

Unusual Behavior in Dense “Guest-Host” Solids: the Study of Alkali Metal-Silicon Clathrates

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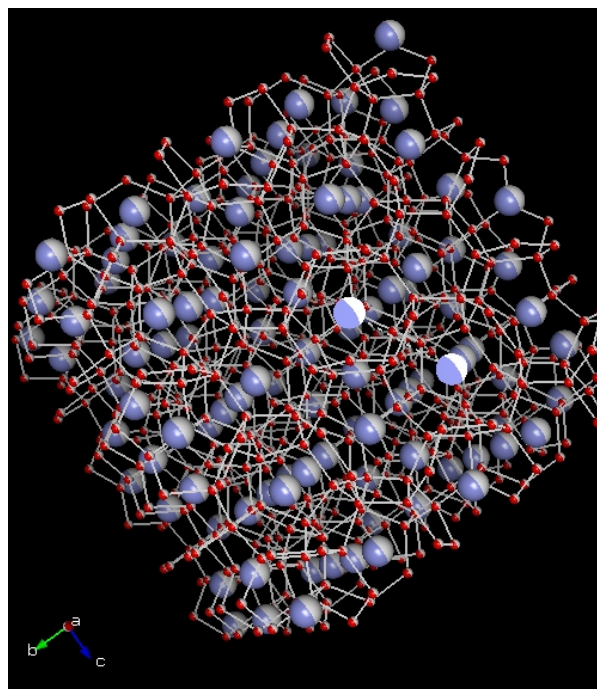
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Probing and Understanding “Guest-Host” Interactions in Solids

Clathrates are “guest-host” systems. For instance, hydrogen-bonded water molecules (host) can be stabilized in cage-like structures (clathrates) in the presence of gaseous species (guest). The best known example is methane clathrate, a gas hydrate commonly found in nature. The enormous energy reservoir represented by methane gas trapped in methane clathrates found in Earth drives currently a considerable research effort [1].

In analogy with gas hydrates, a three-dimensional framework of tetrahedral silicon atoms can be synthesized by a thermal decomposition of alkali metal silicides [2,3]. A “guest-host” system is thus formed between the alkali metal and Si atoms giving rise to structures identical to those adopted by gas clathrate hydrates, hence the term “Si clathrates”. Figure 1 illustrates the Si clathrate structure I. Si (as well as Ge and Sn) clathrates show interesting physical properties: from good electrical conductivity with reduced thermal conductivity (good for thermoelectric applications) to superconductivity [4] and low compressibility [5]. We have undertaken to study the stability of M-Si clathrates (with M = Na, K, and Rb) under high pressure and to characterize their high-density phases in order to better understand “guest-host” interactions in solids. Using the CHESS Facility, we have tested our computational results regarding the guest-host interactions at elevated densities in Si clathrates.

Fig 1: The alkali metal (M)-Si clathrate structure I. The cubic structure I (Pm3n, Z=1), corresponding to M_8Si_{46} , presents two types of Si polyhedra: Si_{20} (tetrakaidecahedron) and Si_{24} (dodecahedron). The unit cell of structure I comprises two Si_{20} and six Si_{24} cages, all centrally occupied at the most by a single alkali metal atom. Structure II (Fd3m, Z=1) is also possible and corresponds to $M_{24}Si_{136}$ with sixteen Si_{20} and eight Si_{28} cages in the unit cell.

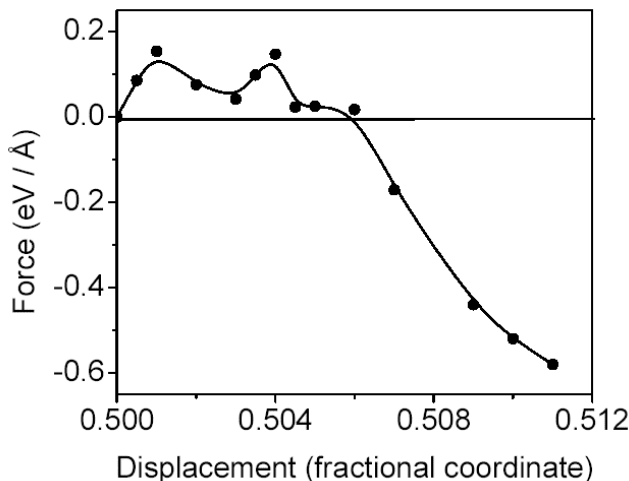


Using Pressure to Tune the “Guest-Host Interactions in Solids”

The increase of pressure represents a very effective means to tune atomic interactions in solids. Samples compressed to very high pressure in gasketed diamond anvil cells are small. With volume of material smaller than $500 \mu\text{m}^3$, the high flux of photons at $\lambda \sim 0.5 \text{ \AA}$ available at the CHESS A2-station is thus ideal to carry out angle dispersive X-ray diffraction experiments at high pressure. Other experimental details are given elsewhere [6]. Angle dispersive X-ray diffraction is used to measure the compressional properties of Si clathrates as well as to study their phase stability at high density. Experimental data are compared to predictions obtained by calculations.

Recent computational results [7] indicate that, among M-Si clathrates (with M = Na, K, and Rb), K-Si represents an atypical case. Although the interactions between the guest atom (K) and the Si-cage framework are similar to those between Na and Rb and Si in the same structure, the analysis of computational results show a contrasting behavior in the former system. In fact, the hybridization between K and Si atoms lead to a strong mixing of the vibrational modes between guest and host atoms at high density. Through phonon band calculations [7], it is shown that as a function of P the vibrational frequencies of guest atoms in large host Si cavities become imaginary, indicating a mechanical instability. The collapse of phonon stability, which occurs at 16 GPa, originates from the displacement of K atoms in the large Si cavities. Force calculations, carried out at 5 and 16 GPa by displacing, for instance, guest K atoms away from their central symmetry position (0.25, 0.50, 0) in the large Si cavities, indicate the development of a positive force which drives K atoms away from the initial central positions upon the application of pressure (Figure 2). This is unusual as one would expect the increase of density to enhance the stability of guest atoms in the centers of Si cavities. Similar computations indicate that the “off-centering” effect is not present in dense isostructural Na- and Rb-Si clathrates.

Fig 2: The calculated force acting on a K atom when displaced from its site symmetry (0.25, 0.5, 0) in a Si_{24} cage of K_6Si_{46} clathrate (cubic structure I) at 16 GPa. The K-atom equilibrium position is found to be 0.06 Å away from the center (.50) along the crystallographic b-axis. The positive force favors displacement against the negative restoring force. Reproduced from [7].



As seen in Figure 3, K-Si clathrate (structure I) is found to be stable against the formation of pure K and Si solid phases to very high pressure. We have observed, however, an anomaly in the equation of state for pressure above 20 GPa: the experimental points deviate substantially from the extrapolated relationship between the relative unit cell volume and pressure. We have indications of an isostructural transition which could be related to the displacement of K atoms in the large cavities as predicted by our calculations. It should be mentioned that the equation of state of Na- and Rb-Si clathrates, measured under the same conditions, do not present the compression anomaly recorded for the case of K-Si clathrate, a result in agreement with our computational results. Hence the unusual response of K-Si clathrate observed at high density.

Although the predicted displacement of K atoms away from the large cavity centers is small (0.06 Å at 16 GPa), it should be possible to observe it by X-ray diffraction or absorption at high pressure. Further experiments are planned to test our calculations.

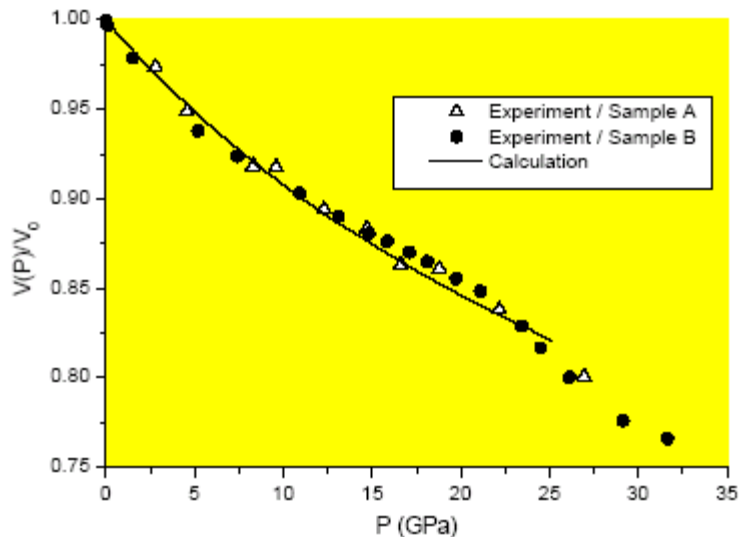


Fig 3: Experimental and calculated isothermal equations of state for K_6Si_{46} . Although no structural transition is inferred by the experimental X-ray diffraction patterns, a clear change of volume compression is recorded for pressures larger than 20 GPa. Reproduced from [7].

Other “Guest-Host” Interaction in Solids: the Case of Gas Clathrate Hydrates

In parallel to our work on alkali metal-silicon clathrates at high pressure, we have also carried out at CHESS structural studies of dense noble gas (Ar, Kr, and Xe) clathrate hydrates (Figure 4). We have established a systematics among the different crystalline structures adopted by the noble gas hydrates. Generally speaking, we have found [8] that the water molecule cage framework stabilized by the presence of guest atomic species (noble gas) becomes unstable against the formation of pure phases, i.e., solid Ar, Kr, and Xe with pure ice VII at high densities corresponding to water molecule cage sizes which can no longer accommodate gaseous species. The phase segregation at high density is found to be fully reversible, i.e., gas clathrates are recovered upon pressure release. In all cases, the phase segregation observed at high density is preceded by a series of solid-to-solid phase transitions, with structures for which the ratio of noble gas atoms to H_2O molecules is reduced from 6 to 2 from low to higher pressure

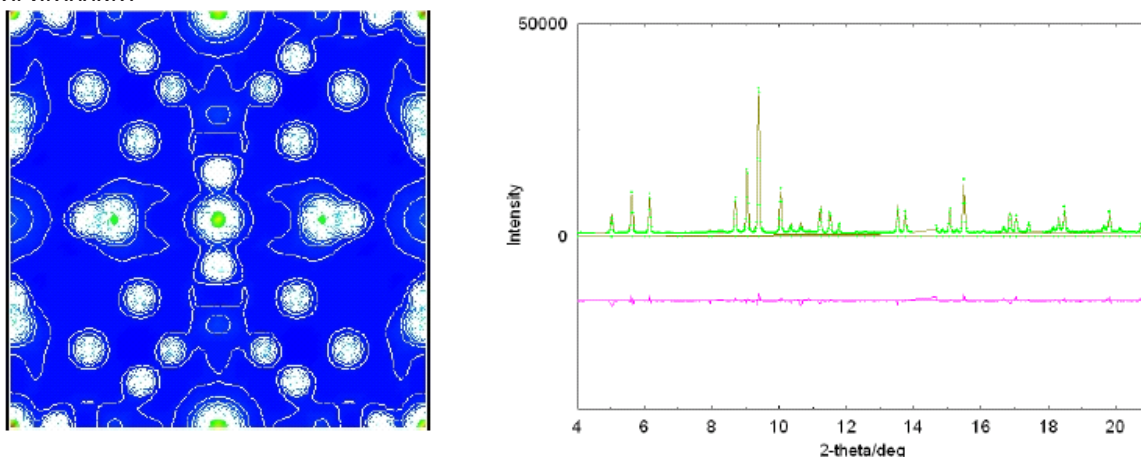


Fig 4: An example of X-ray diffraction data and analysis of noble gas clathrate hydrates at high pressure: Xe clathrate hydrate, $\text{Xe}_8(\text{H}_2\text{O})_{46}$ in the cubic structure I at 0.27 GPa. An electron density map (left, projection along the [100] direction) derived by the maximum entropy method as applied to X-ray diffraction data [9] is used to improve the convergence of structural parameter refinement by full pattern fitting (Rietveld method, right panel; the bottom curve shows the difference between the fitted and the observed X-ray diffraction patterns).

Conclusions

The combination of angle-dispersive X-ray diffraction using synchrotron radiation and advanced high pressure techniques has been central to the study of dense “guest-host” systems such as Si clathrates and noble gas hydrates. Our calculations indicate a displacement of K atoms in the large Si cavities of K_8Si_{46} clathrate at high pressure, leading to an off-centering of guest atoms in host cavities. From data obtained at CHESS, we have experimental indications that support our computational results. Additional X-ray diffraction experiments under high pressure are planned at CHESS to measure, as a function of density, the actual positions of guest atoms in host cage framework in Si-clathrate systems.

We thank our funding agencies, the National Research Council of Canada and the Natural Science and Engineering Research Council of Canada, as well as the entire CHESS staff, not least Drs. Alexander Kazimirov and C.-S. Zha, for their important help.

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