Direct verification of Ga-Ga bond avoidance in the clathrate \( \text{Ba}_8\text{Ga}_{16}\text{Sn}_{30} \) from EXAFS studies

MICHAEL KOZINA, F. BRIDGES, Y. JIANG, UC Santa Cruz, M. AVILA, Universidade Federal do ABC, K. SUEKUNI, T. TAKABATAKE, Hiroshima University — \( \text{Ba}_8\text{Ga}_{16}\text{Ge}_{30} \) and \( \text{Ba}_8\text{Ga}_{16}\text{Sn}_{30} \) are important thermoelectric clathrate materials with low thermal conductivities. In these materials, the Ga/Ge or Ga/Sn atoms occupy three sites in the cage-like lattice, but the Ga are not randomly distributed. Experiments in the past have only been able to suggest that Ga-Ga bonds are not favored within the cage structure of many type I clathrates. Here we show definitive evidence that this is indeed the case for \( \text{Ba}_8\text{Ga}_{16}\text{Sn}_{30} \). Using the EXAFS technique, we are able compare the backscattering functions for the first neighbors about Ga to the calculated functions for Ga-Ga and Ga-Sn bonds. The result is that only \( \sim 15\% \) of the Ga nearest neighbors are Ga. Combining this result with diffraction data on occupational parameters, we propose one possible arrangement of Ga and Sn in the unit cell of \( \text{Ba}_8\text{Ga}_{16}\text{Sn}_{30} \). Additionally, we find significant disorder in the Ga/Sn lattice; the Ga-Sn bond and Ga-Ga bonds are 0.07Å and 0.2Å (respectively) shorter than the average bond length, which must contribute to the smaller thermal conductivity.

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