sato, A. Higashiya, M. Yabashi, K. Tamasaku, D. Miwa, T. Ishikawa, and S. Suga: Phys. Rev. Lett. **98** (2007) 156402.

56) M. Tsubota, S. Tsutsui, D. Kikuchi, H. Sugawara, H. Sato, and Y. Murakami: J. Phys. Soc. Jpn. **77** (2008) 073601.

57) S. Tsutsui, M. Mizumaki, M. Tsubota, H. Tanida, T. Uruga, Y. Murakami, D. Kikuchi, H. Sugawara, and H. Sato: J. Phys.: Conf. Ser. **150** (2009) 042220.