Mössbauer Effect Measurements on Valence Fluctuating Compound Sm₃Se₄

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Magnetic susceptibility¹, ², transport properties³, specific heat², lattice constant² and X-ray LIII absorption⁴ measurements of Sm₃Se₄ reported so far are similar to those of Eu₃S₄ and Sm₃S₄, indicating the thermal activated valence fluctuation.⁵ Ac-conductivity data², however, seem to suggest a quantum-mechanical tunnelling valence fluctuation at lowest temperature of measurement different from the sulphides. The aim of the present work is to study the electronic configuration of Sm₃Se₄ at various temperatures by Mössbauer measurements, in which the isomer shift should provide a data for accurate determination of the 4f configurations in Sm ions. The 4f⁵ and 4f⁶ configurations produce different potentials on the various s electrons, which produce a change of the amplitude of these s electrons on the nucleus and thus give rise to different isomer shifts for the two configurations.

The Mössbauer absorption spectra were obtained in a standard transmission geometry, using a conventional constant-acceleration spectrometer. The temperature of the source and that of the absorber could be changed independently from 4.2 K up to room temperature. Measurements were performed by using the 22.5 keV γ-transition in ¹⁴⁹Eu. The γ-rays were detected by a pure Ge LEP5 (Low-Energy Photon Spectrometer) of 5 cc. The sample velocity was calibrated by detecting the laser light reflected from a mirror attached to the rear end of the source driver. The source consisting of ¹⁴⁹Eu was produced by the (p, 2n) reaction using the cyclotron of Tohoku University. Target was a pressed pellet of ¹⁵⁰Sm₂O₃ containing 280 mg of enriched ¹⁵⁰Sm isotope. The absorber consisted of a polycrystalline sample of Sm₃Se₄ produced from a pure single crystal containing ¹⁴⁹Sm in natural abundance. The same single crystal had been used for previous experiments performed in our laboratory.²

Mössbauer spectra of Sm₃Se₄ were measured at three temperatures 295 K, 77.4 K and 8.0 K. These spectra are plotted in Fig. 1. The isomer shift was evaluated by a least-squares fitting of Lorentzian shape to the data. In the case of the spectra obtained at 295 K and 77.4 K the experimental spectrum consist of a single resonance dip and it is therefore possible to fit the points by a single Lorentzian curve. The spectrum taken at 8.0 K is more complex, but the observed data are adequately described by the sum of two Lorentzians. The intensities of these two components are in a ratio close to 2:1 and their centers of gravity are at 0.50 mm/s and -1.53 mm/s, respectively.
The observed values of the isomer shift and the linewidth for Sm$_3$Se$_4$, as well as those for Sm$_2$Se$_3$ and SmSe$^1$, are collected in Table 1. In the latter two compounds the valencies of samarium are +3 and +2, respectively. Mössbauer absorption measurement in Sm$_3$Se$_4$ at 4.5 K is now in progress. Detailed results and discussions of valence fluctuating state on Sm$_3$Se$_4$ will be published later.

References


Table 1. $^{149}$Sm isomer shift and linewidth

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>$\delta$(mm/sec)</th>
<th>$\Gamma$(mm/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sm$_3$Se$_4$</td>
<td>295 K</td>
<td>-0.28</td>
<td>4.92</td>
</tr>
<tr>
<td></td>
<td>77.4 K</td>
<td>-0.28</td>
<td>4.44</td>
</tr>
<tr>
<td></td>
<td>8.0 K</td>
<td>+0.50</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td>8.0 K</td>
<td>-1.53</td>
<td>3.38</td>
</tr>
<tr>
<td>Sm$_2$Se$_3$</td>
<td>Room Temp.</td>
<td>-0.02</td>
<td>2.56</td>
</tr>
<tr>
<td>SmSe$^1$</td>
<td>Room Temp.</td>
<td>-0.71</td>
<td>2.15</td>
</tr>
</tbody>
</table>

a) Ref. 1.
Fig. 1. Mössbauer spectra of Sm$_2$Se$_4$. The solid line is a Lorentzian least-squares fit to the data.