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# Structural Stability and Phase Transitions in $K_8Si_{46}$ Clathrate under High Pressure

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The structural stability of type-I $K_8Si_{46}$ clathrate has been investigated at high pressure by synchrotron x-ray diffraction. In contrast to that observed in the Na-doped structure-II analogue [A. San-Miguel *et al.*, Phys. Rev. Lett. **83**, 5290 (1999)], no phase separation into the $\beta$-Sn Si structure was identified at 11 GPa. Instead, $K_8Si_{46}$ is found to undergo a transition to an *isostructural* positional disordered phase at around 15 GPa. *Ab initio* phonon band structure calculations reveal a novel phenomenon of phonon instabilities of K atoms in the large cavities is responsible for this transition. Above 32 GPa, the new structure transforms into an amorphous phase.

Open framework clathrate structures composed of group IV or group III/V elements have attracted increasing attention in the last few years [1,2]. This class of compounds, often with enclathrated alkali and/or alkaline metals or halogens, has shown unusual [3] and potentially useful electrical [4] and thermal transport properties [5] and, in some cases, even superconductivity [6]. The electronic structures of these compounds are now reasonably well characterized and understood from a large amount of experimental and theoretical studies [7]. An exciting recent development is the synthesis of a variety of these materials using high-pressure methods [8]. These successes open up a real possibility for the rational design of novel materials with tailored optical band gaps [9]. In the clathrate structure, the (group IV) atoms forming the framework are tetrahedrally bonded, a property expected to enhance the structural stability under high pressure. It was shown recently [10] that the compressibility of a Na-doped Si clathrate with type-II structure is indeed rather low with a corresponding bulk modulus of $90 \pm 5$ GPa, which is comparable to that of Si in the diamond structure. Similar to the pure Si phase in the diamond structure, the Na-doped clathrate also transforms into a dense phase with the $\beta$-Sn structure at 11 GPa [10]. The mechanism for this transformation is not known. This is unlikely to be driven by phonon instability as the empty lattice of structure-II Si clathrate was predicted to be stable up to 30 GPa from phonon band structure calculations [11]. In an attempt to improve the structural stability of empty Si clathrates, we explored the possibility of filling the cavities with alkali metals of larger size. To this end, structure-I Si clathrate doped with K was synthesized [12] and the crystalline structures studied under high pressure. The results are remarkable. No phase transition was observed at 11 GPa. Instead, $K_8Si_{46}$ transforms to a dense structure with the same space group at around 15 GPa. In this Letter, we describe a mechanism for the *isostructural* transformation in $K_8Si_{46}$ using *ab initio* electronic and phonon band structure calculations.

Structure-I K/Si clathrate was prepared by vacuum decomposition of the binary silicide [12]. In agreement with a previous report [12], elemental and Rietveld analysis confirm the stoichiometry to be $K_{7.6}Si_{46}$ ($K_8Si_{46}$ thereafter). Structural studies were carried out by angle dispersive x-ray diffraction (ADXD) using gasketed high-pressure diamond anvil cells at the CHESS beam lines A2 (wiggler) and B2 (bending magnet). To ensure quasihydrostatic conditions and data consistency, two different pressure transferring media—a mixture of methanol:ethanol:water (16:3:1 by volume) and silicone oil— were used. Pressure was measured using the ruby (photoluminescence) and Cu (x-ray diffraction) gauges. Details regarding the experiments are given elsewhere [13].

ADXD patterns are illustrated in Fig. 1 at selected pressures for 2 K-Si clathrate samples. The unit cell volumes relative to those at ambient pressure derived from x-ray diffraction measurements on $K_8Si_{46}$ are shown in Fig. 2. At low pressure the $K_8Si_{46}$ samples compressed normally showing no sign of a phase transition at ca. 11 GPa [10]. At around 15 GPa, a noticeable change in the compressibility indicating a phase transition is observed. Surprisingly, examination of the diffraction patterns shows neither indication of changes in the crystal symmetry nor substantial variation of diffraction peaks intensity associated with the volume reduction (Fig. 1). Apparently, an isostructural phase transition has occurred leaving the crystal symmetry unaltered. The new structure is stable up to at least 32 GPa. At high pressure, $K_8Si_{46}$ becomes amorphous as inferred by the loss of Bragg reflection intensities (see Fig. 1). A small fraction of crystalline sample persists in sample B at 31.7 GPa and upon a complete decompression, as shown in Fig. 1. We believe, however, had the sample been compressed to high enough pressure, a complete amorphization would have occurred.
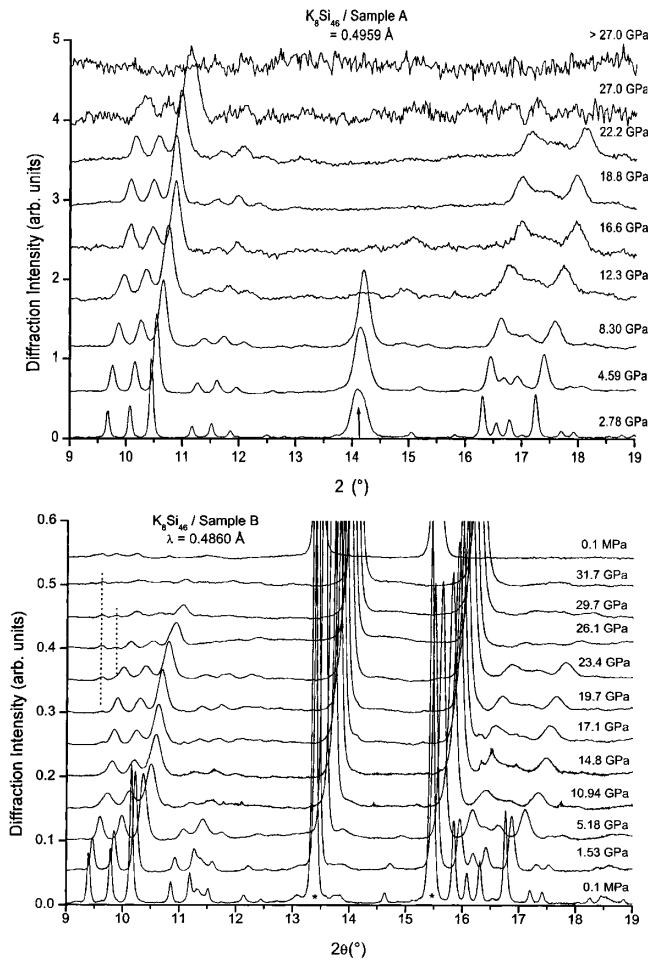
FIG. 1. Angle dispersive x-ray diffraction patterns of $K_8Si_{46}$ at selected pressures at room temperature. Indicated pressures were measured using the ruby and the Cu gauges, for samples A and B, respectively. The vertical arrow and the asterisks indicate a gasket and Cu x-ray diffraction lines, respectively. Vertical dotted lines indicate x-ray diffraction lines which are external to the sample as they do not shift with pressure. The sequences of x-ray diffraction patterns clearly indicate no change of crystalline structure from 15 to 32 GPa and the loss of crystallinity (amorphization) at high pressure. Partial crystallinity is also observed upon complete decompression of sample B.

The absence of a phase transformation to a pure phase of Si (which would be in the $\beta$-Sn structure at 11 GPa) clearly shows that guest elements have an effect on the structural stability of the Si clathrate framework. In view of the size (atomic radius) of K (2.24 Å) is significantly larger than that of Na (1.78 Å) and that the lattice constant for $K_8Si_{46}$ [10.275 18(5) Å] is very similar to that of $Na_8Si_{46}$ [10.181(1) Å], a likely explanation is that the more space filling K atoms help to maintain the framework integrity. However, this suggestion cannot explain the isostructural transition observed in $K_8Si_{46}$ at high pressure. To explore the mechanisms underlying the contrasting behavior of $K_8Si_{46}$ under pressure, *ab initio* elec-
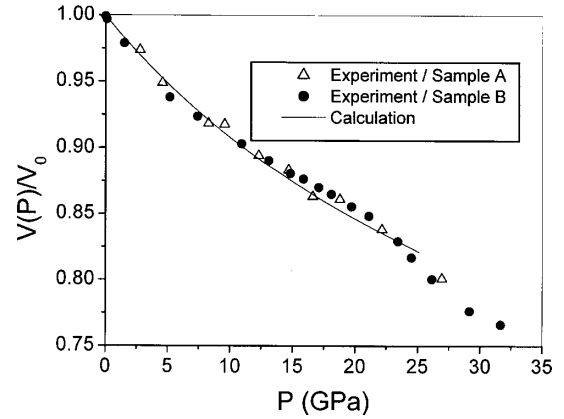


FIG. 2. Comparison of experimental and calculated volume compression curves for $K_8Si_{46}$. Symbols correspond to experimental data points (samples A and B) obtained at 300 K, and the solid line corresponds to the calculated equation of state.

tronic structure and phonon band structure calculations were carried out.

Theoretical calculations were performed with the pseudopotential plane-wave method using gradient-corrected local density functional theory [14]. Details of the computational procedure have been reported previously on similar clathrate systems [14,15]. The starting atomic coordinates were taken from experiment. Both the unit cell and atomic positions were fully optimized at each pressure step. Sufficiently accurate phonon band structures were computed with the supercell [16] method employing a single unit cell since the force constants, evaluated up to ten nearest neighbors, vanish rapidly with interatomic distances. The vibrational spectrum of $Na_8Si_{46}$ calculated in this manner has been shown to reproduce the experimental thermodynamic properties very well [17].

As illustrated in Fig. 2, the calculated volume compression curve for $K_8Si_{46}$ compares favorably with experimental data in the low-pressure region. $K_8Si_{46}$ is found to be slightly more compressible than $Na_8Si_{136}$. For example, at 12 GPa, the observed volume ratio ($V/V_0$) relative to ambient pressure is 0.88 and 0.90 for $K_8Si_{46}$ and $Na_8Si_{136}$ [10], respectively. Significant deviation of the experimental volume ratios from the calculations was observed for pressures higher than 15 GPa. In particular, the experimental results show a distinct discontinuity at 20 GPa indicating a structural change has occurred. The anomalous change in unit cell volume is not due to nonhydrostatic conditions, as we have not observed it in isostructural $Na_8Si_{46}$ and $Rb_6Si_{46}$ studied under similar conditions. The absence of abrupt change of volume associated with the phase transformation suggests that this may be a second order transition. To characterize the structural stability of $K_8Si_{46}$, the phonon band structures were calculated at 5, 14, 16, and 20 GPa.

The phonon band dispersions of $K_8Si_{46}$, in particular, at the low frequency region (Fig. 3), differ markedly from
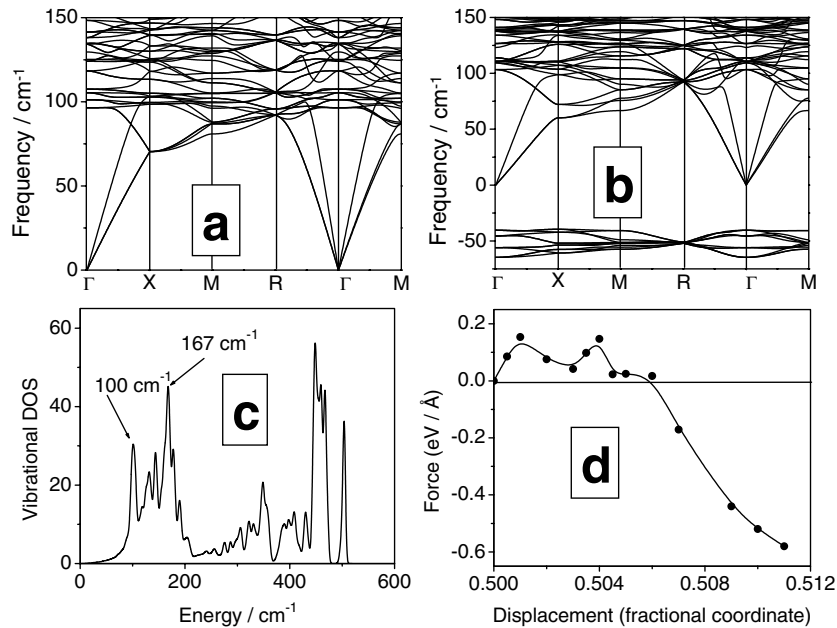
FIG. 3. Theoretical phonon band structure for $K_8Si_{46}$ at (a) 5 GPa, (b) 16 GPa, and (c) phonon vibrational density of states (DOS) at 5 GPa (features at 100 and 167 $cm^{-1}$ are indicated by arrows; see text); (d) the force acting on a K atom at $(1/4, 1/2, 0)$ when displaced from the symmetry site in the large cage along the $b$ direction. Positive force along the crystallographic $b$ axis favors the displacement while negative values indicate restoring forces.

that of $Na_8Si_{46}$ [15]. In $Na_8Si_{46}$, the Na vibrations do not show appreciable dispersion and appear as flat (localized) bands, which intersect or anticross the longitudinal and transverse lattice acoustic branches inside the Brillouin zone [15]. These anticrossings are absent in $K_8Si_{46}$. Moreover, if the interactions between K and the Si framework were similar to the Na analogue, the "localized" vibrations of K are expected to be reduced from the Na vibrations in $Na_8Si_{46}$ by a factor proportional to the square root of their atomic mass ratio ($\sim 0.77$) [18]. No low frequency localized band was predicted in the calculations. Analysis of the theoretical results show strong mixing of K and Si vibrations. This mixing is the consequence of hybridization between K and Si atoms. The calculated phonon band structure of $K_8Si_{46}$ reproduces all the main features in the observed phonon density of states [19]. The experimental vibrational spectrum shows a weak sharp band centered at about 100 $cm^{-1}$ followed by a broad and strong band centered at 170 $cm^{-1}$ [19]. The weak band can be assigned to the relatively flat dispersion along $M \rightarrow R$ at about 90 $cm^{-1}$ and along $\Gamma \rightarrow X \rightarrow M \rightarrow R$ at about 100 $cm^{-1}$. The strong broad band is associated with the optical modes clustered around 100–180 $cm^{-1}$ and peak at 167 $cm^{-1}$. Therefore, the experimental observation fully substantiates the theoretical predictions.

At 16 GPa, the theoretical calculations predict a sudden and dramatic collapse of the entire phonon branch associated with K vibrations in the large cavities of the clathrate. As shown in the phonon band structure (Fig. 3), the vibrational frequencies of the K atoms in the large

cavities become imaginary and are no longer mechanically stable. The phonon instability has an electronic origin where the most favorable K-Si interaction occurs when the K is displaced from the crystallographic symmetry center of the large cage. To verify this proposal, additional total energy and force calculations by moving a K atom $(1/4, 1/2, 0)$ away from its symmetry site were performed [Fig. 3(d)]. These calculations were performed with a larger $6 \times 6 \times 6$ **k**-point set and a much tighter energy convergence criteria ($10^{-7}$ eV). The results show [Fig. 3(d)] that the (positive) force pushes the K atom away from its original position to a local minimum $\approx 0.06$ Å (zero force) at around $(1/4, 0.5065, 0)$. The K atom at the ideal symmetry site is at the energy maximum. The potential energy surface of K in the large cage can be envisaged to resemble a "Mexican hat" with the top of the barrier situated at the crystallographic symmetry site. The site symmetry of K in the large cavities of the type-I structure is $-4m2$. Therefore, the K atoms have equal probability to displace along the crystallographically equivalent directions. Consequently, the K atoms become positional disordered, but the overall crystal symmetry ($Pm$-$3n$) is preserved.

The potential energy surfaces of several metal atoms enclathrated in the type-I Ga/Ge alloyed clathrates have been examined in great detail in a previous report [7]. It was shown that some of the metal atoms are not stable at the center of the cages, while others appeared to be bonded by weak restoring forces. *However, the displacement of K from the symmetry sites upon the application of pressure is unusual.* The unit cell size decreases with

increasing pressure and one would expect the repulsive interactions between K and the Si forming the wall of the cavities to increase and further stabilize the K atoms in their symmetry sites. In contrast, the opposite was predicted. The shift of the K from the center of the large cavity may be interpreted as increased "bonding" interaction when the Si-K separation is decreased, perhaps through polarization. As discussed above, even at low pressure there is already appreciable K-Si hybridization since there are no longer any localized "rattling" vibrations. As the unit cell decreases, the K-Si distance also decreases. At zero pressure, the closest K-Si contact in the large cavity is 3.43 Å and is reduced to 3.23 Å at 17 GPa. The average K-Si distances in the large cavities become shorter favoring interactions between K and Si. Incidentally, a crude estimate of the K-Si "covalent" bond length from the respective covalent radii is 3.07 Å—only 0.16 Å shorter than the Si-K distance if K is at the symmetry site. In view of the consistently good agreement between the calculated and experimental phonon spectra and equation of state, it is highly plausible that the predicted instabilities in the K phonons driven by these interactions initiate the phase transition. A full experimental observation of the displacement of the K atoms and the resulting phonon instability, although difficult, could be done by high-quality powder or single-crystal x-ray diffraction, inelastic neutron or x-ray scattering carried out at high pressure to measure the phonon density of state, or low frequency Raman spectroscopy.

The amorphization of $K_8Si_{46}$ at 32 GPa is similar to that observed in water clathrates [20] and in clathrasils (zeolites) [21] with the same framework structure. The origin of this pressure-induced amorphization has been shown to be due to a mechanical instability of the framework—a consequence of the violation of the Born's conditions for structural stability [22]. It is likely that the same mechanism is responsible for the amorphization transition reported here. In contrast, unlike previous observation, the pressure-amorphized $K_8Si_{46}$ is only partially reversible as the sample crystallinity is not completely recoverable upon decompression (Fig. 1). Thus, the K-Si interactions in the amorphous phase may be different from that in water clathrates and clathrasils. It is also interesting to note that the silicon does not transform to Si(V) [23] or Si(VI) [24] which are the stable crystalline phases in this pressure range.

In conclusion, encaged atoms in clathrate structures display very interesting and novel dynamics. Depending on the size and chemical nature of the encaged atom, the clathrate can exhibit very different physical properties. In this study, a novel phase transition in $K_8Si_{46}$ at high pressures triggered by an anomalous phonon instability of the encaged K atoms was characterized. Furthermore, it is demonstrated that the inclusion of large atoms in the empty cavities helps to enhance the structural stability of the Si framework. This observation may have important implications in the design of new semiconductor materials with increased hardness.

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