

Mechanism of rattling in filled skutterudite compounds RFe_4Sb_{12} ($R=Pr, Nd$) and RRu_4Sb_{12} ($R=Ce, Pr, Nd$) studied by XAFS

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Introduction

Ternary compounds of filled skutterudite RT_4X_{12} (R =rare-earth, $T=Fe, Ru, Os$, $X=P, As, Sb$) shows various physical properties by changing the composition of atoms. These compounds have cage structure consisting of 12 X atoms, including an R atom inside. As the size of cage is large, there is space between cage and R atom. In this cage R atom shows anharmonic and individual vibration, which is called "rattling".

So far, the correlation between rattling motion and size of cage space was shown by XAFS measurement about RO_4Sb_{12} ($R=La, Ce, Pr, Nd, Sm$) [1]. In this report we have measured XAFS ($R L_{III}$ -edge) for RFe_4Sb_{12} ($R=Pr, Nd$) and RRu_4Sb_{12} ($R=Ce, Pr, Nd$) to investigate compounds which have smaller cage space than previous ones.

Experimental and Data analyses

X-ray absorption spectra for $R L_{III}$ -edge were collected at BL9C in KEK-PF. The powder samples of RFe_4Sb_{12} ($R=Pr, Nd$) and RRu_4Sb_{12} ($R=Ce, Pr, Nd$) were measured by transmission mode. Measurement temperature range is from 25K to 300K. EXAFS signal were analyzed by XANADU [2] and FEFF 8.01 code [3].

Results and Discussion

Figure 1 shows the Fourier transforms of $R L_{III}$ -edge EXAFS measured from 25K to 300K. The FT range is from 2 to 10.5\AA^{-1} about $CeRu_4Sb_{12}$, and from 2 to 11\AA^{-1} about other four compounds.

The size of cage space for RRu_4Sb_{12} compounds is larger than that for RFe_4Sb_{12} because of larger lattice constant. On the other hand, if rare-earth ion is replaced within the same T_4Sb_{12} cage, the contribution of lanthanide contraction is dominant, so the size of cage space becomes larger as atomic number increases.

Here we discuss only peak intensity of FT spectrum. The first peak corresponds to the first nearest Sb atom and the second peak corresponds to the second nearest Fe or Ru atom for RFe_4Sb_{12} ($R=Pr, Nd$) and $CeRu_4Sb_{12}$. The first peak contains the first and second nearest Sb and Ru atom for $PrRu_4Sb_{12}$ and $NdRu_4Sb_{12}$. As a whole the first peak for RRu_4Sb_{12} is larger than that for RFe_4Sb_{12} . However, there is a difference in the appearance of peaks, so one cannot compare directly these five compounds about the peak intensity any more.

Next we see the temperature dependence of the peak intensities. The decreases of the peak intensity are shown in all compounds with increase of temperature. This means that the Debye-Waller factor increases due to thermal atomic vibration by increasing temperature. The decrease in the peak intensity is prominent in RRu_4Sb_{12} . This remarkable decrease of peak intensity is expected to be attributed by the rattling motion in RRu_4Sb_{12} compounds with larger cage space.

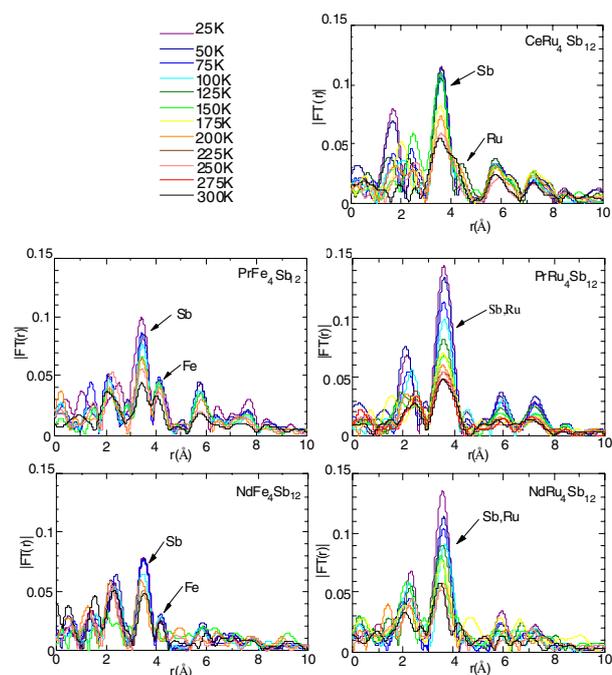


Fig. 1 Temperature dependence of Fourier transform for RFe_4Sb_{12} ($R=Pr, Nd$) and RRu_4Sb_{12} ($R=Ce, Pr, Nd$)

References

- [1] K. Nitta, *et al.*, J. Phys. Soc. Jpn., **77**, 063601 (2008)
- [2] H. Sakane, *et al.* Jpn. J. Appl. Phys. **32**, 4641 (1993).
- [3] A.L. Ankudinov and J.J. Rehr: Phys. Rev. B **62**, 2437 (2000).