

Abstract Submitted
for the MAR11 Meeting of
The American Physical Society

Zintl stabilization and site preference in Ba-Cu-Ge clathrates

SERGIO Y. RODRIGUEZ, XIANG ZHENG, LAZIZ SARIBAEV, JOSEPH H. ROSS, JR., Department of Physics and Astronomy, Texas A&M University — Sn, Ge and Si clathrates have cage-like structures, and many exhibit enhanced thermoelectric performance. To understand Cu substitution and Zintl stabilization in $\text{Ba}_8\text{Cu}_x\text{Ge}_{46-x}$ type-I clathrates with $4 \leq x \leq 6$, we performed NMR measurements coupled with first principles calculations. The ^{63}Cu NMR resonance exhibits a lineshape characteristic of Cu occupation of the high-symmetry $6c$ site. All electron computational results showed that the lowest energy configuration is the one with all the Cu atoms located in the $6c$ site, in agreement with NMR and crystallographic analysis. From bandstructure calculations we find that the preferred structure is a semiconductor, consistent with the observed Zintl stabilization in this material. A direct band gap of about 0.27 eV is found within the Generalized Gradient Approximation formalism. The preferred compositions follow quite closely the valence-counting scheme. From an Atoms In Molecules analysis it is seen that the Ba charge is less than 2^+ , even though the simple electron-counting argument works well. The framework is seen to be composed of a sp^3 bonded network, with strongly polar bonds for Cu. Ba atoms in the large cages are least strongly bonded in the plane of the hexagonal faces, corresponding to ease of rattling as seen for other clathrates. This work is supported by Robert A. Welch Foundation (Grant A-1526).

Sergio Y. Rodriguez
Department of Physics and Astronomy, Texas A&M University

Date submitted: 08 Dec 2010

Electronic form version 1.4