Cs “Rattlers” in Sn-Based Clathrate Semiconductors

Charles W. Myles,1 Jianjun Dong,2 and Otto F. Sankey3

1 Department of Physics, Texas Tech University, Lubbock, TX 79409-1051

2 Department of Physics, Auburn University, Auburn, AL 36849-5311

3 Department of Physics and Astronomy and Materials Research Center, Arizona State University, Tempe, AZ 85287-1504

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 Sn46 and Sn136 and of the Cs-containing, Type I clathrate compounds Cs8Sn46, Cs8Sn44□2, Cs8Zn4Sn42, and Cs8Ga8Sn38. 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 Cs8Ga8Sn38 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.