Thermoelectric clathrates with off-center rattling ions

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Abstract: The field of thermoelectrics has advanced recently because of the strong demand for saving energy. To develop high-performance thermoelectric materials, a guideline is the so-called "Phonon-Glass and Electron-Crystal" concept, where both the thermal conductivity and electrical resistivity should be made simultaneously low by some exotic mechanism. This concept seems to be realized in the intermetallic clathrates with general formula $A_8M_{16}X_{30}$ (A=Sr, Ba, Eu; M=Al, Ga, In; X=Si, Ge, Sn) through the presence of rattler guest ions vibrating in broadened anharmonic potentials with off-center minima.

In this talk, we present our recent findings on the structural, electronic and vibrational behaviors of $Ba_8Ga_{16}Sn_{30}$ and related compounds through thermodynamic and transport measurements [1,2] as well as microscopic techniques such as Raman scattering [3], EXAFS [4], inelastic neutron scattering [5] and others. Type-I clathrate $Ba_8Ga_{16}Sn_{30}$ shows glasslike thermal conductivity that is actually lower than that of amorphous silica glass, while still behaving electrically as a heavily doped semiconducting crystal. The refinements of single-crystal x-ray diffraction data indicate that the Ba atom in the tetrakaidecahedron occupies the off-center 24*k* sites which are 0.43 Å away from the center. This displacement results from the mismatch between the guest ion size and the host cage size. The Ba rattling among off-center positions has a characteristic energy of 20 K whose energy is lowest among type-I clathrates. The low thermal conductivity is therefore ascribed to the strong scattering of acoustic phonons by the low-energy off-center rattling.

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