Abstract Submitted
for the MAR16 Meeting of
The American Physical Society

Formation, properties, and function of vacancies in Si/Ge Clathrates: The importance of broken symmetries AMRITA BHATTACHARYA, CHRISTIAN CARBOGNO, MATTHIAS SCHEFFLER, Fritz Haber Institute of the Max Planck Society — Inclusion compounds, such as clathrates, are cage-like crystal structures that can encapsulate guest atoms. Since this allows to tune their electronic and vibrational properties, they are regarded as interesting materials for thermoelectric applications. Progress in this field is, however, hindered by the fact that filling of group-IV clathrates often results in complex and unexpected structural changes, e.g., the spontaneous formation of vacancies in certain hosts: In Ge_{46} clathrates filled with K or Ba, the most favourable phases K_8Ge_{44}/ Ba_8Ge_{43} feature two/three vacancies. Conversely, the framework of the isoelectronic Si_{46} clathrate remains intact (K_8Si_{46}/Ba_8Si_{46}) upon filling with the exact same guests. Our first-principles calculations of the formation energies and of the thermodynamic phase stabilities confirm this experimental scenario and shed light on the underlying mechanisms. Due to the spatially more delocalized $4sp^3$ orbitals in Ge compared to the more localized $3sp^3$ orbitals in Si, fundamentally different symmetry breaking distortions become possible to stabilize the vacancies. Eventually, we discuss the implications of these findings for the thermoelectric properties of clathrates.

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Date submitted: 06 Nov 2015 Electronic form version 1.4