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First-Principles Study of Guest-Host Bonding in the Type-II Clathrate Compounds A_xSi_{136} (A = Na, K, Rb, Cs; $0 \leq x \leq 24$) CHARLES MYLES, DONG XUE, Texas Tech University — The Type II clathrate-based materials are interesting due to their potential thermoelectric applications. Recently, a synthesis and characterization of Na_xSi_{136} for various x has been reported [1]. Powdered X-Ray diffraction (XRD) data and density functional theory (DFT) studies of Na_xSi_{136} have found a lattice contraction as x increases for $0 < x < 8$ and an expansion as x increases for $x > 8$. This is explained by XRD data showing that, as x increases, the 28-atom Si cages are filled first for $x < 8$ and the 20-atom Si cages are then filled for $x > 8$. We report results of first-principles calculations focused on analyzing the underlying mechanisms relevant to guest-host interactions and to understanding the role of the guest atom to host atom size ratio in this material. We have also studied the compounds A_xSi_{136} (A = Na, K, Rb, Cs; $0 \leq x \leq 24$). Our LDA calculations for K_xSi_{136} ($0 < x < 16$) predict that this material should exhibit a non-monotonic structural response similar to that in Na_xSi_{136}; the lattice should contract and then expand as x increases. We find that the heavier guests (Rb, Cs) vibrate nearer to the center of the Si_{28} cages than do Na and K. Our results also show that Na and K are both strongly coupled to the Si framework in A_xSi_{136} (A = Na, K; x = 4, 8). [1] S. Sefanoski, C.D. Malliakas, M.G. Kanatzidis, G.S. Nolas, *Inorg. Chem.* 51, 8686 (2012).

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