149Sm nuclear resonant inelastic scattering of SmB6

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Abstract. 149Sm nuclear resonant inelastic scattering was carried out in SmB6 in order to investigate the lattice dynamics due to Sm atoms. A sharp phonon excitation associated with Sm atoms is observed around 10 meV, suggesting the presence of a Sm dispersionless mode. The Sm phonon energy shows significant temperature dependence, correlated with temperature dependence of Sm valence state. The nuclear resonant inelastic scattering spectra also indicate that the electronic configuration at the Sm site is 4f5 hybridized with the conduction electrons.

1. Introduction

SmB6 is one of the attractive compounds in a series of hexaborides. This is a valence fluctuating system, as revealed by X-ray absorption spectroscopy, photoemission and 149Sm Mössbauer spectroscopy [1-3]. Anomalous temperature dependence of the lattice constant also suggests the correlation with Sm valence fluctuation. The lattice constant shows a minimum around 150 K, and negative thermal expansion coefficient is observed at lower temperatures [4, 5]. Because the photoemission spectroscopy suggests that the insulator gap opens around 150 K [2], the opening of the insulator gap seems to be correlated with the lattice dynamics in this compound.

Correlation between the lattice dynamics and valence state of the guest atoms is expected by the previous Raman scattering investigation and recent ab initio calculation using the ABINIT package [6-8]. The most significant difference due to the valence state of the guest atoms is the phonon dispersion relation at the zone boundaries. The phonon energies of the guest atomic motion at the zone boundaries are split in divalent hexaborides, whereas they are degenerate in trivalent hexaborides [9]. This affects the phonon density of states (DOS) as shown in figure 1. The partial DOS of the
guest modes clearly depends on the valence state of the guest ions. The calculation suggests that the difference in the phonon energy between divalent and trivalent hexaborides is caused by the number of carriers. Because SmB$_6$ is recognized as a Kondo insulator and as a valence fluctuating system, a temperature dependence of phonon spectra is expected, correlated with the change of the number of carriers.

Nuclear resonant inelastic scattering (NRIS) is a powerful tool to investigate the element-specific partial DOS [10]. Here, nuclear resonance corresponds to the Mössbauer effect. Thus, Sm compounds are available for NRIS measurements, as Sm atom includes several Mössbauer isotopes. In addition, since the elastic scattering in Mössbauer resonance means the probability of recoil-free nuclear resonance [11], the inelastic part of the Mössbauer resonance corresponds to phonon excitation produced by nuclear recoil. Therefore, no excitations except for phonons can be observed by NRIS. As mentioned above, the calculation suggests that the partial DOS of the guest atoms is sensitive to the valence state of the guest ion. When the lattice dynamics in SmB$_6$ is strongly correlated with the Sm valence state and/or electronic configuration, temperature dependence of $^{149}$Sm NRIS spectra is expected. Therefore, the lattice dynamical properties and electronic states of Sm atom have been investigated in this paper by $^{149}$Sm NRIS.

![Figure 1 (a) Calculated phonon density of states in CaB$_6$ convolved with 1.5 meV Gaussian resolution function.](image1a)

![Figure 1 (b) Calculated phonon density of states in LaB$_6$ convolved with 1.5 meV Gaussian resolution function.](image1b)

Figure 2. $^{149}$Sm nuclear resonant inelastic scattering spectra of SmB$_6$ at various temperatures.
2. Experimental setups

$^{149}$Sm NRIS measurements were carried out at the BL09XU beamline of SPring-8. The energy resolution was 1.5 meV at the $^{149}$Sm Mössbauer resonance of 22.494 keV. The details of the X-ray optics are reported in [12]. The detector was a multi-element avalanche photodiode with the large solid angle. The chosen operation mode of SPring-8 was 203 bunches with the interval between the X-ray pulses of 23.6 ns, in order to distinguish nuclear scattering from electronic scattering.

3. Experimental results and discussion

$^{149}$Sm NRIS spectrum of SmB$_6$ at 300 K shows periodic and sharp excitations as shown in figure 2. The line width of the excitation is 3 meV at all temperatures. The calculation shown in figure 1 indicates that the width of the DOS associated with the La atoms is 3 meV in LaB$_6$ and that associated with Ca atoms is 6 meV in CaB$_6$. This demonstrates the presence of the dispersionless modes, as was indicated by the inelastic neutron scattering [13]. This is similar to Sm filled skutterudites [14, 15]. Assuming the Gaussian-shaped partial DOS, the obtained spectrum is well reproduced with multiple phonon contributions [16]. This result does not deny the contribution of Sm atomic motion to the acoustic modes in SmB$_6$, but demonstrates small contribution to the acoustic modes. Because the present result is very similar to the previous $^{161}$Dy NRIS of DyB$_6$ [17], Sm valence expected from the Sm phonon DOS is a trivalent state. This also agrees with the contrast between the cases of the divalent and trivalent hexaborides as shown in figure 1. However, as reported previously [2, 3], the Sm valence state is an intermediate state between divalent and trivalent states. This suggests that the electronic configuration at the Sm site consists of a strong hybridization between 4f and conduction electrons.

Strong temperature dependence of the spectra shown in figure 2 indicates that the excitations at high energies come from multi-phonon contributions [16]. As mentioned above, because the cross section of the NRIS is the only contribution of phonon excitations, the other contributions are ruled out. In addition, the balance of NRIS spectra is caused by the Bose factor. Unless the observed temperature dependence of the spectra correlates with multi-phonon contributions, the intensity of the lower energy excitations is expected to show minor temperature dependence, and the peak of the higher energy excitations must remain even at low temperature. The energy observed at the second excitation around 20 meV agrees well with the unknown dispersionless excitation reported in the neutron scattering experiment [13]. However it might be hard to assert whether or not the unknown excitation comes from a two-phonon contribution in SmB$_6$, because temperature dependence of inelastic neutron scattering measurements has not been reported to our knowledge. Probably, the present result reveals the possible origin of the unknown excitation.

Figure 3 shows temperature dependence of the averaged phonon energy in SmB$_6$. The averaged energy is sensitive to the temperature dependence of the Sm valence state [18]. Above ~ 150 K, the...
energy decreases with the decrease of temperature, suggesting an anharmonic phonon mode. Between ~ 30 and ~ 150 K, the energy increases with decreasing temperature. In this temperature region, the temperature dependence of the averaged Sm valence state indicates an increase of Sm ionic radius towards 30 K. The increase of the phonon energy seems to be correlated with the free space of the Sm ions. In addition, the averaged phonon energy decreases again below ~ 30 K. This also suggests the correlation between Sm valence state and phonon energy associated with the guest free space at the Sm site.

In NRIS measurements, generally, a sum rule exists based on the Mössbauer effect [19]. The inelastic contribution provides the probability of the Mössbauer effect, recoil-free fraction. The relationship between the inelastic contribution of NRIS spectra and the recoil-free fraction is given by

\[
\int E R \int S_{\text{inelastic}}(\omega) d\omega = \int \omega S_{\text{inelastic}}(\omega) d\omega,
\]

where \(E_R = 1.81 \text{ meV}\) is the recoil energy in \(^{149}\text{Sm}\) Mössbauer effect and \(S_{\text{inelastic}}(\omega)\) is an inelastic contribution of the NRIS spectra. The recoil-free fraction \(f\) is written as

\[
f = \exp \left( -\frac{4\pi^2}{\lambda^2} \langle x^2 \rangle \right),
\]

where \(\lambda\) is the wavelength of Mössbauer resonance and \(\langle x^2 \rangle\) is the atomic displacement factor at the probe atomic site, the Sm site in the present case. The obtained atomic displacement factor is plotted against temperature in figure 4. This dependence agrees with the reported neutron diffraction data [4]. It also demonstrates one of the reasons not only for the adaptability of the sum rule [19] but also for denying any contribution of the observed excitations except for phonons. The temperature dependence of the atomic displacement factor shows no anomalies at about 25, 50 and 150 K where the slope of the averaged Sm valence changes with temperature.

4. Summary
We have succeeded in the direct measurement of the Sm phonon energy in SmB\(_6\). The present results demonstrate the presence of the dispersionless modes around 10 meV at 300 K. This agrees with the calculation in LaB\(_6\) [7] and with the \(^{161}\text{Dy}\) NRIS of DyB\(_6\) [17]. Therefore, the presence of the dispersionless modes infers that a possible electronic configuration at Sm site is a mixture between 4f\(^6\) and conduction electrons. The temperature dependence of the dispersionless mode energy indicates that the Sm mode is anharmonic in SmB\(_6\). Besides, the temperature dependence of the Sm phonon energy shows significant temperature dependence associated with the averaged Sm valence state.

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