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^{149}Sm and ^{57}Fe nuclear resonant inelastic scattering of filled skutterudites $SmFe_4X_{12}$ (X: pnictogen)

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Abstract ^{149}Sm and ^{57}Fe nuclear resonant inelastic scattering (NRIS) measurements were carried out on $SmFe_4P_{12}$, $SmFe_4As_{12}$ and $SmFe_4Sb_{12}$. A clear dip structure of the ^{57}Fe NRIS spectrum was found in $SmFe_4P_{12}$, which was not clearly observed for $SmFe_4As_{12}$ and $SmFe_4Sb_{12}$. On the other hand, the line width of the phonon excitation in the ^{149}Sm NRIS spectrum increases with increasing the ionic radius of the pnictogen. These findings imply that the hybridization between the Sm and Fe phonon modes is correlated to changes in the ionic radius of the pnictogen.

Keywords Filled skutterudite · Nuclear resonant inelastic scattering · Element-specific phonon spectrum

1 Introduction

Cage-structured compounds such as filled skutterudites and clathrates have attracted considerable interest owing to their strongly correlated electron systems and

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application as thermoelectric materials. One of the key features of these compounds is the presence of a low-lying optical mode associated with the atoms inserted into the cage structure, which is called a guest mode. Since the phonon-glass-electron-crystal model was first proposed [1], the importance of guest modes for thermal insulation has been discussed [2–5]. In strongly correlated electron systems, on the other hand, superconductivity in β-pyrochlore compounds is an example of superconductivities correlated with low-lying guest modes [6].

Nuclear resonant inelastic scattering (NRIS) is a unique technique for investigating element-specific phonon spectra in materials. It can be applied to a limited number of elements including Mössbauer isotopes that can be excited by sunchrotron radiation X-rays. However, it is a useful tool for elucidating atomic dynamics in cage-structured compounds. In the present work, the atomic dynamics in filled skutterudites were investigated by performing ^{149}Sm and ^{57}Fe NRIS experiments.

2 Experimental procedure

NRIS measurements were carried out at BL09XU of SPring-8 in Japan. ^{57}Fe NRIS measurement of $SmFe_4P_{12}$ at 300 K was carried out with 3.5 meV resolution using a Si(5 1 1)-Si(9 7 5) nested-type high-resolution monochromator (HRM) and those of $SmFe_4As_{12}$ and $SmFe_4Sb_{12}$ at 300 K were carried out with 1.6 meV resolution using a Ge(4 2 2)-Si(9 7 5)-Si(9 7 5) HRM [7]. ^{149}Sm NRIS measurements of $SmFe_4P_{12}$ and $SmFe_4Sb_{12}$ at 25 K ($SmFe_4As_{12}$ at 9 K) were carried out with 1.5 meV resolution using a Si(4 4 0)-Si(16 8 8)-Ge(4 2 2) HRM (a Si(4 4 0)-Si(16 8 8) nested-type HRM) [7, 8].

3 Experimental results and discussion

The ^{149}Sm NRIS spectra of $SmFe_4X_{12}$ (X: P, As and Sb) are shown in Fig. 1a. All the spectra obtained exhibit relatively sharp excitation, suggesting the presence of a dispersionless mode similar to an Einstein mode. Similar spectra have already been reported for other filled skutterudites [4, 9]. The excitation energy decreases with increasing ionic radius of X, whereas the line width increases with increasing X ionic radius. With respect to the excitation energy, the present results indicate that the guest-free space is an important parameter. This was also suggested by the results of other experiments on filled skutterudites [10–12].

The ^{57}Fe NRIS spectra of $SmFe_4X_{12}$ at 300 K are shown in Fig. 1b. Unlike the ^{149}Sm NRIS spectra, the contribution of the Fe atoms to the acoustic modes was clearly observed in the ^{57}Fe spectra. As was reported Ref. [9], a dip structure was found in the ^{57}Fe NRIS spectrum of $SmFe_4P_{12}$ in spite of the inferior energy resolution of 3.5 meV. The energy at which the dip structure was found is in good agreement with that of Sm phonon excitation observed by ^{149}Sm NRIS, although the Sm phonon energy is slightly shifted, mainly due to the shirinkage of the unit cell volume with decreasing temperature [13]. The presence of the dip structure is evidence that the guest modes are hybridized with the acoustic modes. This was supported by the reasonable agreement between the energy of the dipstructure in the ^{57}Fe NRIS spectra and the Einstein temperature obtained by EXAFS experiments

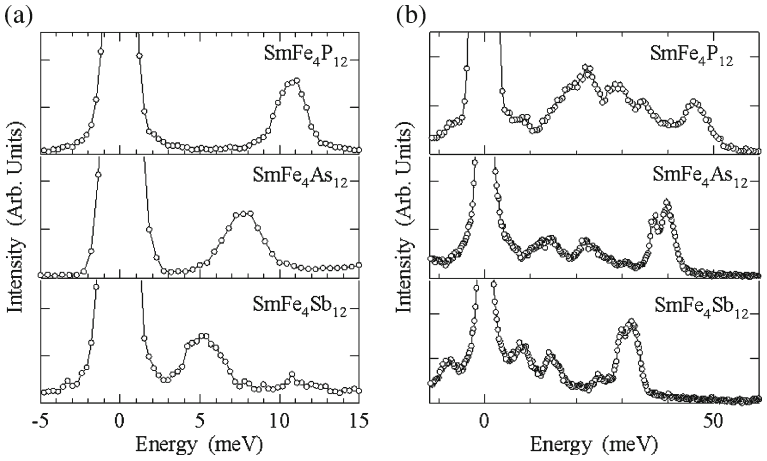

Fig. 1 **a** [149]Sm nuclear resonant inelastic scattering spectra of $SmFe_4P_{12}$ at 25 K, $SmFe_4As_{12}$ at 9 K and $SmFe_4Sb_{12}$ at 25 K. **b** [57]Fe nuclear resonant inelastic scattering spectra of $SmFe_4P_{12}$, $SmFe_4As_{12}$ and $SmFe_4Sb_{12}$ at 300 K

on the series of RFe_4P_{12} (R: rare-earth). On the other hand, the dip structure in the $SmFe_4As_{12}$ or $SmFe_4Sb_{12}$ spectrum was less clearly observed than that in the $SmFe_4P_{12}$ spectrum. The result for $SmFe_4Sb_{12}$ is very similar to that for $EuFe_4Sb_{12}$ [14, 15]. In addition, the X-ray absorption spectrum of $SmFe_4Sb_{12}$ ($EuFe_4Sb_{12}$) using the Sm (Eu) L_3-edge demonstrates that the Sm (Eu) is trivalent (divalent) [16, 17]. These findings imply that the Fe atomic dynamics are correlated to the X atoms in the series of $SmFe_4X_{12}$ compounds.

Hereafter, we discuss the X-dependence of the dip structure in the [57]Fe NRIS spectrum and the line width in the [149]Sm NRIS spectra of $SmFe_4X_{12}$ compounds. We interpret the dip structure and the line width in terms of the change in the hybridization between the Sm modes and acoustic modes including the Fe atoms. When the sum rule for NRIS measurements [18] is applied to the present results, the average force constants are 293 ± 10, 189 ± 2 and 156 ± 4 N / m for $SmFe_4P_{12}$, $SmFe_4As_{12}$ and $SmFe_4Sb_{12}$, respectively, at the Fe site. This infers that the cage consisting of Fe and X atoms is softened by changes in the atomic radius of X. This softening leads to strong hybridization between the Sm modes and acoustic modes, i.e., the contribution of the Fe atoms to the acoustic modes. Consequently, the line width in the Sm NRIS spectra, which reflects the density of states at the Sm site, is the broadened by the dispersion of the Sm modes as guest modes.

4 Summary

We carried out [149]Sm and [57]Fe NRIS measurements on the series of $SmFe_4X_{12}$. The X-dependence of the NRIS spectra is interpreted in terms of the X-dependence of the hybridization between Fe modes, which partially play the role of acoustic modes, with Sm modes as guest modes.

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