Direct Observation of Motion in Atom Cage

Thermoelectricity requires materials that are electrically conducting but thermally insulating. While important technologically, such materials are difficult to realize because electrons usually act as both electronic and thermal conductors. One option for their realization is a material which has low lattice conductivity, whereby the lattice contribution to thermal transport is removed. Since the proposal of the phonon-glass-electron-crystal (PGEC) model [1], cage compounds, such as filled skutterudites (see Fig. 1) and clathrates have been considered potential thermoelectric materials because of their low thermal conductivity. The central idea is that localized vibrational modes of the atoms inserted into the cages reduces thermal conductivity.

We employ a combination of two synchrotron techniques to investigate precisely the motions of atoms in cages of filled skutterudites. These materials, having the formula RT_4X_{12} (R: rare earth or actinide, T: transition metal, X: pnictogen), have a cage about atom "R" (see Fig. 1), which may lead to localized motion and reduce thermal conductivity. Using meV-resolved inelastic X-ray scattering (IXS), we show that nearly dispersionless modes exist, and using atom-specific nuclear resonant inelastic scattering (NRIS), we show that these modes are precisely those of the guest atom in the cage [2], as discussed below.

The left and middle panels of Fig. 2 show the phonon dispersion relations in $SmRu_4P_{12}$ obtained by IXS at beamline **BL35XU**. We found dispersionless modes in both longitudinal and transverse modes along the (1 0 0) and (1 1 0) directions. The obtained dispersion relations also show that the dispersionless modes hybridize with the heat-carrying acoustic modes. Meanwhile, the right panel of Fig. 2 shows the Sm PDOS in $SmRu_4P_{12}$ obtained by ^{149}Sm NRIS at beamline **BL09XU**. A strong single peak in the Sm

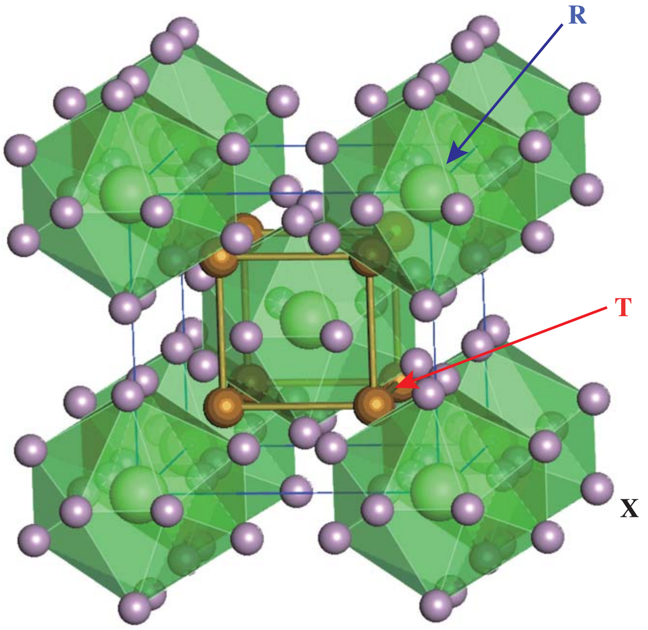

Fig. 1. Crystal structure of filled skutterudites. A rare earth atom (R), a Sm atom in the present case, is surrounded by 12 pnictogen atoms (X), P atoms in the present case, forming an icosahedral cage. A transition metal atom (T), Ru in the present case, is located between the icosahedral cages.

PDOS, suggesting the presence of a dispersionless mode, and its energy, 9 meV, agrees with that of the modes observed by IXS. This indicates that the dispersionless modes at 9 meV correspond to Sm atomic motion. The sharp PDOS also means that the contribution of Sm motion to the acoustic modes is small, similar to the localized mode.

To understand the thermoelectricity in filled skutterudites, the relation between the dispersionless mode and the heat-carrying acoustic modes is important. Investigating the precise atomic motion makes it possible to clarify the contribution of the phonon to the reduction of the thermal conductivity. In particular, the hybridization of the dispersionless mode with the acoustic mode, as we observe here, is not expected from the PGEC model, which is one of the candidate theories for explaining the reduction of thermal conductivity [1]. Our recent work suggested that such hybridization is the common property in the series of filled skutterudites [3-6], as did subsequent neutron scattering work [7,8]. Since the temperature dependence of the NRIS spectra indicates that the Sm modes in $SmRu_4P_{12}$ are anharmonic [6], the present work hints that the hybridization of the anharmonic dispersionless modes owing to the inserted atoms with acoustic modes might reduce the thermal conductivity due to phonons in cage-structured compounds.

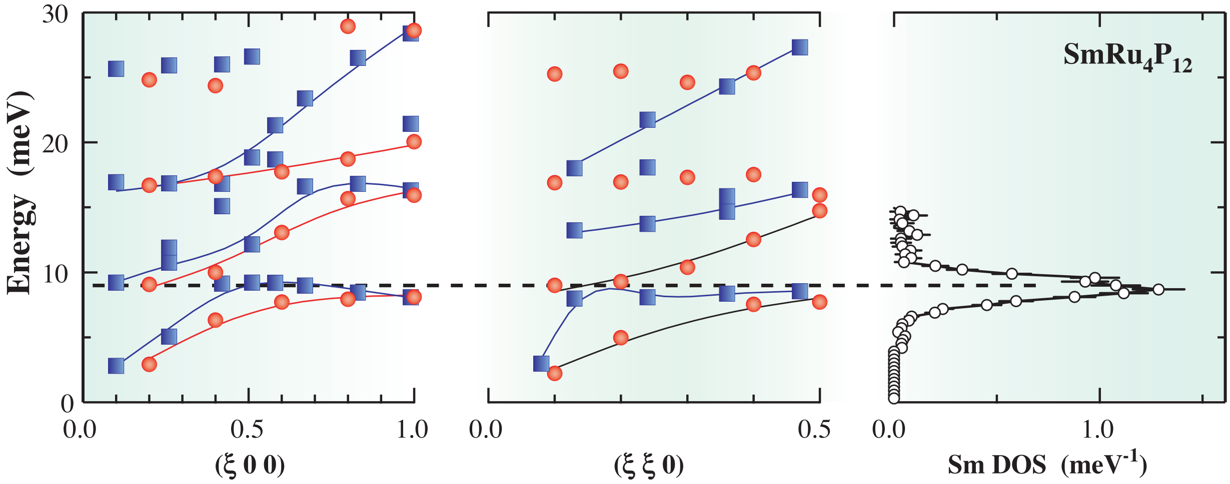

Fig. 2. Phonon dispersion in higher symmetry directions in $SmRu_4P_{12}$ obtained by IXS (left and middle) and measured partial phonon density of states associated with Sm atomic motion (right). The blue squares (red circles) show the phonon energy of the longitudinal (transverse) modes in each direction. The solid curves are guides for the eye. The dotted line is the excitation energy observed by ^{149}Sm NRIS.

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