Inelastic X-ray scattering of filled-skutterudite compounds

Satoshi Tsutsui

Japan Synchrotron Radiation Research Institute, SPring-8

Filled-skutterudite compounds attracted many researchers' interests both as strongly correlated electron systems and for the industrial applications. These compounds show interesting physical properties in strongly correlated electron system, multipolar ordering including magnetic ordering, superconductivity, heavy fermion behavior and so on. They are also considered as candidates for next-generation thermoelectric materials. Their chemical form is written as RT_4X_{12}, where R is rare-earth, actinide, alkaline and alkaline-earth elements, T is transition metal elements and X is pnicogen elements. The crystal structure contains a cage structure like clathrate compounds. R atoms stay in the icosahedral cage of X atoms. The cages including R atoms consist of bcc structure.

The cage structure in filled-skutterudite compounds suggests the presence of an Einstein-like localized mode. The presence of an Einstein-like mode has been one of important parameters to understand their physical properties in strongly correlated electron systems as well as for the application to thermoelectric materials. The correlation between the presence of Einstein modes and the reduction of thermal conductivity has been discussed in these compounds since the discussion about the presence of Einstein modes in filled-Skutterudite antimonides [1]. On the other hand, the recent results of the ultrasound measurements have been discussed the correlation between atomic motion in antimony icosahedral cage and superconductivity with heavy electrons in $PrOs_4Sb_{12}$ [2, 3]. The heavy fermion system insensitive to applied magnetic field was discovered in $SmOs_4Sb_{12}$ [4]. These are also considered as the correlation with Einstein-like modes.

The contribution of an Einstein-like mode to thermoelectricity is also crucial to reduce the thermal conductivity. The high electric conductivity and low thermal conductivity are needed for good thermoelectric materials. The merit of thermoelectricity ZT is written as

$$ZT = S^2 T\sigma/\kappa ,$$

where T is temperature, S is Seebeck constant, σ is electric conductivity and κ is thermal conductivity. In addition, thermal conductivity is written as

$$\kappa = \kappa_{el} + \kappa_{ph} ,$$

where κ_{el} is thermal conductivity due to electrons and κ_{ph} is that due to phonon. Since the κ_{el} is proportionate to the electric conductivity, low thermal conductivity due to phonon is needed. It is believed up to now that the heat-carrying acoustic phonons are effectively scattered by the Einstein modes in filled-skutterudite compounds.

The heavy fermion behavior induced by the strong electron-phonon coupling was proposed in superconductor of V_3Si [5, 6]. Recently, the similar model was proposed in filled-skutterudite compounds by Mitsumoto and Ohno [7]. These models are based on the strong coupling between the low-lying Einstein modes and conduction electrons. The presence of Einstein modes are crucial to understand the heavy fermion behavior induced by strong electron-phonon coupling by these scenarios.

We have investigated the phonon dispersion of Sm-filled skutterudite compounds by meV-resolution inelastic x-ray scattering (IXS) at BL35XU in SPring-8. We used Si(11 11 11) backscattering reflection as a high resolution monochrometer, whose energy resolution is about 1.5 meV. We measured IXS spectra at room temperature. The samples are a single crystal prepared by a flux method. The size of every sample is about 1 mm^3.

We found low-lying dispersionless modes in $SmFe_4P_{12}$, $SmRu_4P_{12}$ and $SmOs_4Sb_{12}$ along [1 0 0], [1 1 0] and [1 1 1]. This suggests the presence of the Einstein-like modes in these compounds. These are observed at 11 meV in $SmFe_4P_{12}$, 9 meV in $SmRu_4P_{12}$ and ~ 3 meV in $SmOs_4Sb_{12}$. Such a mode is observed in both longitudinal and transverse geometries. This mode crosses the acoustic modes in every direction of $SmFe_4P_{12}$ and $SmRu_4P_{12}$. This indicates that the dispersion curves expected from the crystal structure seems to be realized in filled-skutterudite phosphides. The correlation between Einstein-like modes and acoustic modes in $SmOs_4Sb_{12}$ is different from that in the filled-skutterudite phosphides. The difference in the dispersion between phosphides and antimonides are probably correlated with the size of the icosahedral cages, because antimony cages are larger than phosphorus ones.

We have also carried out ^{149}Sm nuclear resonant inelastic scattering of $SmFe_4P_{12}$ and $SmRu_4P_{12}$ at BL09XU in SPring-8 [8]. The spectra obtained show a strong peak at the energies of the dispersionless modes. This indicates that the Sm atoms vibrate in the icosahedral cage by the energy where the flat dispersions are observed.

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