EXAFS study of filled skutterudites
RT₄Sb₁₂(R:La, Ce, Pr, Nd, Sm, T:Fe, Ru, Os)

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Abstract.
The filled skutterudites RT₄X₁₂ (R: rare-earth, T: transition metal, X: pnictogen) show a variety of intriguing features by changing the combination of R, T, and X. Among them, some compounds shows characteristic feature called "rattling" that is considered as anharmonic oscillation or off-centered motion of rare-earth ions accommodated in the icosahedron cages made from pnictogen and "rattling" is suggested to contribute to the various features of this system. We applied extended X-ray absorption fine structure (EXAFS) on this system to clarify the microscopic mechanism of "rattling" motion [1]. Temperature dependence of EXAFS thermal (Debye-Waller) factors of R-Sb and T-Sb atomic pairs were analyzed by Einstein model. Thermal oscillation and static distortion are analyzed independently. From this study, we could know systematic information about "rattling" as a large amplitude oscillation of rare-earth ions and static distortion that has two types of cage space dependence.

1. Introduction
Ternary compounds of filled-skutterudites are attracted a lot of attention by its interesting physical properties. Especially in this compounds, characteristic feature called "rattling" is observed by ultrasonic measurement[2], Raman scattering[3] and other methods. "Rattling" is considered as anharmonic oscillation or off-centered motion of rare-earth ions accomodated in the icosahedron cages and suggested to contribute to the formation of heavy fermion state, scattering of heat carrying acoustic phonons and formation of superconductive cooper pair. And it is possible to create excellent materials(e.g, superconductive material, thermoelectric material, etc.) by understanding dynamics of "rattling" and control physical property mentioned above. On the other hand, temperature dependent study of EXAFS reveals the contribution to atomic fluctuation separated from thermal vibrations or static distortions and various studies have been presented[1, 4]. In this paper, we show the result of EXAFS measurements on RT₄Sb₁₂ (R=La, Ce, Pr, Nd, Sm, T=Fe, Ru, Os) to clarify the microscopic mechanism and the relationship between the physical properties and lattice dynamics from the more unified perspective, especially a role of the rare-earth motion and static distortion of the Sb icosahedron cage systematically.
2. Experimental and data analysis

Single crystals of the filled skutterudites RT₄Sb₁₂ were grown by the Sb-flux method [5]. La L₃(5.48keV), Ce L₃(5.72keV), Pr L₃(5.96keV), Nd L₃(6.21keV), Sm L₃(6.72keV), Fe K(7.11keV), Ru K(22.1keV) and Os L₃(10.9keV) edge X-ray absorption spectra for the powder sample prepared from the single crystals were obtained at BL9A, BL9C and BL12C (Si(111) monochromator) at PF and NW10A (Si(311)monochromator) at PF-AR(KEK). The measurements were carried out in transmission mode with the detector of the ionization chambers in the temperature range from 25K to 300K. The XAFS analyses were performed by XANADU[6] code and REX2000[7] software. In order to obtain the structural parameters, non-linear-least-square-fitting was applied to the experimental data by fitting usual EXAFS function, and theoretical parameters of phase shift, backscattering amplitude and electron mean free path are used from FEFF8.10[8].

Figure 1. k³χ(k) spectra(a) and their Fourier transform (|FT|) (b) of R L₃-edge EXAFS for NdT₄Sb₁₂ at 25K(T: Fe, Ru and Os).

Figure 1 shows k³χ(k) spectra(a) and their Fourier transforms (|FT|)(b) of Nd L₃-edge EXAFS for NdT₄Sb₁₂ (T=Fe, Ru, Os) measured at 25K. In the k³χ(k) spectra, the phase of the EXAFS function of NdFe₄Sb₁₂ is different from the others, which indicates the distance between Nd and Sb changes when the transition metal is Fe. In the |FT| spectra, the position and the height of the peaks appearing near 3 ∼ 4Å depend on sample. That suggests the local structure around Nd ion of these samples is different each other.

To know the details of local structure, the non-linear least-square fitting have been carried out to inverse Fourier transformed spectra of the peak at the range of 2.9 ∼ 4.2Å for R L₃-edge and 1.5 ∼ 3.2Å for Fe K, Ru K and Os L₃-edge using two-shell model of R-Sb and R-T for the former, one-shell model of T-Sb for the latter. From the fitting, the parameters r, N, C₂, C₃ were determined.

3. Result and discussion

In this paper, our attention is focused on the motion of rare-earth ions in the Sb icosahedron cage. So we have tried to analyze the motion of R ions as a harmonic vibration model as we have already done[1]. The harmonic vibrator can be described by Einstein model represented as C₂ = h²coth(θₑ/2T)/(2μkₑθₑ) + C₂(static), where, μ is the reduced mass of the Einstein vibrator, θₑ is the Einstein temperature, T is the temperature and C₂(static) is the static distortion (temperature independent part) in the system.

Figure 2 shows temperature dependence of EXAFS Debye-Waller factor C₂ for CeT₄Sb₁₂ obtained from the fitting. Results of Einstein fitting are also shown by solid lines. From Einstein fitting, we could obtain the information of static distortion and Einstein temperature.
For example, in figure 2, CeFe$_4$Sb$_{12}$ has the largest static distortion and highest Einstein temperature, in contrast, CeRu$_4$Sb$_{12}$ has the smallest static distortion and lowest Einstein temperature. We analyzed all EXAFS Debye-Waller factor obtained from experiment like this way.

Figure 3 shows Einstein temperature $\Theta_E$ (a) and the static distortion $\sigma_{\text{static}} = \sqrt{C_2(\text{static})}$ (b) for R-Sb and T-Sb as a function of the one-dimensional cage space defined by $r_{R-Sb} - r_{R^{3+}} - r_{Sb}$, where $r_{R-Sb}$ is a distance between R and Sb, $r_{R^{3+}}$ and $r_{Sb}$ are the ionic and atomic radius for $R^{3+}$ ions and Sb atom [9]. In SmOs$_4$Sb$_{12}$, Sm ion shows charge fluctuation[10], and the ionic radius used in this study is $r_{\text{Sm}^{2.76+}}$. Solid circles, triangles, squares, inverted triangles and diamonds correspond to La, Ce, Pr, Nd and Sm, respectively. Solid, dashed and dotted lines correspond to RFe$_4$Sb$_{12}$, RRu$_4$Sb$_{12}$, ROs$_4$Sb$_{12}$, respectively. Open triangles, squares and circles shows the results of Fe $K$-, Ru $K$- and Os $L$-III-edges. It is clear in figure 3 (a) that Einstein temperatures of T-Sb atomic pairs are higher than that of R-Sb atomic pairs. That means T-Sb bond is more stiff and stable than R-Sb bond. For R $L$-III edges, Einstein temperature seems to decrease with increasing cage space. It is reasonable that the longer the distance of R-Sb, the weaker the bond strength. Static distortion in figure 3 (b) includes key information for “rattling”. Linear relation between $\sigma_{\text{static}}$ and the cage space is observed for the results of R $L$-III-edges in the compounds which have same cage and different guest ions. On the other hands, $\sigma_{\text{static}}$ of Fe-Sb atomic pairs($\triangle$) are larger than that of Ru-Sb($\Box$) and Os-Sb($\bigcirc$) atomic pairs and that may affect to the static distortion of R-Sb atomic pairs.

To understand the static distortions of rare-earth ions without distortion of cages. We simply defined effective static distortion as the difference between static distortion for R-Sb and average
rate of static distortions of T-Sb that have same cages. Figure 4 shows the cage space dependence of effective static distortion. It is interesting that the behavior of effective static distortion has two regions of cage space dependence. In the small cage region below \( \sim 0.55\text{Å} \), effective static distortion is almost constant, while in the larger cage space region, effective static distortion increases linearly as cage space. These two groups are almost the same with that the second order Raman scattering which is due to independent vibration ("rattling") of rare-earth ions was observed or not.

4. Conclusion
Temperature dependence of EXAFS gives us the informations of dynamics around absorption atoms through its thermal factor. Einstein temperature obtained from EXAFS thermal factor analysis for R-Sb atomic pairs is smaller than that of T-Sb atomic pairs, suggesting that R ions have large amplitude of oscillation in the stiff cage. In addition, the effective static distortion obtained from the difference between static distortions of R-Sb and T-Sb atomic pairs can be separated by the cage space and it corresponds to the second order Raman scattering was observed or not. The effective static distortion due to the anharmonic oscillation or off-centered motion of rare-earth ions appear when the cage space is larger than 0.55Å.

Acknowledgments
This study was partially supported by a Grant-in-Aid for Scientific Research in Priority Area § Skutterudite § (No.15072206) of MEXT, Japan. The synchrotron radiation experiments were performed at Photon Factory at KEK under Proposal No.2005G198, 2006G036 and 2008G629

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