Cs "Rattlers" in Sn-Based Clathrate Semiconductors

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We have studied the electronic and vibrational properties of some of the Sn-based clathrate materials using LDA electronic structure methods. These framework materials have open cages which can contain guest impurities, and these guests can produce local ("rattling") vibrational modes. These modes may scatter the extended, heat carrying acoustic modes of the framework, potentially reducing the thermal conductivity. We present results for the electronic bandstructures and for the vibrational spectra of the Type I and Type II clathrate frameworks Sn_{46} and Sn_{136} and of the Cs-containing, Type I clathrate compounds Cs_8Sn_{46}, $Cs_8Sn_{44}\square_2$, $Cs_8Zn_4Sn_{42}$, and $Cs_8Ga_8Sn_{38}$. We have also theoretically identified the infrared- and Raman-active modes in some of these materials and have computed their Raman spectra. Focusing on the on vibrational frequencies of the Cs guests, we compare the experimental Raman spectrum of $Cs_8Ga_8Sn_{38}$ with the theoretical spectrum. By this means, we are able to unambiguously identify the low frequency, Cs guest-related "rattling" vibrational modes in this material.