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Atomic dynamics of low-lying rare-earth guest modes in heavy fermion filled skutterudites $R\mathrm{Os}_4\mathrm{Sb}_{12}$ (R = light rare-earth)

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The atomic dynamics of the guest modes in heavy fermion filled skutterudites $R\mathrm{Os}_4\mathrm{Sb}_{12}$ were investigated by inelastic x-ray scattering. Comparison of the phonon dispersion relations for the filled skutterudite $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ with those for the unfilled skutterudite IrSb_3 indicates that the guest modes in filled skutterudites are observed as additional modes in the unfilled skutterudites. The dispersion relations for IrSb_3 and $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ agree reasonably well with the results obtained by *ab initio* calculations for IrSb_3 and $\mathrm{LaOs}_4\mathrm{Sb}_{12}$, respectively. The rare-earth dependence of the inelastic x-ray scattering spectrum in the series of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds is difficult to interpret in terms of changes in the atomic mass and electron number of the rare-earth atom inserted into the Sb cage. The combination of inelastic x-ray scattering and x-ray absorption spectroscopy reveals a correlation between the guest mode energy and the guest free space in these compounds. The rare-earth dependence of the inelastic x-ray scattering spectrum indicates the mediation of heavy fermion behavior by the atomic motion of the guest in some $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds and the electron-phonon coupling between the guest modes with $4f$-electrons and conduction electrons in the series of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds.

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I. INTRODUCTION

Heavy fermion (HF) behavior is one of many important problems in strongly correlated electron systems (SCES), particularly, those in rare-earth and actinide compounds. Many HF compounds have already been found among the rare-earth and actinide intermetallics. A common feature of HF compounds is a large electronic specific heat coefficient γ of over 100 mJ mol^{-1} K^{-2}, reflecting the mass enhancement of conduction electrons. For conventional HF compounds, the origin of the large mass enhancement comes from a formation of the Fermi-liquid state through the Kondo effect. Most of the HF compounds are located near a quantum critical point in Doniach's phase diagram[1] where the Ruderman-Kittel-Kasuya-Yosida interaction and the Kondo effect compete against each other. This interpretation is based on the correlation of HF behavior with the magnetism at rare-earth or actinide sites. Thus, such large γ values have been approximately understood as a transformation of the magnetic degrees of freedom of the f electrons. In such a case, γ values are generally proportional to the inverse of the Kondo temperature T_{K}. Typical values of T_{K} in conventional HF compounds are $\sim$100 K or less. On the other hand, theoretical models of phonon-mediated HF behavior, which is free from magnetic degrees of freedom, unlike conventional HF behavior, have been proposed.[2–4] These models require the presence of low-lying Einstein modes coupled with conduction electrons. In reality, this indicates that HF behavior may be driven by a low-lying dispersionless mode coupled with conduction electrons that can be treated as an Einstein mode. In these models, the energy characteristic of HF behavior is an Einstein temperature θ_{E}, which corresponds to the Kondo temperature T_{K}. The origin of the mass enhancement comes from the electron-phonon coupling between a low-lying dispersionless mode and the conduction electrons. To realize phonon-mediated HF behavior, the Einstein temperature, corresponding to the phonon energy of low-lying optical modes, should be $\theta_{\mathrm{E}} < \sim 100$ K.

The roles of low-lying optical modes in SCES have been discussed in recent years for cage-structured compounds, such as filled skutterudites, clathrates, β-pyrochlore, and rare-earth hexaboride compounds.[5–8] The crystal structure of these compounds allows the presence of an Einstein-like mode because the cage size is sufficiently large for one atom to be inserted into the cage structure as a guest atom. In this case, the guest atom in the cage structure behaves as an Einstein oscillator with a low Einstein temperature. Concerning filled skutterudites and clathrates, much attention was originally paid to low-lying optical modes from the viewpoint of their thermal insulation due to phonons in the phonon-glass-electron-crystal (PGEC) model.[9] Many investigations were carried out by both macroscopic and microscopic measurements. For the filled skutterudites, observations of low-lying dispersionless modes below $\sim$10 meV in inelastic neutron and x-ray scattering experiments[10–17] and those of Einstein temperatures below $\sim$100 K in specific heat, x-ray diffraction, extended x-ray absorption fine structure (EXAFS), and nuclear magnetic resonance (NMR)/nuclear quadrupole

TABLE I. Electronic specific heat coefficient γ reported in the literature and the line broadening of the guest modes obtained in the present paper for the series of $R\mathrm{Os_4Sb_{12}}$ compounds.

		Line broadening (meV)		
Compound	γ (mJ mol^{-1} K^{-2})	$H(L)$ point	$N(T)$ point	References
$\mathrm{LaOs_4Sb_{12}}$	36–56	0.43 ± 0.15	0.32 ± 0.10	35 and 36
$\mathrm{CeOs_4Sb_{12}}$	92–180	0.35 ± 0.06	0.00 ± 0.20	37 and 39
$\mathrm{PrOs_4Sb_{12}}$	310–750	0.51 ± 0.09	0.09 ± 0.17	38, 40, and 41
$\mathrm{NdOs_4Sb_{12}}$	520	0.63 ± 0.09	0.36 ± 0.22	42
$\mathrm{SmOs_4Sb_{12}}$	820–880	0.91 ± 0.16	0.75 ± 0.28	29 and 43
$\mathrm{EuOs_4Sb_{12}}$	135	0.26 ± 0.09	0.09 ± 0.13	44

resonance (NQR) experiments have been reported.[18–25] At the beginning of the investigation of low-lying optical modes in filled skutterudites,[6,10,12,26–28] which are called guest modes hereafter, it was discussed whether or not the guest modes were localized. This means that the presence of an Einstein-like localized mode is important in proving the validity of the PGEC model. The phonon dispersion relations clarified by inelastic neutron and x-ray scattering experiments demonstrate that the guest modes are hybridized with acoustic modes.[13,14] In other words, the observation of hybridization between the Einstein-like dispersionless mode and an acoustic mode denies the presence of localized modes predicted from the PGEC model.[13–15] It also invalidates the presence of Einstein modes in the PGEC model and implies the necessity for reconsidering the thermal insulation mechanism in thermoelectric materials.

The discovery of HF behavior in $\mathrm{SmOs_4Sb_{12}}$ provided a good opportunity to investigate the correlation between large γ values and guest modes in filled skutterudites.[29] The γ value for $\mathrm{SmOs_4Sb_{12}}$ is insensitive to the applied magnetic field. This implies that nonmagnetic degrees of freedom are a plausible origin of the HF behavior in this compound. One of the candidates in the nonmagnetic origin of HF behavior is an Einstein-like phonon with low energy that has been theoretically predicted.[2–4] However, $\mathrm{SmOs_4Sb_{12}}$ is not the only possible phonon-mediated HF compound in filled skutterudites. In fact, the presence of low-lying guest modes has already been reported for some $R\mathrm{Os_4Sb_{12}}$ compounds.[30–34] In addition, the γ values for the series of filled skutterudites $R\mathrm{Os_4Sb_{12}}$ are large as shown in Table I.[29,35–44] The compounds that contain $4f$-electrons have a γ value of over 100 mJ mol^{-1} K^{-2}, which is a typical γ value in HF compounds. Even for $\mathrm{LaOs_4Sb_{12}}$, which contains no $4f$-electrons, the γ value is about 50 mJ mol^{-1} K^{-2}and varies slightly in the literature.[35,36] Furthermore, the γ value for $\mathrm{EuOs_4Sb_{12}}$, 135 mJ mol^{-1} K^{-2},[36] is also anomalously large among the Eu compounds. $\mathrm{EuOs_4Sb_{12}}$ undergoes ferromagnetic ordering below 9 K.[35] In general, no reduction in the ordered magnetic moments due to the effect of the crystal electric field (CEF) or the Kondo effect, such as those observed in the other rare-earth compounds has been predicted for Eu compounds. This means that $\mathrm{EuOs_4Sb_{12}}$ has few magnetic degrees of freedom that can cause the enhanced γ value. These facts infer that the mass enhancement of the conduction electrons is correlated with the crystal structure of the filled skutterudites.

The investigation of the phonon dispersion in the guest mode of cage-structured compounds has already been carried out in $\mathrm{CeB_6}$ from the viewpoint of its electronic structure.[45] However, the purpose of the previous paper was not to investigate electron-phonon coupling but to estimate the lattice contribution to the specific heat because the lattice contribution of the guest modes at low temperatures was always large in such cage-structured compounds. The same problems tend to mislead interpretation of the lattice contribution to the specific heat in filled skutterudites as pointed out by Matsuhira *et al.*[46] In addition, second-order Raman scattering signals suggest a rare-earth dependence of the guest mode, making it difficult to discuss the direction dependence.[47] From this viewpoint, a systematic investigation of the guest modes in filled skutterudites is required to estimate the lattice contribution to the specific heat as well as to discuss the correlation between the γ value and the guest mode energy.

In the present paper, we carried out inelastic x-ray scattering (IXS) experiments on the series of $R\mathrm{Os_4Sb_{12}}$ compounds and the unfilled skutterudite $\mathrm{IrSb_3}$ at 300 K. The phonon dispersion relations of $\mathrm{SmOs_4Sb_{12}}$ and $\mathrm{IrSb_3}$ agree reasonably well with the calculated dispersion relations of $\mathrm{LaOs_4Sb_{12}}$ and $\mathrm{IrSb_3}$, respectively. The atomic motion of Sm was found to involve low-lying dispersionless modes by the comparison of experimental results as was also predicted by the comparison of calculated results. The IXS spectrum at zone boundaries showed rare-earth dependence. The guest mode energies in $\mathrm{SmOs_4Sb_{12}}$ and $\mathrm{EuOs_4Sb_{12}}$ deviated from the linear relation observed for $\mathrm{LaOs_4Sb_{12}}$, $\mathrm{CeOs_4Sb_{12}}$, $\mathrm{PrOs_4Sb_{12}}$, and $\mathrm{NdOs_4Sb_{12}}$. The combination of the IXS experiments with x-ray absorption spectroscopy (XAS) using rare-earth L_{III}-edges clarified that the guest mode energy in $R\mathrm{Os_4Sb_{12}}$ correlated with the guest free space, which means the space between the guest atoms and the cage surrounding it, in the Sb icosahedral cage. By comparing the experimental and calculated results, it was found that two types of contributions of the electronic states to the IXS spectra via electron-phonon coupling are essential for understanding the rare-earth dependence. One is the correlation of the guest mode spectrum with the presence of $4f$-electrons, and the other is the correlation between the phonon linewidth and the γ value in the series of $R\mathrm{Os_4Sb_{12}}$ compounds.

II. EXPERIMENTS AND RESULTS

A. IXS measurements

1. Experimental setup

IXS measurements of the series of $R\mathrm{Os_4Sb_{12}}$ compounds and $\mathrm{IrSb_3}$ were carried out at BL35XU of SPring-8 in Japan.[48]

The chosen experimental setup in the present paper was the Si(11 11 11) backscattering setup, whose energy resolution was 1.5 meV at 21.747 keV. The typical **Q** resolution in the measurements was $\Delta\mathbf{Q} \sim (0.13\ 0.12\ 0.08)$ in the reciprocal lattice unit of each compound. The measured temperature was 300 K for each compound.

The samples measured were single crystals fabricated by a Sb self-flux method.[36,49] Their typical sizes were about 1 mm^3 or less, and their rocking curve widths were $\sim 0.02°$, close to the resolution limit of the IXS spectrometer in BL35XU. This means that the uncertainty of the **Q** resolution due to the quality of the sample is negligible in the present paper.

2. *Experimental results*

IXS spectra obtained near the zone center of the unfilled skutterudite $\mathrm{IrSb_3}$ and filled skutterudite $\mathrm{SmOs_4Sb_{12}}$ at 300 K are shown in Figs. 1(a) and 1(b), respectively. The energy of the phonon excitation observed in $\mathrm{IrSb_3}$ increases when the $\boldsymbol{q}$ vector approaches a zone boundary, indicating an acoustic mode. On the other hand, two excitations are found in the low-energy region of the $\mathrm{SmOs_4Sb_{12}}$ spectra. One mode propagated with changes in the $\boldsymbol{q}$ vector as observed in $\mathrm{IrSb_3}$, and the other remained at nearly the same energy of about 5 meV. Since the crystal structures of both $\mathrm{IrSb_3}$ and $\mathrm{SmOs_4Sb_{12}}$ are identical except for the Sm atom in the icosahedral Sb cage, the low-lying mode represents the atomic vibration of Sm in the Sb cage.

Phonon dispersion relations obtained from the IXS spectra of $\mathrm{IrSb_3}$ and $\mathrm{SmOs_4Sb_{12}}$ are shown in Figs. 2(a) and 2(b), respectively. Comparison of the dispersion relation of $\mathrm{SmOs_4Sb_{12}}$ with that of $\mathrm{IrSb_3}$ clarified that the modes associated with the atomic motion of Sm were observed from 2 to 5 meV as additional modes with low energy in each high-symmetry direction of the unfilled skutterudite $\mathrm{IrSb_3}$, except for small energy differences in the acoustic modes due to the difference in the lattice constant between these compounds.[36,50] The dispersion relation of the guest mode is slightly different from that of the rare-earth filled skutterudites $\mathrm{CeRu_4Sb_{12}}$ and $\mathrm{SmRu_4P_{12}}$.[13,14,33] Although the guest mode energy is nearly independent of $\boldsymbol{q}$ in these compounds, that in $\mathrm{SmOs_4Sb_{12}}$ is dispersive in every high-symmetry direction. In addition, unlike the dispersion relation for $\mathrm{SmRu_4P_{12}}$,[14,33] the guest mode energies at zone boundaries show direction dependence. The highest guest mode is observed in the longitudinal [1 0 0] direction [$\Gamma-$H(L) direction], and the lowest one is observed in the transverse [0 1 1] direction polarized in the [1 0 0] direction [$\Gamma-$N(T) direction]. These findings infer that the interatomic interaction between the guest mode and the cage is different for $\mathrm{SmOs_4Sb_{12}}$ and $\mathrm{SmRu_4P_{12}}$.

Figure 3 shows phonon spectra around (9 0 0) and (8 0.5 0.5) at 300 K. These reciprocal points correspond to the H point in the $\Gamma-$H(L) direction [H(L) point] and the N point in the $\Gamma-$N(T) direction [N(T) point] of the filled skutterudites $R\mathrm{Os_4Sb_{12}}$ (R: light rare-earth element) at 300 K, respectively. Phonon excitations shown by closed arrows are guest modes in all the $R\mathrm{Os_4Sb_{12}}$ compounds, whereas, those shown by open arrows are acoustic modes. The former excitations in both the $\Gamma-$H(L) and the $\Gamma-$N(T) directions show strong rare-earth dependence, particularly in their excitation energies.

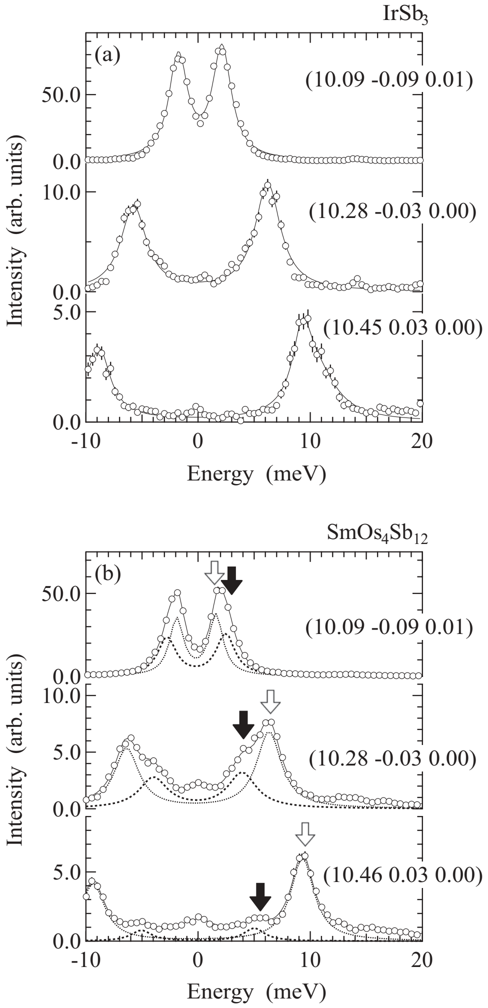

FIG. 1. (a) IXS spectra of $\mathrm{IrSb_3}$ at selected **Q** positions at 300 K. (b) IXS spectra of $\mathrm{SmOs_4Sb_{12}}$ at selected **Q** positions at 300 K. Closed (open) arrows show excitations of the Sm guest mode (acoustic mode).

The latter excitations remain at nearly the same energy in the $\Gamma-$H(L) direction, but those in the $\Gamma-$N(T) direction show rare-earth dependence similar to that of the guest modes. The rare-earth dependence of the spectra is observed in the excitation intensity as well as the phonon energy of the guest modes. These findings imply a correlation between the phonon spectra and the electronic states in the series of $R\mathrm{Os_4Sb_{12}}$ compounds. If there was no contribution of the electronic states to the phonon spectra, no rare-earth dependence of the integrated intensity and linewidth would be expected, except for the shift in the phonon energy due to the atomic mass of the rare earth because the scattering cross section of IXS is based on Thomson scattering.

The rare-earth dependence of the guest mode energy in $R\mathrm{Os_4Sb_{12}}$ at 300 K is plotted against the atomic number in Fig. 4. The guest mode energy changes linearly from $\mathrm{LaOs_4Sb_{12}}$ to $\mathrm{NdOs_4Sb_{12}}$, although the values for $\mathrm{SmOs_4Sb_{12}}$ and $\mathrm{EuOs_4Sb_{12}}$ deviate from this linear relationship. With respect to the IXS spectra at the $\Gamma-$H(L) points, the guest mode energy agrees with the Einstein temperature obtained by x-ray diffraction experiments.[20,51] In most series of rare-earth-

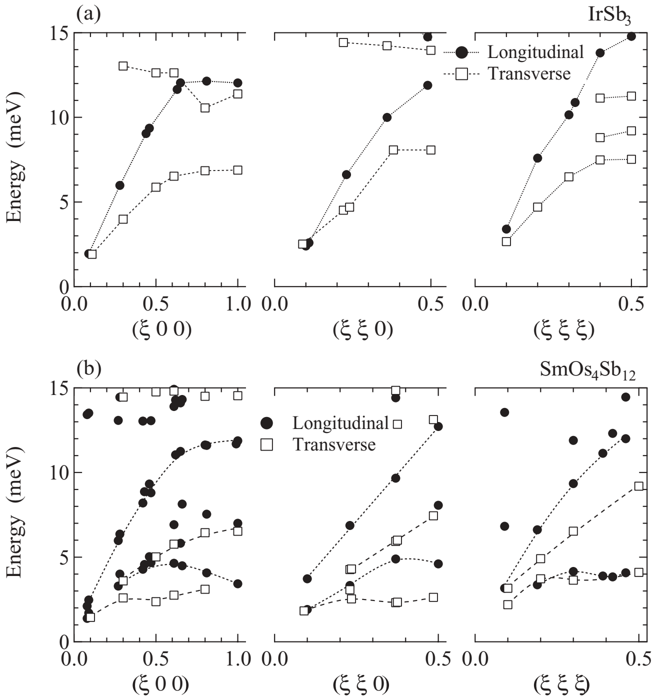

FIG. 2. (a) Phonon dispersion relations for IrSb$_3$ at 300 K. Closed circles (open squares) show the data obtained in the longitudinal (transverse) direction. The solid curves are guide to the eyes. (b) Phonon dispersion relations for SmOs$_4$Sb$_{12}$ at 300 K. Closed circles (open squares) show the data obtained in the longitudinal (transverse) direction. The solid curves are guides to the eyes.

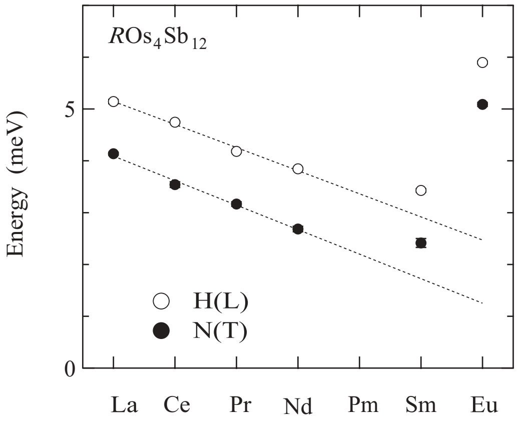

FIG. 4. Rare-earth dependence of guest mode energy in ROs$_4$Sb$_{12}$ compounds at 300 K. Open (closed) circles are the data taken at the H(L) [N(T)] position.

based intermetallic compounds, the rare-earth dependence of the lattice constant indicates the valence state of the rare earth in these compounds. In addition, most La, Pr, and Nd intermetallic compounds have no degrees of valence freedom at the rare-earth sites. These facts mean that the valence state of the rare earth is trivalent in these compounds. In the case of filled skutterudites ROs$_4$Sb$_{12}$, the lattice constants of LaOs$_4$Sb$_{12}$, PrOs$_4$Sb$_{12}$, and NdOs$_4$Sb$_{12}$ show a linear relationship with the atomic number of the rare earth, but those of CeOs$_4$Sb$_{12}$, SmOs$_4$Sb$_{12}$, and EuOs$_4$Sb$_{12}$ deviate from this relationship.[19,20,36,52] The lattice constants of these compounds indicate that the Ce valence state is a mixed state between the trivalent and tetravalent states and that the Sm and Eu valence states are located between the divalent and trivalent states. The ionic radius of the rare earth is changed by the valence states. For example, the ionic radius of the divalent state in Eu and Sm atoms is ∼20% larger than that of the trivalent one. In addition, the relationship between the guest mode energy and

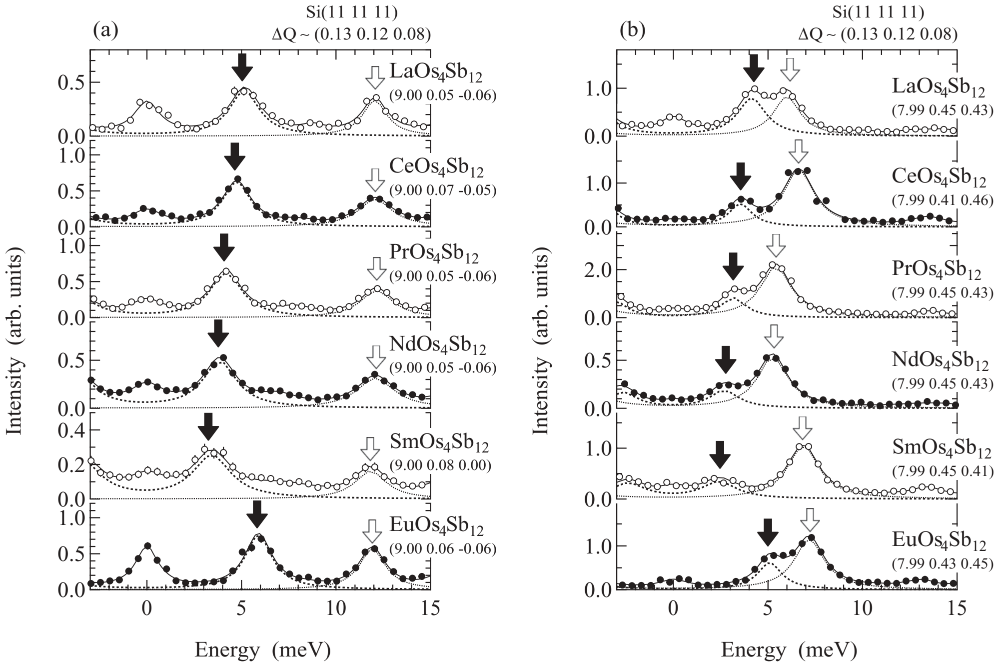

FIG. 3. IXS spectra of filled skutterudites ROs$_4$Sb$_{12}$ (R: light rare-earth element) at 300 K. Closed (open) arrows show excitations of the Sm guest mode (acoustic mode). (a) Spectra of ROs$_4$Sb$_{12}$ compounds were measured around $\mathbf{Q} = (9.00\ 0.00\ 0.00)$. (b) Spectra of ROs$_4Sb_{12}$ compounds were measured around $\mathbf{Q} = (8.00\ 0.45\ 0.45)$.

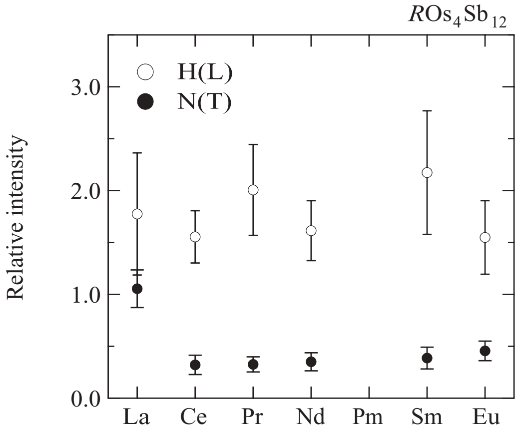

FIG. 5. Rare-earth dependence of relative integrated intensity of the guest mode to that of the acoustic mode in $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds at 300 K. Open (closed) circles show the data taken at the H(L) [N(T)] position.

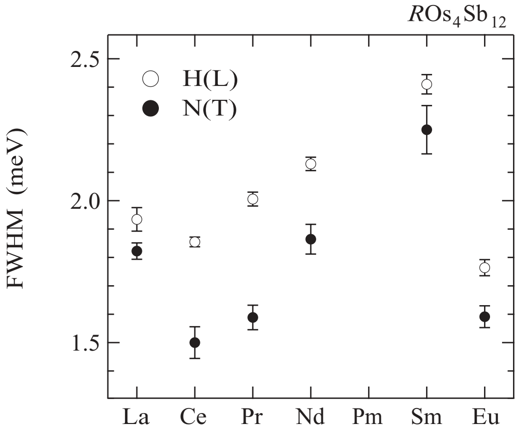

FIG. 6. Rare-earth dependence of guest mode linewidth [full width at half maximum (FWHM)] in $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds at 300 K. Open (closed) circles show the data taken at the H(L) [N(T)] position.

the guest free space was already discussed by the specific heat and EXAFS measurements in filled skutterudites.[18,24] In this sense, the rare-earth dependence of the guest mode energy can be explained by the guest free space in the Sb cage of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds, except for the case of $\mathrm{CeOs}_4\mathrm{Sb}_{12}$.

The IXS spectrum $S(\mathbf{Q},\omega)$ at a certain $\mathbf{Q}$ position is generally given by

$$S(\mathbf{Q},\omega) = \sigma(\mathbf{Q},\omega)BF(\omega,T)/\omega, \tag{1}$$

where $\sigma(\mathbf{Q},\omega)$ is the cross section of phonons at the $\mathbf{Q}$ position and $BF(\omega,T)$ is the Bose factor at measured temperature T. This means that the observed intensity is correlated with the phonon energy and measured temperature. Here, the ratio of the integrated intensity of the guest mode (closed arrow) to that of the acoustic mode (open arrow) is defined as the relative intensity of the guest mode in Fig. 3. A plot of the relative intensity at the zone boundaries against the atomic number is shown in Fig. 5. The rare-earth dependence of the relative intensity is different at the H(L) and N(T) points. The relative intensity in the longitudinal direction is independent of the rare earth. On the other hand, that in the transverse direction depends on whether or not the rare earth contains $4f$-electrons. Since the scattering cross section of IXS spectra is based on Thomson scattering, which is proportional to the number of electrons in atoms, the present results indicate that the guest modes at the $\Gamma-$N(T) points are coupled with $4f$-electrons of rare-earth ions.

The linewidth of the guest modes is plotted against the atomic number in Fig. 6. The linewidth in each compound is obtained by spectral analysis using the Lorentzian function. The linewidth at the H(L) point at the zone boundary of each compound is broader than that at the N(T) point. Since the effect of the mosaic of the samples is small, the broadening is caused by the effect of the dispersion and not by the uncertainty of $\mathbf{Q}$ in the measurements. In addition, the linewidth at the N(T) point was very close to the resolution of the IXS measurements for $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ and $\mathrm{PrOs}_4\mathrm{Sb}_{12}$, and significant line broadening was observed in $\mathrm{NdOs}_4\mathrm{Sb}_{12}$ and $\mathrm{SmOs}_4\mathrm{Sb}_{12}$. This variation in the linewidth in the series of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds, which have the same structure, is difficult to understand by any factor other than electron-phonon coupling. Furthermore, the rare-earth dependence of the linewidth of the guest modes resembles that of the γ value, estimated by specific heat measurements as shown in Table I. This indicates a correlation between the electron-phonon coupling and the γ value in $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds.

B. XAS measurements

1. Experimental setup

XAS experiments were carried out using the transmission method at BL01B1 and BL39XU of SPring-8 in Japan. The incident x-ray is monochromatized by a double crystal monochromator equipped with Si (1 1 1) [diamond (1 1 1)] at BL01B1 (BL39XU). The measured samples were crushed into powder. The spectra were measured at 300 K. The energy was calibrated by CeO_2 for the Ce L_{III}-edge, by $\mathrm{Sm}_2\mathrm{O}_3$ for the Sm L_{III}-edge, and by $\mathrm{Eu}_2\mathrm{O}_3$ for the Eu L_{III}-edge.

2. Experimental results

The L_{III}-edge XAS spectra of $\mathrm{CeOs}_4\mathrm{Sb}_{12}$, $\mathrm{SmOs}_4\mathrm{Sb}_{12}$, and $\mathrm{EuOs}_4\mathrm{Sb}_{12}$ at 300 K are shown in Fig. 7. As mentioned above, these compounds contain valence degrees of freedom in the rare-earth elements. The rare-earth dependence of the lattice constants suggests that the rare-earth valence in these compounds is a mixed state.[19,20,36,52] Mixed valence states of the rare-earth ions were reported in $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ and $\mathrm{EuOs}_4\mathrm{Sb}_{12}$.[44,53–55] However, the results obtained in the present paper indicate that the Ce valence state in $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ is purely trivalent and that the Eu valence state in $\mathrm{EuOs}_4\mathrm{Sb}_{12}$ is purely divalent. The mixed valence state of the rare-earth ions is only observed in $\mathrm{SmOs}_4\mathrm{Sb}_{12}$.

The results of XAS measurements of $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ and $\mathrm{EuOs}_4\mathrm{Sb}_{12}$ are plausible to explain the previous papers as follows. The result in $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ agrees with that of the photoemission spectroscopy within the experimental error.[56] The results of a neutron scattering experiment also suggest that $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ undergoes antiferromagnetic ordering

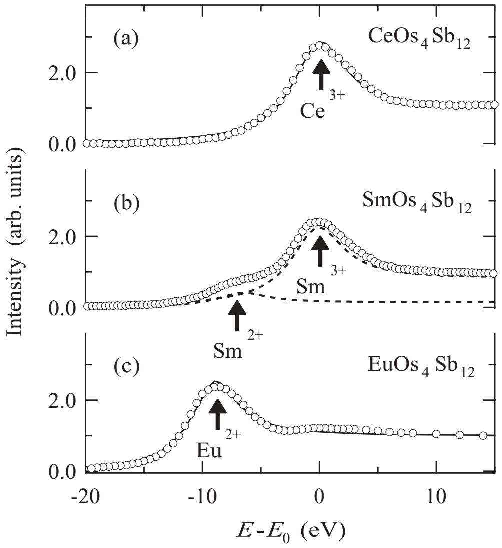

FIG. 7. Rare-earth L_{III}-edge x-ray absorption spectra of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds at 300 K. Zero energy is the energy of the absorption edge in each rare-earth element. (a) Ce L_{III}-edge x-ray absorption spectrum of $\mathrm{CeOs}_4\mathrm{Sb}_{12}$. (b) Sm L_{III}-edge x-ray absorption spectrum of $\mathrm{SmOs}_4\mathrm{Sb}_{12}$. (c) Eu L_{III}-edge x-ray absorption spectrum of $\mathrm{EuOs}_4\mathrm{Sb}_{12}$.

because of the observation of the magnetic reflection at $\boldsymbol{q} = (1\ 0\ 0)$ at 0.1 K.[57] This is also consistent with the result of the present XAS experiment on $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ because Ce^{3+} is a magnetic ion. Since $\mathrm{EuOs}_4\mathrm{Sb}_{12}$ shows ferromagnetic ordering below 9 K,[44] the divalent state of the Eu ion, whose ground state is purely magnetic, is consistent with the ground state of $\mathrm{EuOs}_4\mathrm{Sb}_{12}$. The absence of the trivalent state in the Eu L_{III}-edge XMCD spectrum also supports the pure divalent state of the Eu atoms in $\mathrm{EuOs}_4\mathrm{Sb}_{12}$.[58] The deviation from the linear relationship in the lattice constant of $\mathrm{CeOs}_4\mathrm{Sb}_{12}$ may be related to strong hybridization between $4f$- and conduction electrons. The present results also imply that the linear relationship for the guest modes in $R\mathrm{Os}_4\mathrm{Sb}_{12}$ is correlated with the valence state of rare-earth ions.

III. CALCULATIONS

Ab initio calculations were carried out for the unfilled skutterudite IrSb_3 and filled skutterudite $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ using the ABINIT code, the results of which are shown in Fig. 8.[59] The calculated results agree with the reported experimental results in the $\Gamma-$H(L) direction of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$, whose guides are different from the dispersion relations shown in Fig. 8.[32,60] The calculated IXS spectra shown in Fig. 9 demonstrate reasonable agreement with the experimental results shown in Fig. 3. These findings allow us to conclude that the calculation of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ in the present paper successfully reproduces the experimental results. The dispersion relations of $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ agree with the calculated results in $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ except for the guest mode energy. However, the difference between the guest mode energies of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ and $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ can be explained by the results of Raman scattering and x-ray diffraction experiments.[19,20,47] While the guest modes are observed as second-order signals in Raman scattering, this suggests that the energy difference between the guest mode energies of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ and $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ is about 2 meV. The results of x-ray diffraction experiments suggest that the difference in the Einstein temperature estimated from the atomic displacement factor at the $2a$ site is about 25 K, corresponding to about 2 meV. These results agree with the present IXS results for $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ and $\mathrm{SmOs}_4\mathrm{Sb}_{12}$ as shown in Fig. 3. Such an energy shift due to the filled rare-earth atom was observed not only in $\mathrm{SmOs}_4\mathrm{Sb}_{12}$, but also in the other $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds. Hereafter, the energy shift in the guest mode will be mainly discussed.

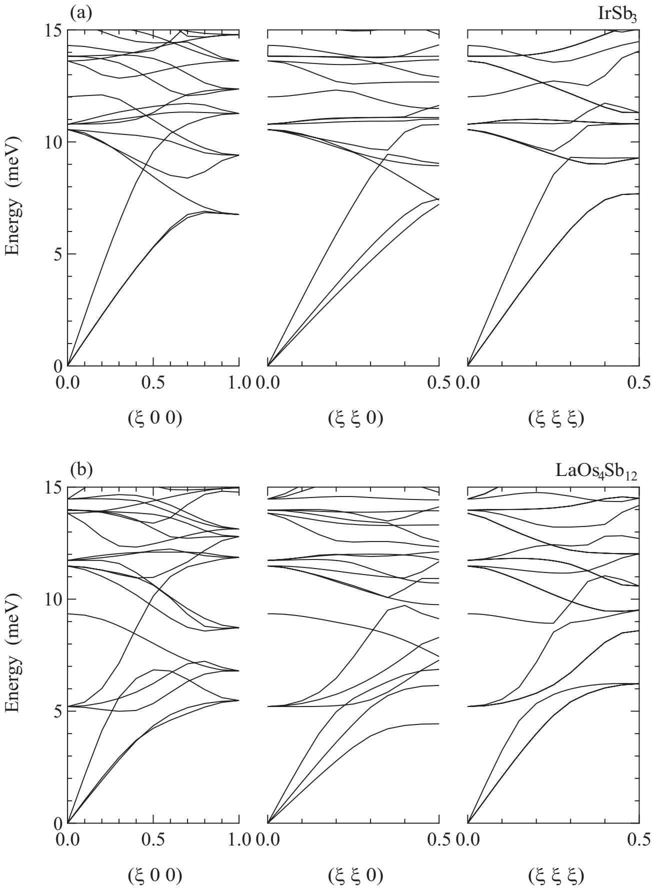

FIG. 8. Calculated phonon dispersions in (a) unfilled skutterudite IrSb_3 and (b) filled skutterudite $\mathrm{LaOs}_4\mathrm{Sb}_{12}$.

Since each compound in the series of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds has the same structure, the dynamical structure factor $S(\mathbf{Q},\omega)$ at any $\mathbf{Q}$ position should be identical before considering the effects of the atomic mass and scattering cross section of the rare earth on $S(\mathbf{Q},\omega)$. To consider their effects on the IXS spectrum, calculation of the IXS spectra was carried out using the force constant matrices obtained for $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ at the measured $\mathbf{Q}$ positions. The calculated results at (9.00 0.00 0.00) [(8.00 0.45 0.45)], which correspond to the H(L) [N(T)] point, are shown in Fig. 9(a) [Fig. 9(b)]. For both (9.00 0.00 0.00) and (8.00 0.45 0.45), the calculated spectrum is hardly affected by the electron number and atomic mass of the rare-earth atom. The calculated energy shift with the electron number and atomic mass of the rare-earth atom is much smaller than the measured shift. In addition, the peak heights of the calculated spectra appear to be different from the measured heights. This may be due to the effect of the $\mathbf{Q}$ resolution or to

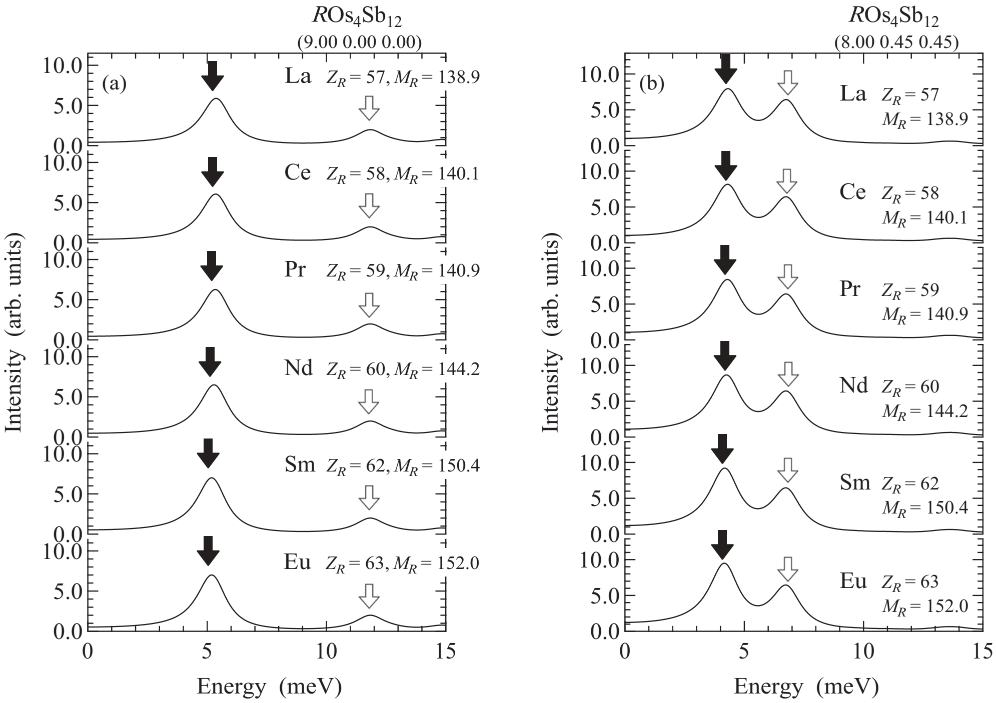

FIG. 9. Calculated IXS spectra at (a) (9.00 0.00 0.00) and (b) (8.00 0.45 0.45) obtained using various atomic masses and electron numbers at the 2*a* site in $LaOs_4Sb_{12}$. Closed (open) arrows show excitations of the Sm guest mode (acoustic mode).

the effect of the electronic states or hybridization among the phonon modes. With respect to the former case, the calculated peak heights at (8.00 0.45 0.45) are in better agreement with the measured heights than with those at (9.00 0.00 0.00). The **Q** resolution of the measurements is $\Delta\mathbf{Q} \sim (0.13\ 0.12\ 0.08)$ in the present paper. Both the measured results for $SmOs_4Sb_{12}$ and the calculated results for $LaOs_4Sb_{12}$ demonstrate that the dispersion relations in the $\Gamma-$H(L) direction are more dispersive than those in the $\Gamma-$N(T) direction. Therefore, an effect of the **Q** resolution in the measurements cannot be ruled out. As shown in Fig. 6, however, the rare-earth dependence of the linewidth in the measured spectra is also a significant factor for explaining the rare-earth dependence of the peak height because the linewidths in the calculated spectra are determined only by the energy resolution of 1.5 meV chosen in the experimental setup of the present paper.

A comparison between the energy shifts in the guest modes for the measured and calculated results is shown in Fig. 10. The calculated shift is much smaller than the measured shift when the guest mode energy in each direction of $LaOs_4Sb_{12}$ is set as the standard energy. This means that the shift in the guest mode cannot be explained by the change in the atomic mass of the inserted rare-earth. In addition, the calculated shift decreases with increasing atomic number, whereas, the measured shift changes signs between the atomic numbers of 62 and 63, corresponding to Sm and Eu, respectively. This indicates that the contribution of the rare-earth mass to the guest mode energy is small.

The relative intensity of the guest modes to the acoustic modes also shows different rare-earth dependence between the calculation and the measurements. The relative intensity is normalized by that of $LaOs_4Sb_{12}$ at the H(L) and N(T) points. Plots of the calculated and measured results at the H(L) [N(T)] point against the atomic number of the inserted rare earth are shown in Fig. 11(a) [Fig. 11(b)]. At the H(L) point, the

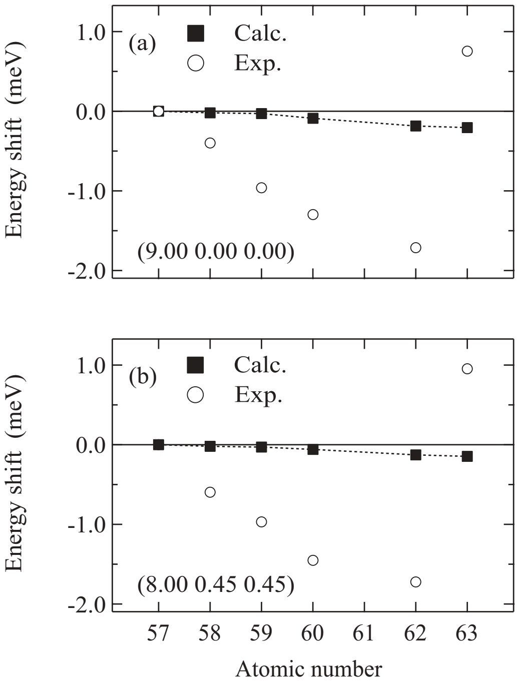

FIG. 10. Calculated phonon energy of the guest modes at (a) (9.00 0.00 0.00) and (b) (8.00 0.45 0.45). Closed squares (open circles) show calculated (experimental) results. The dotted line is a guide to the eyes.

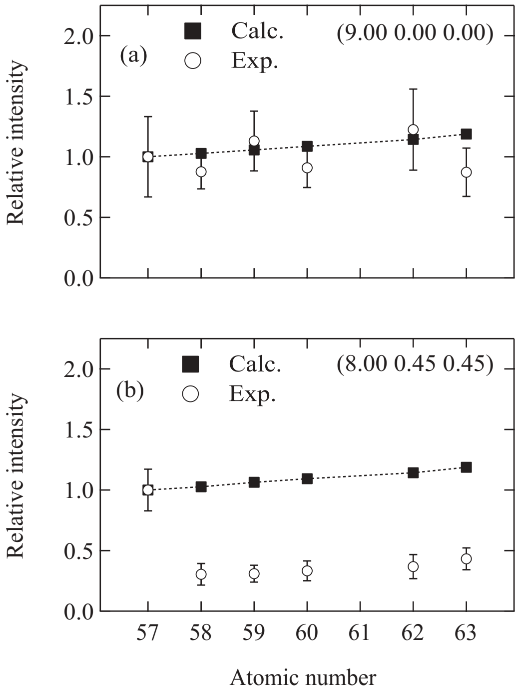

FIG. 11. Calculated relative intensities of the guest modes at (a) (9.00 0.00 0.00) and (b) (8.00 0.45 0.45). Closed squares (open circles) show calculated (experimental) results. The dotted line is a guide to the eyes.

rare-earth dependence of the relative intensity agrees with the calculated results despite the large error bars. This indicates that, except for the line broadening due to factors independent of the crystal structure, such as electron-phonon coupling and hybridization among phonon modes, the integrated phonon intensity depends on the total numbers of electrons predicted from the cross section based on Thomson scattering. However, the rare-earth dependence of the relative intensity at the N(T) point is different from that at the H(L) point. The relative intensity of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds other than $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ measured at the N(T) point is 30% of that of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$. The different behavior at the H(L) and N(T) points implies the presence of mode-selective coupling between the guest modes and the $4f$-electrons of the rare earth.

IV. DISCUSSION

The IXS spectra obtained in the present paper show evident rare-earth dependence of the guest mode energy, intensity, and linewidth. The IXS spectra calculated from the force constant matrices of $\mathrm{LaOs}_4\mathrm{Sb}_{12}$ demonstrate that the shift in the guest mode energy, expected from the change in the atomic mass and the increase or decrease in the guest mode intensity expected from the change in the atomic number, is too small to explain the experimental results. Rare-earth dependence of the guest mode linewidth is not expected according to the calculated results. The calculation in the present paper indicates that the dependences of the IXS spectra on the f-electron and the radius of the guest atom, which are excluded in the calculation, have a strong effect on the guest mode spectra observed by IXS measurements. The combination of the IXS measurements with XAS measurements revealed the correlation between the guest mode energy and the guest free space at the rare-earth site. The rare-earth dependence of the guest mode linewidth implies the correlation between the guest mode and the HF behavior through electron-phonon coupling in some $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds when the lowest excitation is a guest mode excitation. A detailed discussion is given as follows.

A. Rare-earth dependence of the guest mode energy

The guest mode energies determined in the present paper fulfill the condition required by previous theories on phonon-mediated HF behavior.[2–4] Nearly flat dispersions of the guest mode exist in all the $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds, which can be treated as an Einstein mode in the specific heat of the lattice. As shown in Fig. 4, the energy of the guest mode in each compound is nearly equal to the Kondo temperature in typical HF compounds below 100 K. The present results show that the guest mode energy itself is not correlated with the HF behavior, unlike the Kondo temperatures in conventional HF compounds because no correlation is found between the guest mode energy and the γ value in each $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compound.

The rare-earth dependence indicates the origin of the guest mode energy. The combination of the results of IXS and XAS measurements demonstrates that the guest free space at the $2a$ site where the rare-earth atom is located is one of the most important parameters in determining the guest mode energy. Since the atomic position parameter at the $24g$ site where Sb atoms are located in $R\mathrm{Os}_4\mathrm{Sb}_{12}$ is nearly equal among the series of $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds,[19,20,27,36,52,61] the rare-earth dependence of the Sb cage size is small. Therefore, the main factor, determining the guest free space, is the radius of the atoms inserted into the Sb cage. When the valence state of the rare-earth ion is the same in all the compounds, the radii of the rare-earth atoms decrease with increasing atomic number because of the lanthanide contraction. However, the XAS measurements indicate that the Sm valence state is an intermediate state between the divalent and the trivalent states and that the Eu valence state is trivalent, whereas, the valence state of the rare-earth is purely trivalent in the other $R\mathrm{Os}_4\mathrm{Sb}_{12}$ compounds. This means that the guest free space is reduced by the difference in the atomic radius because divalent ions are larger than trivalent ions in general. The results of the XAS and IXS measurements agree with the predicted relationship between the guest mode energy and guest free space. The correlation between the guest mode energy and the guest free space has already been pointed out from the results of the specific heat and EXAFS measurements of filled skutterudites.[18,24] These findings imply that the relationship between the guest free space and the guest mode energy is common to all filled skutterudites.

The relationship between the guest free space and the guest mode energy also indicates the instability of the filled skutterudite structure in heavy rare-earth filled skutterudites. As shown in Fig. 4, the slope of the guest mode energy plotted against the atomic number of the rare earth is negative at the H(L) and N(T) points. The phonon energy at the N(T) point reaches zero near the atomic number of Tb or Dy if a linear relationship between the phonon energy and the atomic number holds. Since Tm and Yb have valence degrees of freedom, compounds filled with Tm and Yb ions may exist. However, the present results imply that it is difficult for rare-earth elements heavier than Tb or Dy to maintain a skutterudite structure at ambient pressure.

B. Guest mode linewidth and electron-phonon coupling

Previous theories have suggested that electron-phonon coupling between low-lying Einstein-like modes and conduction electrons as well as the presence of low-lying Einstein-like modes is important when discussing the origin of phonon-mediated HF behavior.[2–4] Electron-phonon coupling is usually observed as the line broadening of phonon excitations. Since no line broadening is expected from the calculations in the present paper, the observed broadening is caused by electron-phonon coupling as mentioned above. However, three factors can be considered to have resulted in the observation of broadened excitations. One is the uncertainty of the momentum transfer **Q** due to the mosaic of each measured sample, another is the effect of the phonon dispersion on the **Q** resolution, and another is related to the presence of electron-phonon coupling.

The observed line broadening is caused by electron-phonon coupling. The first factor is ruled out by the rocking curve width of the samples as mentioned above. The difference between the experimental and the calculated linewidths of the guest mode was greater at the H(L) point than at the N(T) point for every $R\text{Os}_4\text{Sb}_{12}$. An effect of the **Q** resolution on the line broadening in the guest modes is supported by the phonon dispersions shown in Figs. 2(b) and 8(b). However, the rare-earth dependence of the linewidth is difficult to understand in terms of the **Q** resolution. As mentioned above, the rare-earth dependence is very similar to the trend of the γ values in the series of $R\text{Os}_4\text{Sb}_{12}$ compounds as shown in Table I. Among the $4f$-containing $R\text{Os}_4\text{Sb}_{12}$ compounds, the broadening is smallest in $\text{CeOs}_4\text{Sb}_{12}$ and is largest in $\text{SmOs}_4\text{Sb}_{12}$. The fact that the linewidth in $\text{CeOs}_4\text{Sb}_{12}$ is close to the resolution limit demonstrates that the electron-phonon coupling is not the only factor causing the mass enhancement in $R\text{Os}_4\text{Sb}_{12}$.

To the best of our knowledge, whether or not electron-phonon coupling really occurs in the guest mode has never been discussed by using phonon measurements. To resolve this problem, it is helpful to consider the nesting condition of the Fermi surfaces. In the present paper, the phonon spectra were measured at specific **Q** positions, corresponding to $\boldsymbol{q} = (1\ 0\ 0)$ and $(0.5\ 0.5\ 0)$. The Fermi surfaces at $\boldsymbol{q} = (1\ 0\ 0)$, which correspond to the H point, do not necessarily satisfy the nesting conditions in $R\text{Os}_4\text{Sb}_{12}$ compounds, such as $R\text{Fe}_4\text{P}_{12}$ and $R\text{Ru}_4\text{P}_{12}$,[62] although the propagation vectors of the antiferromagnetic ordering in $\text{CeOs}_4\text{Sb}_{12}$ (Ref. 57) and the field-induced ordered phase in $\text{PrOs}_4\text{Sb}_{12}$ (Ref. 63) are $\boldsymbol{q} = (1\,0\,0)$. On the other hand, the Fermi surfaces at $\boldsymbol{q} = (0.5\,0.5\,0)$, which correspond to the N point, do not satisfy the nesting condition in any of the filled skutterudites. This means that the phonon anomalies observed in the present paper, which include the reduction in the guest mode intensity, are not caused by the Fermi surface nesting but by electron-phonon coupling between the guest mode and the conduction electrons. Because of the complexity of the phonon dispersion relations in filled skutterudites, discussion of the electron-phonon coupling is difficult for the guest mode. The presence of low-lying guest modes causes the hybridization with acoustic modes. Therefore, a reciprocal point **Q** where the contribution of the guest modes is large is difficult to find in the middle of the Brillouin zones. Fortunately, however, the calculation in the present paper indicates that the contribution of the guest atoms to the lowest modes assigned as the guest modes is large in the spectra at the zone boundaries of $\boldsymbol{q} = (1\ 0\ 0)$ and $(0.5\ 0.5\ 0)$. This is the reason that we discuss the relationship between phonon anomalies and electron-phonon coupling at the H(L) and N(T) points.

C. Origin of the heavy fermion behavior in the series of $R\text{Os}_4\text{Sb}_{12}$ compounds

What is the origin of the HF behavior in the series of $R\text{Os}_4\text{Sb}_{12}$ compounds? The observation of guest modes with low energy and the presence of electron-phonon coupling correlated with the guest modes imply the possibility of phonon-mediated HF behavior in $R\text{Os}_4\text{Sb}_{12}$ compounds. However, the present results indicate that electron-phonon coupling, causing the broadened linewidth of the guest modes, is not the only origin of the HF behavior in the series of $R\text{Os}_4\text{Sb}_{12}$ compounds. Another possible origin is another type of low-energy excitation, such as spin excitation, CEF excitation, and so forth. Hereafter, the contribution of other low-lying excitations in each $R\text{Os}_4\text{Sb}_{12}$ compound will be considered to clarify the contribution of the guest mode to the HF behavior.

The γ value of $\text{LaOs}_4\text{Sb}_{12}$ is approximately $50\,\text{mJ}\,\text{mol}^{-1}\,\text{K}^{-2}$ as mentioned above.[35,36] Such mass enhancement of the conduction electrons can be explained by the results of the band calculation.[64] The cyclotron effective mass obtained by de Haas–van Alphen effect measurements supports such large γ values.[36] The present results demonstrate the presence of the low-lying Einstein-like mode required in theoretical predictions.[2–4] The mass enhancement observed in $\text{LaOs}_4\text{Sb}_{12}$ is, thus, caused by electron-phonon coupling.

No low-energy excitations have yet been found in $\text{CeOs}_4\text{Sb}_{12}$, except for phonons.[65] Unlike $\text{LaOs}_4\text{Sb}_{12}$, $\text{CeOs}_4\text{Sb}_{12}$ has $4f$-electrons with degrees of freedom as suggested by the XAS spectrum shown in Fig. 7. In fact, the ground state of $\text{CeOs}_4\text{Sb}_{12}$ is an antiferromagnetic ordered state as suggested by the results of a neutron scattering experiment,[57] which was originally predicted on the basis of an NMR/NQR.[66] The magnitude of the Ce magnetic moment is smaller in the ordered state than in the paramagnetic state. The suppression of ordered magnetic moments is one of the most common features among itinerant f-electron systems, including HF systems. In addition, the absence of CEF excitations according to the inelastic neutron scattering (INS) experiment suggests the itinerancy of $4f$-electrons in $\text{CeOs}_4\text{Sb}_{12}$.[65] On the other hand, since the linewidth of the guest mode obtained in the present paper is close to the resolution, the electron-phonon coupling associated with the guest mode is weak. Therefore, the correlation between the enhancement of the γ value and the electron-phonon coupling in the guest mode is weak in $\text{CeOs}_4\text{Sb}_{12}$.

In the case of $\text{PrOs}_4\text{Sb}_{12}$, the energy of the lowest CEF excitation is much lower than those of other phonon excitations, including those of the guest modes.[67] If the lowest excitation is the main origin of HF behavior in the series of ROs$_4$Sb$_{12}$ compounds, the correlation between line broadening and the γ value can be explained as for the case of CeOs$_4$Sb$_{12}$. In addition, in several papers, the ground state of PrOs$_4$Sb$_{12}$ has been suggested to have unconventional superconductivity.[41,68–71] A correlation between HF behavior and CEF degrees of freedom was suggested to be one of the suitable mechanisms of Cooper pairing. Furthermore, on the basis of a recent NMR experiment, it was proposed that the origin of HF behavior was low-lying CEF excitations.[72] Considering the role of heavy quasiparticles in unconventional superconductivity,[67,70] the small amount of line broadening in the present paper does not contradict the correlation of the HF behavior with low-lying CEF excitations.

NdOs$_4$Sb$_{12}$ contains guest modes with a large linewidth compared with those of other ROs$_4$Sb$_{12}$ compounds. This is consistent with the presence of electron-phonon coupling between the guest mode and the conduction electrons. Therefore, the evident contribution of the guest mode to HF behavior is acceptable, but the Kondo effect cannot be ruled out as a possible origin of the HF behavior in NdOs$_4$Sb$_{12}$. On the other hand, INS spectra suggest that the $4f$-electrons of the Nd atoms are well localized.[73] The combination of the INS measurements with the magnetic susceptibility measurements revealed that the CEF ground state of the Nd atom is a Γ_8 quartet. The CEF levels were clearly observed at a low temperature. Since the hybridization between f- and conduction electrons often broadens CEF excitation peaks, the absence of broadened INS spectra suggests that the hybridization is weak. Unlike the case of PrOs$_4$Sb$_{12}$, the CEF excitations can be ruled out as the candidates because the lowest CEF excitation was reported to be observed at 23 meV.[73] These experimental results support the possibility of HF behavior mediated by the guest mode in NdOs$_4$Sb$_{12}$.

In the case of SmOs$_4$Sb$_{12}$, it is difficult to propose the conventional mechanism as the origin of the HF behavior. The linewidth of the guest mode is the broadest in the series of ROs$_4$Sb$_{12}$ compounds. The observed linewidth indicates the presence of electron-phonon coupling between the guest modes and the conduction electrons. As mentioned in Ref. 74, the HF behavior in SmOs$_4$Sb$_{12}$ is completely different from that in conventional HF compounds, such as CeCu$_6$. The robustness of the HF behavior to an applied magnetic field suggests that magnetic degrees of freedom can be ruled out as a possible origin. Although the g-factor is small in Sm compounds, the robustness of the HF behavior up to 30 T or higher implies that it is difficult to use the effect of the small g-factor to explain the magnetic-field dependence of the HF behavior from the viewpoint of magnetic degrees of freedom. In other words, nonmagnetic degrees of freedom are strong candidates for the origin of the HF behavior in SmOs$_4$Sb$_{12}$. The low-lying guest modes are another possible origin. The present paper revealed the presence of low-lying guest modes that are coupled with conduction electrons through electron-phonon coupling. However, the contribution of the CEF excitations cannot be ruled out. The results of magnetization and specific heat measurements suggest the presence of low-lying CEF excitations,[43,75] which correspond to the transition from the Γ_{67} ground state to the Γ_5 excited state or from the Γ_7 ground state to the Γ_8 excited state, depending on the literature. Since the energy of the lowest guest mode is close to that of the lowest CEF excitation, one or both of them may be the origin of the HF behavior in SmOs$_4$Sb$_{12}$.

The case of EuOs$_4$Sb$_{12}$ is more difficult to understand than those of the other ROs$_4$Sb$_{12}$ compounds. A previous paper[35] and the XAS measurement in the present paper indicate that this compound has Eu atoms with low degrees of magnetic and valence freedoms and that the reduction of the saturated magnetic moment is small. Also, the XAS spectrum at room temperature indicates that the Eu valence is purely divalent. The amount of line broadening, suggesting the presence of electron-phonon coupling, is small, even compared with that in LaOs$_4$Sb$_{12}$, whose γ value is similar to that of EuOs$_4$Sb$_{12}$. Considering the guest mode energy, the mass enhancement expected from electron-phonon coupling is difficult to explain in the present paper.

As discussed above, the HF behavior, which plausibly originates from the guest modes, is not realized in all the ROs$_4$Sb$_{12}$ compounds. Since the results for CeOs$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$ indicate that the effect of electron-phonon coupling on the HF behavior is much weaker than that in the other ROs$_4$Sb$_{12}$ compounds, one proposed explanation for the origin of the HF behavior is based on the relationship between the low-lying guest modes and other excitations, such as spin excitations, CEF excitations, and so forth. A good example of the relationship between the guest modes and the other excitations is the difference between the ground states of PrRu$_4$Sb$_{12}$ and PrOs$_4$Sb$_{12}$. Both the guest free space and the lattice constant are nearly equal in these compounds.[36,52] Both compounds exhibit superconductivity at low temperatures. The superconductivity in PrRu$_4$Sb$_{12}$ is BCS-type superconductivity,[76] whereas, that in PrOs$_4$Sb$_{12}$ is unconventional superconductivity.[41,68–71] The different ground states of these compounds may correlate with the difference between the d-electron nature of Ru and Os atoms. Concerning the low-energy excitations in these compounds, however, the guest mode energy is lower than the lowest CEF excitation in PrRu$_4$Sb$_{12}$ (Refs. 16 and 77) and higher in PrOs$_4$Sb$_{12}$ (Refs. 16, 30, and 68). Considering the HF behavior produced by the renormalization between conduction electrons and low-energy excitations, an important point in explaining the origin of the HF electrons in these compounds is the excitation found at the lowest energy of each ROs$_4$Sb$_{12}$ compound. Although the CEF level schemes in SmOs$_4$Sb$_{12}$ have not yet been investigated, judging from the reported level schemes in PrOs$_4$Sb$_{12}$ and NdOs$_4$Sb$_{12}$, the present results demonstrate that the lowest excitation is correlated with the HF behavior in ROs$_4$Sb$_{12}$ compounds.

V. SUMMARY

IXS experiments were carried out on the series of ROs$_4$Sb$_{12}$ compounds at 300 K. Dispersion relations of the unfilled skutterudite IrSb$_3$ and the filled skutterudite SmOs$_4$Sb$_{12}$ are in reasonable agreement with the results of a calculation using the ABINIT code for the unfilled skutterudite IrSb$_3$ and filled skutterudite LaOs$_4$Sb$_{12}$, respectively. The most apparent difference between the results of the calculation for LaOs$_4$Sb$_{12}$ and the experimental results for SmOs$_4$Sb$_{12}$ is the guest mode energy. This can be explained by the difference between the measured guest mode energies of LaOs$_4$Sb$_{12}$ and SmOs$_4$Sb$_{12}$. Some of the experimental results are difficult to explain without taking into account the electron-phonon coupling between the guest modes and the conduction electrons in the calculation. The strong effects of rare-earth atoms on the linewidth and relative intensity imply the presence of electron-phonon coupling between low-lying guest modes and conduction electrons. The results obtained in the present paper satisfy the theoretical prerequisites required to support phonon-mediated HF behavior.[2–4] The following details were clarified in the present paper.

(1) The guest mode energy shows evident rare-earth dependence. Considering the valence state and guest mode energy, the main factor in determining the guest mode energy is the free space of the guest site, i.e., the $2a$ site of the filled skutterudite structure. The difference between the guest mode energy in $\mathrm{LaOs_4Sb_{12}}$ and that in the other $R\mathrm{Os_4Sb_{12}}$ compounds is not small and can exceed 20 K as the Einstein temperature. Therefore, this affected the estimation of the electronic contribution in specific heat measurements as pointed out previously[44] because the present results indicated that the lattice contribution of the guest mode to the specific heat in the low-temperature region was large for the filled skutterudites $R\mathrm{Os_4Sb_{12}}$.

(2) The rare-earth dependence of the guest mode intensity implies that the $4f$-electrons are coupled with the guest modes at the N(T) point in $4f$-containing $R\mathrm{Os_4Sb_{12}}$ compounds. Since the rare-earth dependence at the H(L) point agrees with the calculated result, the lack of rare-earth atoms at the $2a$ site is ruled out. The observation of the reduction in the integrated intensity indicates that the electron-phonon coupling with the guest mode is stronger at the N(T) point than at the H(L) point but that the role of the coupling between the guest mode and the $4f$-electrons has not been clarified yet.

(3) The rare-earth dependence of the linewidth is very similar to that of the γ value among the series of $R\mathrm{Os_4Sb_{12}}$ compounds. Considering the dispersion relations of $\mathrm{SmOs_4Sb_{12}}$, which is isostructural with other $R\mathrm{Os_4Sb_{12}}$ compounds and the nesting conditions of the Fermi surface in the filled skutterudites, this also implies the occurrence of electron-phonon coupling between the guest mode and the conduction electrons rather than the Kohn anomaly at specific reciprocal points. The linewidth of the guest modes in $\mathrm{CeOs_4Sb_{12}}$ and $\mathrm{PrOs_4Sb_{12}}$ indicates that electron-phonon coupling is not necessarily important for enhancing γ values in the series of $R\mathrm{Os_4Sb_{12}}$ compounds, although the linewidth of the guest mode is significant in $\mathrm{NdOs_4Sb_{12}}$ and $\mathrm{SmOs_4Sb_{12}}$. This means that an important factor for enhancing the γ values in $R\mathrm{Os_4Sb_{12}}$ compounds is the excitation that has the lowest energy in every compound.

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[1] S. Doniach, Physica B&C **91**, 231 (1977).

[2] C. C. Yu and P. W. Anderson, Phys. Rev. B **29**, 6165 (1984).

[3] H. Kusunose and K. Miyake, J. Phys. Soc. Jpn. **65**, 3032 (1996).

[4] K. Mitsumoto and Y. Ono, Physica C **426–431**, 330 (2005).

[5] 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**, 180511 (2004).

[6] R. P. Hermann, V. Keppens, P. Bonville, G. S. Nolas, F. Grandjean, G. J. Long, H. M. Christen, B. C. Chakoumakos, B. C. Sales, and D. Mandrus, Phys. Rev. Lett. **97**, 017401 (2006).

[7] Z. Hiroi, J. Yamaura, and K. Hattori, J. Phys. Soc. Jpn. **81**, 011012 (2012).

[8] K. Iwasa, R. Igarashi, K. Saito, C. Laulhé, T. Orihara, S. Kunii, K. Kuwahara, H. Nakao, Y. Murakami, F. Iga, M. Sera, S. Tsutsui, H. Uchiyama, and A. Q. R. Baron, Phys. Rev. B **84**, 214308 (2011).

[9] G. A. Slack, *CRC Handbook of Thermoelectrics*, edited by D. Rowe (CRC, Boca Raton, FL, 1995), p. 407.

[10] 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 (London) **395**, 876 (1998).

[11] R. P. Hermann, R. Jin, W. Schweika, F. Grandjean, D. Mandrus, B. C. Sales, and G. J. Long, Phys. Rev. Lett. **90**, 135505 (2003).

[12] G. J. Long, R. P. Hermann, F. Grandjean, E. E. Alp, W. Sturhahn, C. E. Johnson, D. E. Brown, O. Leupold, and R. Rüffer, Phys. Rev. B **71**, 140302 (2005).

[13] C. H. Lee, I. Hase, H. Sugawara, H. Yoshizawa, and H. Sato, J. Phys. Soc. Jpn. **75**, 123602 (2006).

[14] S. Tsutsui, H. Kobayashi, D. Ishikawa, J. P. Sutter, A. Q. R. Baron, T. Hasegawa, N. Ogita, M. Udagawa, Y. Yoda, H. Onodera, D. Kikuchi, H. Sugawara, C. Sekine, I. Shirotani, and H. Sato, J. Phys. Soc. Jpn. **77**, 033601 (2008).

[15] M. M. Koza, M. R. Johnson, R. Viennois, H. Mutka, L. Girard, and D. Ravot, Nat. Mater. **7**, 805 (2008).

[16] K. Iwasa, Y. Mori, L. Hao, Y. Murakami, M. Kohgi, H. Sugawara, and H. Sato, J. Phys. Conf. Ser. **92**, 012122 (2007).

[17] S. Tsutsui, H. Kobayashi, Y. Yoda, H. Sugawara, C. Sekine, T. Namiki, I. Shirotani, and H. Sato, Hyperfine Interact. **206**, 67 (2012).

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

[19] M. Tsubota, S. Tsutsui, D. Kikuchi, H. Sugawara, H. Sato, and Y. Murakami, J. Phys. Soc. Jpn. **77**, 073610 (2008).

[20] J. Yamaura and Z. Hiroi, J. Phys. Soc. Jpn. **80**, 054601 (2011).

[21] D. Cao, F. Bridges, S. Bushart, E. D. Bauer, and M. B. Maple, Phys. Rev. B **67**, 180511 (2003).
[22] D. Cao, F. Bridges, P. Chesler, S. Bushart, E. D. Bauer, and M. B. Maple, Phys. Rev. B **70**, 094109 (2004).
[23] D. Cao, R. H. Heffner, F. Bridges, I.-K. Jeong, E. D. Bauer, W. M. Yuhasz, and M. B. Maple, Phys. Rev. Lett. **94**, 036403 (2005).
[24] M. Mizumaki, S. Tsutsui, T. Uruga, H. Tanida, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **80**, 074603 (2011).
[25] Y. Nakai, K. Ishida, H. Sugawara, D. Kikuchi, and H. Sato, Phys. Rev. B **77**, 041101 (2008).
[26] S. Tsutsui, J. Umemura, H. Kobayashi, T. Tazaki, S. Nasu, Y. Kobayashi, Y. Yoda, H. Onodera, H. Sugawara, T. D. Matsuda, D. Kikuchi, H. Sato, C. Sekine, and I. Shirotani, Hyperfine Interact. **168**, 1073 (2006).
[27] S. Tsutsui, H. Kobayashi, J. Umemura, Y. Yoda, H. Onodera, H. Sugawara, D. Kikuchi, H. Sato, C. Sekine, and I. Shirotani, Physica B **383**, 142 (2006).
[28] S. Tsutsui, Y. Yoda, and H. Kobayashi, J. Phys. Soc. Jpn. **76**, 065003 (2007).
[29] S. Sanada, Y. Aoki, H. Aoki, A. Tsuchiya, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74**, 246 (2005).
[30] K. Iwasa, M. Kohgi, H. Sugawara, and H. Sato, Physica B **378–380**, 194 (2006).
[31] C. Yang, H. Wang, K. Iwasa, M. Kohgi, H. Sugawara, and H. Sato, J. Phys.: Condens. Matter **19**, 226214 (2007).
[32] 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**, 257 (2008).
[33] S. Tsutsui, H. Kobayashi, J. P. Sutter, A. Q. R. Baron, T. Hasegawa, N. Ogita, M. Udagawa, Y. Yoda, C. Sekine, I. Shirotani, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Conf. Ser. **92**, 012171 (2007).
[34] S. Tsutsui, H. Uchiyama, J. P. Sutter, A. Q. R. Baron, H. Sugawara, J. Yamaura, Z. Hiroi, A. Ochiai, and H. Sato, J. Phys. Conf. Ser. **200**, 012213 (2010).
[35] E. D. Bauer, A. Slebarski, E. J. Freeman, C. Sirvent, and M. B. Maple, J. Phys.: Condens. Matter **13**, 4495 (2001).
[36] H. Sugawara, S. Osaki, S. R. Saha, Y. Aoki, H. Sato, Y. Inada, H. Shishido, R. Settai, Y. Ōnuki, H. Harima, and K. Oikawa, Phys. Rev. B **66**, 220504 (2002).
[37] T. Namiki, Y. Aoki, H. Sugawara, and H. Sato, Acta Phys. Pol. B **34**, 1161 (2003).
[38] M. B. Maple, E. D. Bauer, V. S. Zapf, E. J. Freeman, N. A. Frederick, and R. P. Dickey, Acta Phys. Pol. B **32**, 3291 (2001).
[39] E. D. Bauer, A. Slebarski, E. J. Freeman, N. A. Frederick, B. J. Taylor, C. Sirvent, and M. B. Maple, Physica B **312–313**, 230 (2002).
[40] E. D. Bauer, N. A. Frederick, P.-C. Ho, V. S. Zapf, and M. B. Maple, Phys. Rev. B **65**, 100506 (2002).
[41] R. Vollmer, A. Faißt, C. Pfleiderer, H. V. Löhneysen, E. D. Bauer, P.-C. Ho, V. Zapf, and M. B. Maple, Phys. Rev. Lett. **90**, 057001 (2003).
[42] H. Sugawara, M. Kobayashi, S. Osaki, S. R. Saha, T. Namiki, Y. Aoki, and H. Sato, Phys. Rev. B **72**, 014519 (2005).
[43] 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**, 104402 (2005).
[44] E. D. Bauer, A. Ślebarski, N. A. Frederick, W. M. Yuhasz, M. B. Maple, D. Cao, F. Bridges, G. Giester, and P. Rogl, J. Phys.: Condens. Matter **16**, 5095 (2004).
[45] S. Kunii, M. Effantin, and J. Rossat-Mignot, J. Phys. Soc. Jpn. **66**, 1029 (1997).
[46] K. Matsuhira, M. Wakeshima, Y. Hinatsu, C. Sekine, I. Shirotani, D. Kikuchi, H. Sugawara, and H. Sato, J. Magn. Magn. Mater. **310**, 226 (2007).
[47] N. Ogita, T. Kondo, T. Hasegawa, Y. Takasu, M. Udagawa, N. Takeda, K. Ishikawa, H. Sugawara, D. Kikuchi, H. Sato, C. Sekine, and I. Shirotani, Physica B **383**, 128 (2006).
[48] A. Q. R. Baron, Y. Tanaka, S. Goto, K. Takeshita, T. Matsushita, and T. Ishikawa, J. Phys. Chem. Solids **61**, 461 (2000).
[49] N. Takeda and M. Ishikawa, Physica B **259–261**, 92 (1999).
[50] A. Kjekshus and G. Pedersen, Acta Crystallogr. **14**, 1065 (1961).
[51] S. Tsutsui, H. Uchiyama, J. P. Sutter, A. Q. R. Baron, J. Yamaura, H. Sugawara, and H. Sato, J. Phys. Conf. Ser. (to be published).
[52] D. J. Braun and W. Jeitschko, J. Less-Common Met. **72**, 147 (1980).
[53] M. Mizumaki, S. Tsutsui, H. Tanida, T. Uruga, D. Kikuchi, H. Sugawara, and H. Sato, Physica B **383**, 144 (2006).
[54] M. Mizumaki, S. Tsutsui, H. Tanida, T. Uruga, D. Kikuchi, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **76**, 053706 (2007).
[55] A. Yamasaki, S. Imada, H. Higashimichi, H. Fujiwara, T. Saita, T. Miyamachi, A. Sekiyama, H. Sugawara, D. Kikuchi, H. Sato, A. Higashiya, M. Yabashi, K. Tamasaku, D. Miwa, T. Ishikawa, and S. Suga, Phys. Rev. Lett. **98**, 156402 (2007).
[56] M. Matsunami, R. Eguchi, T. Kiss, K. Horiba, A. Chainani, M. Taguchi, K. Yamamoto, T. Togashi, W. Watanabe, X.-Y. Wang, C.-T. Chen, Y. Senba, H. Ohashi, H. Sugawara, H. Sato, H. Harima, and S. Shin, Phys. Rev. Lett. **102**, 036403 (2009).
[57] K. Iwasa, S. Itobe, C. Yang, Y. Murakami, M. Kohgi, K. Kuwahara, H. Sugawara, H. Sato, N. Aso, T. Tayama, and T. Sakakibara, J. Phys. Soc. Jpn. **77** Suppl. A, 318 (2008).
[58] M. Mizumaki *et al.* (unpublished).
[59] X. Gonze, J.-M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.-M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.-Y. Raty, and D. C. Allan, Comput. Mater. Sci. **25**, 478 (2002).
[60] T. Hasegawa, Y. Takasu, N. Ogita, and M. Udagawa, J. Phys. Soc. Jpn. **77** Suppl. A, 248 (2008).
[61] C. B. H. Evers, W. Jeitschko, L. Book, D. J. Braun, T. Ebel, and U. D. Scholtz, J. Alloys Compd. **224**, 184 (1995).
[62] H. Harima, J. Phys. Soc. Jpn. **77**, Suppl. A, 114 (2008).
[63] M. Kohgi, K. Iwasa, M. Nakajima, N. Metoki, S. Araki, N. Bernhoeft, J.-M. Mignot, A. Gukasov, H. Sato, Y. Aoki, and H. Sugawara, J. Phys. Soc. Jpn. **72**, 1002 (2003).
[64] H. Harima and K. Takegahara, Physica B **388–389**, 555 (2003).
[65] C. Yang, M. Kohgi, K. Iwasa, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74**, 2862 (2005).
[66] M. Yogi, H. Kotegawa, G.-q. Zheng, Y. Kitaoka, S. Ohsaki, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **74**, 1950 (2005).
[67] K. Kuwahara, K. Iwasa, M. Kohgi, K. Kaneko, S. Araki, N. Metoki, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **73**, 1438 (2004).
[68] M. B. Maple, P.-C. Ho, V. S. Zapf, N. A. Frederick, E. D. Bauer, W. M. Yuhasz, F. W. Woodward, and J. W. Lynn, J. Phys. Soc. Jpn. **71**, Suppl., 23 (2002).
[69] K. Izawa, Y. Nakajima, J. Goryo, Y. Matsuda, S. Osaki, H. Sugawara, H. Sato, P. Thalmeier, and K. Maki, Phys. Rev. Lett. **90**, 117001 (2003).
[70] Y. Aoki, A. Tsuchiya, T. Kanayama, S. R. Saha, H. Sugawara, H. Sato, W. Higemoto, A. Koda, K. Ohishi, K. Nishiyama, and R. Kadono, Phys. Rev. Lett. **91**, 067003 (2003).

[71] K. Kuwahara, K. Iwasa, M. Kohgi, K. Kaneko, N. Metoki, S. Raymond, M.-A. Méasson, J. Flouquet, H. Sugawara, Y. Aoki, and H. Sato, Phys. Rev. Lett. **95**, 107003 (2005).

[72] H. Tou, Y. Inaoka, M. Doi, M. Sera, K. Asaki, H. Kotegawa, H. Sugawara, and H. Sato, J. Phys. Soc. Jpn. **80**, 074703 (2011).

[73] K. Kuwahara, M. Takagi, K. Iwasa, S. Itobe, D. Kikuchi, Y. Aoki, M. Kohgi, H. Sato, and H. Sugawara, Physica B **403**, 903 (2008).

[74] H. Sato, J. Phys. Soc. Jpn. online—News and Comments (2009) and references therein.

[75] Y. Aoki, S. Sanada, H. Aoki, D. Kikuchi, H. Sugawara, and H. Sato, Physica B **378–380**, 54 (2006).

[76] M. Yogi, H. Kotegawa, Y. Imamura, G.-q. Zheng, Y. Kitaoka, H. Sugawara, and H. Sato, Phys. Rev. B **67**, 180501 (2003).

[77] D. T. Adoroja, J.-G. Park, E. A. Goremychkin, N. Takeda, M. Ishikawa, K. A. McEwen, R. Osborn, A. D. Hillier, and B. D. Rainford, Physica B **359–361**, 983 (2005).