

Abstract Submitted  
for the MAR15 Meeting of  
The American Physical Society

**Effect of Alkaline Metal Filling on the Structural Properties of Type-II Clathrate  $A_xM_{136}$  ( $A = Na, K, Rb, Cs$ ;  $M = \text{Group IV Atom}$ ;  $0 \leq x \leq 24$ )** CHARLES MYLES, DONG XUE, Texas Tech University — Early investigations of the properties of the Type II clathrate  $Na_xSi_{136}$  ( $0 < x < 24$ ) [1] have found that, as the composition  $x$  increases, the  $Si_{136}$  lattice exhibits framework contraction upon filling ( $0 < x < 8$ ), followed by an expansion of the unit cell volume ( $9 < x < 24$ ). Stimulated by this discovery of a non-monotonic structural response to cage filling by the guests, we have performed a systematic, first-principles study of the guest-framework interaction in the large and small cages in the Type II clathrates  $Si_{136}$ ,  $Ge_{136}$ , and  $Sn_{136}$ . Our calculations are based on the VASP code and we have considered Na, K, Rb, and Cs guests for  $0 \leq x \leq 24$ . An emphasis in our study is on how the guest atom size affects the dynamical behavior of the host material. We focus on the host lattice structural expansion or compression as  $x$  increases. We also present and discuss calculations of the effective potential energy curves for the guest-host interactions in these materials. Our results are correlated with the harmonic (or anharmonic) oscillations of the guests. These results are useful as an indication of the expected behavior of the guest “rattling” phonon modes in these materials. Among other results, we find that some guests are weakly bonded in the host cages and others are unstable around the cage centers.

[1] Beekman, Nenghabi, Biswas, Myles, Baitinger, Grin, Nolas, *Inorganic Chemistry* 49, 5338 (2010).

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Date submitted: 13 Nov 2014

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