High Pressure Behavior of Silicon Clathrates: A New Class of Low Compressibility Materials

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The high pressure evolution of silicon clathrates is studied at room temperature by x-ray diffraction up to 15 GPa. Remarkably, no transition towards the diamond structure is observed and the clathrate phase transforms directly into the β-tin metallic phase at 11 GPa. Further, the bulk modulus is found to be 90 ± 5 GPa, that is, only (8 ± 5)% smaller than the one of the diamond phase. These results are in good agreement with *ab initio* calculations which predict further that carbon clathrates, if synthesized, should be less compressible than cubic BN.

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There is a great experimental and industrial interest [1,2] in obtaining low-compressibility structures having large hardness [3]. Nature provides the best known example of such a material: the carbon diamond phase. Unfortunately, the precious gem is rare and the industrial production is quite limited. Consequently, much work has been devoted to predicting novel forms of low compressibility materials. For example, on the basis of empirical and theoretical considerations relating the bulk modulus of a material to its structural and electronic properties, a candidate β-C_3N_4 carbon-nitride compound was proposed [3] in analogy with the existing β-Si_3N_4 structure. Even though the synthesis of carbon-nitride materials has proven to be difficult, the idea of using known silicon-based compounds as a "template" to design novel carbon-based structures is a motivating line of work.

In this paper, we present a joint experimental and theoretical study of the stability and structural properties under pressure of silicon clathrates. Such low-density phases, recently synthesized [4] for the Si and Ge elements, are metastable at ambient conditions and have been predicted [5] to have a cohesive energy larger than that of the β-tin structure [6]. However, the equation of state of such compounds has never been studied experimentally, leaving the phase diagram of Si incomplete on the low-density side of the diamond phase. Beyond this fundamental motivation for the study of Si clathrates, our study reveals further that such compounds display unique properties under pressure. We show, in particular, that such a material is characterized by a transition pressure towards denser phases equivalent or even larger than that of the corresponding diamond structure. In addition, the compressibility of clathrates is close to the one of the diamond phase. These two results indicate therefore a novel route towards the synthesis of low-compressibility materials, providing much incentive in attempting to synthesize carbon-based clathrates.

Silicon clathrates are cagelike crystals that can be assimilated to the large family of zeolite-network systems. The structure studied in this work, labeled Si-34 [7], is characterized by the 3D periodic arrangement of (Si_{20}-I_h) and (Si_{28}-T_d) cages having shared faces (see Fig. 1). All atoms are hybridized in a nearly sp^3 configuration without dangling bonds. This geometry leads to very large predominance of fivefold rings (87%) that induces a 0.7 eV opening of the band gap as compared to Si-2 [8]. Si clathrates are synthesized by thermal decomposition of NaSi precursor under vacuum or argon at high temperatures, leading to Na-"intercalated" Na_x@Si-34 ($0 < x < 24$) clathrates [9]. The Na atoms, which are located inside the cages, can be subsequently removed to produce relatively pure Si-34 phases. The main crystallographic data and some relevant properties of Si-34 compared with Si-2 can be found in Ref. [10]. Presently, both silicon or germanium clathrates are currently produced

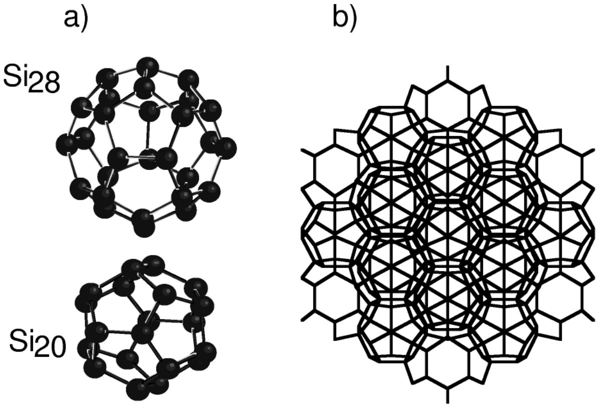

FIG. 1. Structure of silicon clathrate (Si-34). (a) Elementary building blocks of the structure. We note that we have omitted the "sticks" representing the bonding of each Si atom outside the fullerene-type cages, linking by shared faces these basic blocks. (b) Projection of the structure following the (111) direction. The structure can be seen as a fcc staking of Si_{28} building blocks. The contact between the Si_{28} units gives rise to the Si fourfold coordination as in the diamond structure. The remaining voids of the fcc staking form Si_{20} cages.

following this synthesis process, but unfortunately there is as yet no precursor to synthesize carbon clathrates.

We first perform an energy-dispersive x-ray diffraction experiment using the DW11 beam line of the LURE synchrotron (Orsay, France). The white beam was collimated down to 50 μm × 50 μm before the sample. Membrane diamond-anvil cells [11] were used as high-pressure generators. Fine grained powdered samples (250 mesh) of Na_x@Si-34 with $x < 0.5$ were loaded in 250 μm diameter holes drilled in stainless steel placed between the diamond anvils. The sample was embedded in a pressure transmitting fluid to ensure quasihydrostatic conditions. Pressure was measured using the linear ruby-shift scale [12]. In order to discard any influence of the pressure transmitting media on our results, we have used silicon oil, 16:3:1 methanol-ethanol-water mixture, and 2:11 *n*-pentane-isopentane. We have also studied Si-2 and Si-34 grains together in the same high pressure cell as another way to avoid any spurious influence of the transmission media. This experimental protocol gives directly the relative compressibility of the Si-34 structure with respect to the Si-2 one.

We show in Fig. 2 some selected diffraction patterns of Si-34 at different pressures. The atomic volume obtained as a function of the applied pressure is depicted in Fig. 3. The most striking result is that the clathrate structure is extremely stable under pressure. As shown in Figs. 2 and 3, we do not observe any transition from Si-34 towards Si-2. In fact, the clathrate structure becomes unstable with respect to the metallic β-Sn one at 11.0 ± 0.5 GPa, a value that is very close to recent values reported for the Si-2 → β-Sn transformation in hydrostatic conditions (i.e., 11.7 GPa [13], 11.3 ± 0.2 GPa [14]). This is consistent with an early study of the electrical behavior of Na_x@Si-34 sodium-silicon clathrates under pressure [15] showing a transition towards a metallic phase at 11 GPa for $x = 3$ and between 15 and 18 GPa for $x = 11$, suggesting further that "intercalated"-clathrate structures could be even more stable under pressure than the diamond phase [16]. We note further that the direct transition from Si-34 to the β-Sn structure yields a huge $1/3$ volume reduction. This is, to our knowledge, the largest volume change observed upon phase transformation of a covalent crystal.

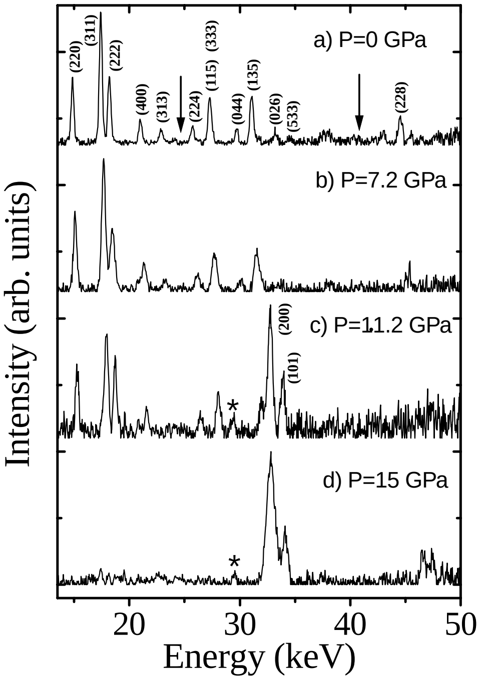

FIG. 2. Energy dispersive x-ray diffraction patterns of Si-34 at different pressures and room temperature. Patterns (a) and (b) were taken at ambient conditions and $P = 7.2$ GPa, respectively. In curve (a) the more intense reflections observed in the clathrate phase are labeled with their corresponding (hkl) indices. The transition pressure to the β-Sn structure has been estimated as $P = 11$ GPa [curve (c)], where the mixture between the Si-34 and β-Sn structures is observed and the two more intense peaks of this last phase are labeled. Curve (d) shows the diffraction pattern at $P = 15$ GPa for which the reflection positions are compatible with a mixture of *Imma* and simple hexagonal phases as for the phase diagram of Si-2 (Ref. [13]). The arrows in pattern (a) point to the location of the (111) and (220) Si-2 structure reflections at ambient conditions, to note the absence of this phase at all pressures. The peak labeled "*" can be assigned to the most intense peak of the Na_8Si-46 phase (see text).

The absence of transition under pressure towards the diamond structure is quite surprising since Si-34 is less stable and dense than Si-2. Further, on the basis of thermodynamics, and in the absence of a metastable behavior, the Si-34 to β-Sn transition should occur at a significantly lower pressure than the diamond to β-Sn transformation. This suggests that there exists a rather large energy barrier for the structural transformation from the clathrate to the cubic diamond and β-Sn phases. In fact, the clathrate lattice is built from tetrahedra packed in an eclipsed mode while, in β-Sn or in Si-2, they are found in a staggered configuration. Consequently, any of these two transformations involves the crossing of the so-called tetrahedral "rotation barrier" [17] which is not present in the Si-2 → β-Sn transition. A more detailed understanding of the atomistic mechanisms taking place during the phase transformations seems necessary to decide if the equality of transition pressure at 11 GPa for both the Si-34 and diamond to β-Sn transformation is fortuitous or not.

A second important result is that the clathrate structure, despite its low-density and fullerenelike structure, displays a compressibility which is close to the one of the diamond phase. The pressure variation of the atomic volume has been fitted using a Murnaghan equation of state (EOS). Our data spread does not allow the determination of the first derivative of the bulk modulus, B'. We have fixed its value to our calculated one, 3.6 (see below). Compiling the different results obtained with the different transmitting media, we find for Si-34 a bulk modulus $B_0 = 90 \pm 5$ GPa with B' fixed to 3.6. This value can be compared with the best results for Si-2 based on

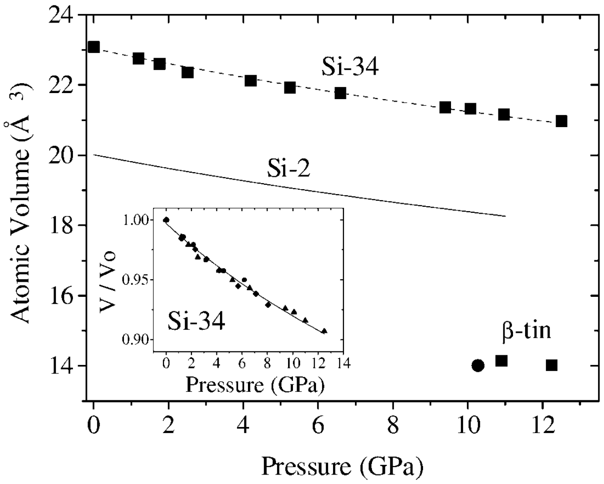

FIG. 3. Evolution of the atomic volume of Si-34 as a function of the applied pressure. The squares show our experimental values for the clathrate phase and the β-Sn one after the phase transition at 11 GPa. The discontinuous line is the Murnaghan equation of state (EOS) fit of the Si-34 phase data that gives a bulk modulus of $B_0 = 90 \pm 5$ GPa with B' fixed to 3.6. Also shown (circle) is an experimental value of the atomic volume in the β-Sn phase obtained after the Si-2 → β-Sn transformation (Ref. [13]). The Si-2 Murnaghan EOS from Ref. [19] is shown for comparison (solid line). The inset shows the pressure variation of the reduced volume of Si-34 for the ensemble of our experimental data and the fitted Murnaghan EOS.

elastic constant data [19] ($B_0 = 97.88$ GPa, $B' = 4.24$). We obtain therefore a value for Si-34 B_0 which is only 8 ± 5 smaller than the one of Si-2. We note that, as shown in Fig. 2, in the pressure domain explored, the phase diagram of Si-34 after transformation to the β-Sn phase matches the one of Si-2 [13]. The diffraction peak labeled "*" in panels 2(c) and 2(d) can be explained by the structuration of the Na_8@Si-46 phase around Na impurities at the Si-34 destabilization [16].

In order to corroborate the present experimental results, we perform *ab initio* calculations within the local density approximation [20] to density functional theory (DFT) [21]. A standard norm-conserving pseudopotential [22] is used for Si and the wave functions are expanded on a plane-wave basis with kinetic energy up to 20 Ry. We first minimize the internal energy of the Si-34 system with respect to both cell size and atomic positions and find a lattice constant of 27.55 a.u., that is, ~0.8% smaller than the experimental lattice constant. Comparing the internal energy at the equilibrium geometry to the one observed for the diamond within the same formalism, we find that the Si-34 phase is less stable than Si-2 by ~0.08 eV per atom, in excellent agreement with the results of Ref. [5] within their plane-wave-based approach. Therefore, at ambient pressure, the clathrate phase is significantly more stable than the β-tin phase which can be shown to have a cohesive energy ~0.25 eV smaller than the one of Si-2. Using a Murnaghan fitting analysis of the data points around the equilibrium volume, we find further that the bulk modulus of Si-34 is equal to 87.7 GPa and $B' = 3.6$. This bulk modulus is 9.5% smaller than the value obtained for Si-2 within the same approach (96.9 GPa). This ratio is rather close to the 10.5% difference obtained in a former calculation based on a tight-binding approach [18], but the absolute values for the respective bulk moduli were found to be ~8% larger than those given by the present first-principles calculations.

Both the experimental and theoretical results lead to conclude that the clathrate structure yields materials "softer" than their diamond analogs, but the rather small difference between the two bulk moduli still allows one to classify the clathrate structure as a "low compressible" one. As a matter of fact, the present DFT calculations performed on the hypothetical C-34 clathrate predict that such a phase, if synthesized, would exhibit a bulk modulus ~14% smaller than the one of cubic diamond (398 GPa instead of 462 GPa, calculated values). This can be compared to the case of cubic BN, the second less-compressible material after diamond, which has a bulk modulus ~17% smaller than the one of diamond. Further, the present results seem to indicate that such a material could be as stable under pressure as carbon diamond and potentially more stable if intercalated. These considerations, even though speculative at this stage, lend support to the idea that the clathrate phase is a potential novel candidate structure for the synthesis of low-compressibility materials. The recently reported synthesis of cagelike 3D carbon covalent crystals [23,24] strongly suggests that such materials are within reach of current synthesis techniques. The graphite to diamond transition at high pressure leads to propose, as a possible route for the production of C-34, the hydrothermal collapse of the LiC_6 intercalated graphite compound. The alkali atoms are expected [25] to frustrate the production of diamond and serve as templates to form the carbon cages.

We discuss now the effect of both the change in density and structure on the bulk modulus of Si-34 as compared to Si-2. A semiempirical formula was proposed by Cohen [26] to simply relate the bulk modulus and the interatomic distance (d) of tetrahedral semiconductors, namely, $B_0 = 1971 d^{-3.5}$ GPa (d in Å). In the clathrates, the spreading of the dihedral angles and the first neighbors distances are low enough to take a mean value. Applying the law given above to Si-34 and Si-2, one obtains, respectively, 96 and 99 GPa for the bulk modulus. The general trend is therefore respected but this simple relation, which works remarkably well for column IV materials in the diamond phase, appears to overestimate the Si-34 to Si-2 bulk modulus ratio and predict the Si-34 B_0 to be only ~3% smaller than that of diamond. Even if the density difference could explain the observed bulk moduli difference, other mechanisms are likely to participate.

The specific topology of Si-34, namely, the large percentage of pentagonal rings, has been shown to significantly affect the electronic and phonon density of states [8,10] and is therefore expected to influence as well the compressibility of clathrates as compared to diamond. Even though the relation between topology and compressibility is not straightforward, one notes that in Si-2 all moments are even, while in Si-34 we have odd and even moments. It is further well known [27] that odd moments appearing in tetrahedral structures are the mark of a charge transfer as in ionocovalent systems. As a matter of fact, there are three nonequivalent Si atoms in the Si-34 unit cell. Such a charge transfer is expected to induce a decrease of the bulk modulus [28] as compared to the purely covalent Si-2 system. Consequently, one should not neglect a possible electronic origin participating in the reduction of the bulk modulus of Si-34 with respect to the one of Si-2.

In conclusion, we have shown that the Si-34 clathrate phase not only exhibits a rather large bulk modulus, 8 ± 5% smaller than the one of Si diamond, but is also very stable under pressure. In particular, no transformation into diamond could be observed. In fact, the only transition observed is the transformation into β-tin at 11 GPa, that is, the same transition pressure as the Si diamond to β-tin transformation. Our results, corroborated by *ab initio* calculations, strongly suggest that, if carbon clathrates can be synthesized, they would show a compressibility close to the diamond one, smaller, for example, than the one of cubic BN.

Note added.—The bulk modulus of Si-46 and C-46 has been previously calculated using similar *ab initio* techniques (see Ref. [29]). In good agreement with the present results, the reported bulk modulus of C-46 was found to be 85% of that of the diamond structure.

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