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Thermoelectrics of Kondo Semiconductors and Intermetallic Clathrates

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We report a systematic study of thermoelectric properties in two systems; Kondo semiconductors and intermetallic clathrates. Kondo semiconductors based on rare-earth elements have an extremely narrow pseudogap at the Fermi level as a result of anisotropic hybridization of $4f$ electronic states with conduction bands. The development of a V-shaped density of states with decreasing temperature allows enhancement of thermopower while maintaining the electrical conduction metallic. Among the isostructural compounds CeTX with the ϵ-TiNiSi-type orthorhombic structure, the transport property changes from semiconducting CeRhAs, semimetallic CeRhSb and CeNiSn, to metallic CePtSn and CeBiPt [1]. In this sequence, both the Kondo temperature and the gap width decrease, whereas the phonon thermal conductivity at high temperatures increases. Opening of the pseudogap in CeRhAs and CeRhSb enlarges the thermopower, and leads to the thermoelectric figure of merit 1.0×10^{-3}/K at 115 K and 1.7×10^{-3}/K at 12 K, respectively. There results are compared with those of Ce-filled skutterudite $CeOs_4Sb_{12}$ and Yb-based Kondo semiconductor YbB_{12}.
The other is intermetallic clathrates $A_8Ga_{16}X_{30}$ (A=Sr, Ba; X=Si, Ge, Sn) where guest A atoms are loosely bound to the cage formed by Ga and X atoms. The structural and vibrational properties were studied through thermodynamic and transport measurements [2], [3] as well as microscopic techniques such as Raman scattering [4], EXAFS [5], inelastic neutron scattering [6] 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 $24k$ 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 vibration 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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