Large local distortions around the Ba site in $\text{Ba}_8\text{Ga}_{16}\text{X}_{30}$, $\text{X}=\text{Si, Sn}$

TREVOR KEIBER, Univ of California-Santa Cruz, FRANK BRIDGES, PATRICK NAST, UC Santa Cruz, SCOTT MEDLING, Australian National University, TOSHIRO TAKABATAKE, Hiroshima University — We report an Extended X-ray Absorption Fine Structure (EXAFS) analysis of thermoelectric type-I clathrates, $\text{Ba}_8\text{Ga}_{16}\text{X}_{30}$, $\text{X}=\text{Sn, Si}$. These clathrates have a cage-like crystal structure filled with “rattler” atoms (Ba) located near the center of the cages (Ga-X). In contrast to the results for $\text{Ba}_8\text{Ga}_{16}\text{Ge}_{30}$, our results show that for $\text{X}=\text{Sn, Si}$ the average pair distances within the cages (Ga-Sn, Ga-Ga, Ga-Si, Sn-Sn) are significantly different than the average distances found from diffraction. Direct measurements of the Ba K edge suggests that the environment about Ba is very highly disordered for $\text{X}=\text{Sn, Si}$ compared to $\text{X}=\text{Ge}$, with surprisingly short Ba-X/Ga distances; likely the Ba2 site is significantly off center. For Si, the Ba K first neighbor peak is substantially reduced in size and shifted to lower $r$ due to interference effects from many different Ba neighbor distances. For $\text{X}=\text{Sn}$ the Ba-Ga/Sn distances are even shorter, and there is a split peak with very low amplitude suggesting a very disordered environment. The mixed distances of the cage atoms, the very short Ba-Ga/X distances, as well as the disorder about the Ba site, suggest that the cage structure is buckled. This disorder will lead to increased scattering for both phonons and electrons.

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