

High-pressure phases of germanium

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2001 J. Phys.: Condens. Matter 13 35

(<http://iopscience.iop.org/0953-8984/13/1/304>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.226

The article was downloaded on 16/05/2010 at 08:16

Please note that [terms and conditions apply](#).

High-pressure phases of germanium

A Mujica^{1,3}, S Radescu¹, A Muñoz¹ and R J Needs^{2,3}

¹ Departamento de Física Fundamental II, Universidad de La Laguna,
La Laguna E-38205, Tenerife, Spain

² Theory of Condensed Matter group, Cavendish Laboratory, University of Cambridge,
Cambridge CB3 0HE, UK

E-mail: amujica@marengo.dfis.ull.es (A Mujica), rjll@phy.cam.ac.uk (R J Needs)

Received 1 September 2000, in final form 15 November 2000

Abstract

We report a first-principles study of high-pressure phases of Ge finding that a Cmca phase is stable in the pressure range 91–155 GPa, while at higher pressures the hcp phase has lower enthalpy. The structural parameters of the Cmca phase are similar to those of other Cmca phases found in Si (Si-VI) and Cs (Cs-V). Our results challenge the experimental report of a transition from the simple hexagonal phase to a double hexagonal close-packed phase in this material.

1. Introduction

Much less effort has gone into studying the high-pressure behaviour of Ge than the chemically similar element Si⁴. For Si, experiments up to pressures of ~250 GPa have led to the discovery of 12 different structural phases, both stable and metastable under different conditions of applied pressure, of which only three are currently lacking a precise crystallographic characterization. In particular, a large and well established body of experimental evidence indicates the following sequence of transitions between stable phases in Si upon increase of pressure: cd→ β -Sn→Imma→sh→Cmca→hcp→fcc.⁵ For Ge, experimental high-pressure studies have reached a pressure of ‘only’ ~125 GPa and the observed sequence of transitions has been accepted as cd→ β -Sn→Imma→sh→dhcp. (See, however, the *Note Added* at the end of the paper for a reassessment of the experimental situation.)

The correct structural identification of phase VI of Si, which is intermediate between the sh and hcp phases and is named Cmca after its space group, was until recently precluded by

³ Authors to whom correspondence should be addressed.

⁴ See [1] for a recent review of the experimental situation in Si and Ge. This review was written prior to the identification of the Cmca–Si phase.

⁵ The nomenclature used for the different structural phases is as follows: (cubic) diamond (cd), simple (or primitive) hexagonal (sh), (mono)-hexagonal close-packed (hcp), double-hexagonal close-packed (dhcp), face-centred cubic (fcc), body-centred cubic (bcc), body-centred cubic (bct), and simple cubic (sc); Imma and Cmca refer to the space group of the corresponding phases; bc8 is a body-centred cubic structure with eight atoms per primitive cell, r8 is rhombohedral with eight atoms, and st12 is simple tetragonal with 12 atoms; and β -Sn indicates the same structure as the β phase of tin. Details of these structures can be found in [1] and the literature cited therein; for Cmca see [8].

its very complexity. It was initially suggested that it could consist of a simple restacking of hexagonal close-packed layers as in dhcp [2] (although this suggestion has proved incorrect), and later to have the same structure as the so called *X* phase of the alloy $\text{Bi}_{0.8}\text{Pb}_{0.2}$ [3]⁶. It is now known to consist of a base-centred orthorhombic lattice, with space group *Cmca* and 16 atoms in the conventional orthorhombic cell, occupying 8(d) and 8(f) Wyckoff positions [5]. A similar structure had been found previously in Cs at high pressures (Cs-V) [6] and later in Rb (Rb-VI) [7]. At variance with studies of Si, a single experimental study of Ge has reported a transition from the sh phase to a phase identified as dhcp [8]. This phase remained stable up to the highest pressure achieved in the experiment of ~ 125 GPa. In other aspects, however, the behaviour under compression of Si and Ge shows remarkable similarities, as evidenced by the sequence of structural phases observed with increasing pressure, by the structural identity of the metastable phases Si-III and Ge-IV (bc8) obtained upon decompression, and by the further observation of another similar low-pressure structure to which both of these metastable phases later transform [1]. There are also some significant differences in their properties under compression because Ge has a larger and more polarizable core containing the 3d electrons which gives an additional inter-atomic repulsion leading to higher transition pressures than in Si [9,10]. It is therefore important to assess theoretically the possibility of the formation of a *Cmca* phase in Ge which would motivate further experimental work on this material for which there is currently a scarcity of experimental studies at high pressures.

2. Method of calculation

As part of an ongoing systematic theoretical study of the high-pressure behaviour of the group IVa and IIIa–Va semiconductors we have studied the energetics and structural properties of Ge under compression, including the *Cmca* phase. We have used the plane-wave (PW) pseudopotential (PP) implementation of the density functional theory within the local density approximation (LDA). The details of the calculation are similar to those reported in previous work⁷. Although we are primarily concerned with Ge, we also present results for Si both for the sake of comparison and to demonstrate the capability of the PWPP method in reproducing the results of very accurate experimental studies of *Cmca*-Si, and by extension to predict the stability of a similar structural phase in Ge.

3. Description of the *Cmca* structure

The *Cmca* structure was first described after its identification as Cs-V ([6]) and Si-VI ([5]), where it was interpreted in terms of layers of octahedra which share corners and which are stacked in an approximately close-packed fashion along the *a* axis, with octahedra within one layer being rotated with respect to their neighbours. The atomic positions in *Cmca* are illustrated in figure 1, where we have chosen to show views along the different Cartesian axes (see also figure 2 of [6] for other representations of this structure). At fixed volume *Cmca* has five structural degrees of freedom: the internal parameters *x* (relative to the 8(d) sites at (*x*,0,0) etc), *y* and *z* (relative to the 8(f) sites at (0,*y*,*z*) etc); and the two axial ratios *b/a* and

⁶ A recent reassessment of the structure of this *X* phase (made after the identification of Si-VI) confirms that both structures are indeed isotopic. See [4].

⁷ We used the Ceperley–Alder form of the LDA and full structural relaxations were performed using the atomic forces and stress tensor. The Ge^{4+} ion was represented by a norm-conserving PP which included non-linear core exchange-correlation corrections. The Brillouin zone integrations for the metallic *Cmca* phase were performed by summing over a $10 \times 10 \times 10$ mesh and we used a PW energy cutoff of 24 Ry. See [11] for a fuller account and details of other phases.

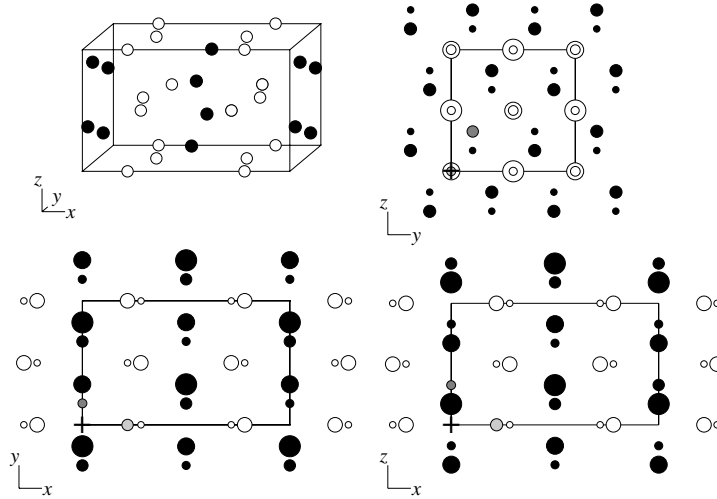


Figure 1. The Cmca structure represented in perspective and viewed along the Cartesian axes. The configuration shown corresponds to the experimental values of the structural parameters found in Si-VI (see table 1). Black and white ‘atoms’ indicate, respectively, the positions of the 8(f) and 8(d) sites. In the projections of the structure, the sites in the different perpendicular planes are represented by atoms of the same size, with the size indicating the distance to a reference plane. The standard origin has been indicated in the projections by means of a cross, and the 8(d) site $(x,0,0)$ and the 8(f) site $(0,y,z)$ have been marked using grey atoms, which make it possible to identify the positional parameters. For reference the conventional orthorhombic unit cell is also represented.

c/a . The ‘invariances’⁸ of Cmca with respect to the values of its structural parameters imply the existence of certain equilibrium configurations at special values of these parameters⁹ and also allows us to restrict the ranges of these parameters in the relaxation of the structure.

The five degrees of freedom of Cmca allow a variety of configurations with very different bonding arrangements. For the actual values of the structural parameters obtained from experiments on Si-VI and Cs-V, each 8(d) site has 10 nearest neighbours with a number of slightly different bond lengths, while each 8(f) site is approximately 11-fold coordinated. The coordination is thus intermediate between the eight-fold coordination of sh, which precedes Cmca in the sequence of transitions, and the twelve-fold coordination of the higher pressure close-packed phases. We will see that these structural features are approximately preserved in Ge.

⁸ By an invariance we mean that for two different sets of parameters the corresponding configurations are related by a point group operation and thus the relative distances between atoms are strictly preserved. Consequently, the internal energies of both configurations are the same and they are equivalent from the point of view of an energetic study. For example, concerning the y and z parameters, the sets (y,z) , $(0.5-y,0.5-z)$, $(-y,z)$, $(y,-z)$, $(1-y,z)$, and $(y,1-z)$ are equivalent.

⁹ For example, regarding the y and z parameters, the configuration $y = 0.25$, $z = 0.25$, which for $b/a = c/a$ corresponds to a tetragonal structure (bct when $x = 0.25$, and fcc when in addition $b/a = c/a=1$). The configuration $x = 0.25$, $y = 0.25$, $z = 0.5$, and $b/a = 1/\sqrt{3}$ corresponds to the sh structure, with the axis of the hexagonal cell orientated along the z -axis (along the y -axis if $x = 0.25$, $y = 0.5$, $z = 0.25$ and $c/a = 1/\sqrt{3}$).

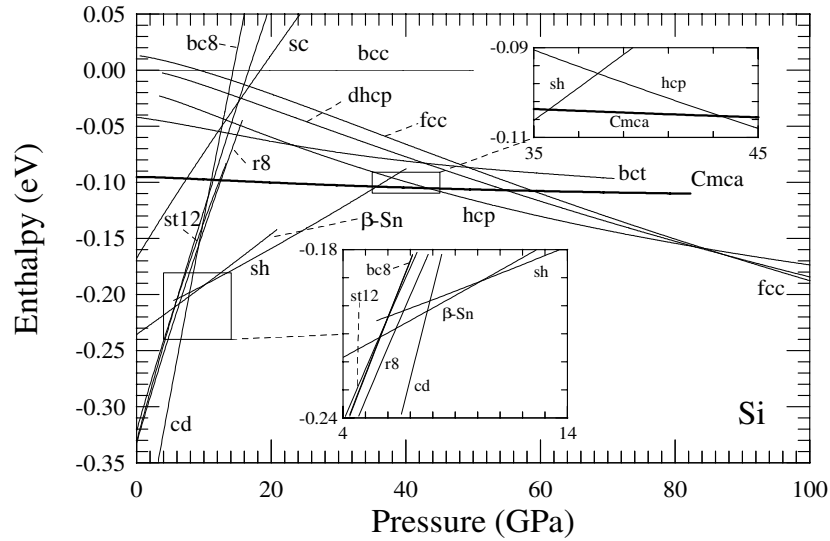


Figure 2. Enthalpy–pressure curves for different phases of Si (see footnote 5 for the nomenclature). For clarity the enthalpy of a reference phase (bcc) has been subtracted from each curve. Enlarged areas correspond to the relevant regions where transitions take place, and the curve for the Cmca phase is shown in bold.

4. Results and discussion

In figures 2 and 3 we show the calculated enthalpy, H , as a function of pressure, p , for fourteen phases (see footnote 5) of Si and Ge. For both materials the initial sequence of transitions $cd \rightarrow \beta\text{-Sn} \rightarrow \text{Imma} \rightarrow \text{sh}$ is correctly described¹⁰. For Si, our results show an interval of pressures between 36.0 GPa and 43.5 GPa in which the Cmca phase has a lower enthalpy than any other phase considered; the subsequent transitions would then be $\text{sh} \rightarrow \text{Cmca} \rightarrow \text{hcp}$. This is in almost perfect agreement with the experimental results for Si [5] which locate the onset for the $\text{sh} \rightarrow \text{Cmca}$ transition at 38.0 GPa and that for the $\text{Cmca} \rightarrow \text{hcp}$ transition at 42.5 GPa. The calculated volume changes at the coexistence $\text{sh} \rightarrow \text{Cmca}$ and $\text{Cmca} \rightarrow \text{hcp}$ pressures (5.2% and 2%, respectively) are also in excellent agreement with the observed volume reductions of 5.4% and 1.9% [5]. These results for Si agree with those obtained by Christensen *et al* [12] and by Ahuja *et al* [13] using the all-electron full-potential linearized muffin tin orbital (FP-LMTO) method.

The results of our calculations for Ge indicate that at pressures just below 100 GPa the Cmca phase has a lower enthalpy than any other phase considered; the predicted transition would then be from sh to Cmca with a calculated coexistence pressure of 91 ± 2 GPa and a small reduction in volume of $\sim 1.4\%$. As pressure is further increased, the enthalpy of the hcp phase becomes lower than that of the Cmca phase at 155 ± 5 GPa; the calculated volume reduction for this transition is $\sim 0.5\%$.

¹⁰ See also [11] for Si. We have chosen not to include the results for the Imma phase in figures 2 and 3, which on the scale of this figure would be indistinguishable from those of the $\beta\text{-Sn}$ and sh phases (to which Imma is intermediate) within the relevant range of stability of this phase. At low pressures we find that the favoured structure within the Imma class is in fact $\beta\text{-Sn}$ in agreement with the experimental observation [1] but at variance with the theoretical study of [10], where a small distortion from $\beta\text{-Sn}$ is reported.

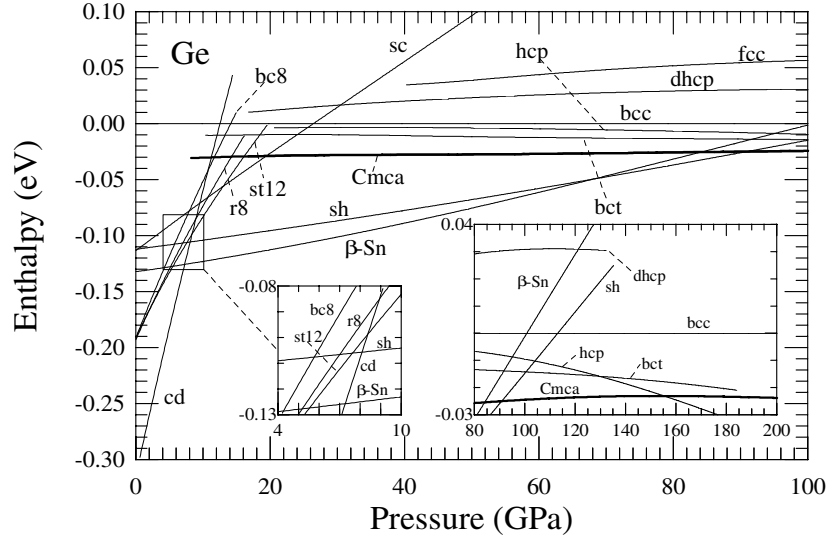


Figure 3. Same as figure 2, for the different phases of Ge.

The fcc, dhcp, bcc, hcp, bct, and Cmca phases of Ge are calculated to have nearly parallel $H(p)$ curves at low pressures, but some downward curvature of $H(p)$ is apparent in the inset to figure 3 for the hcp and bct phases at high pressures. The enthalpy of the dhcp phase is, however, significantly higher than that of the Cmca phase (by ~ 0.055 eV per atom at ~ 100 GPa); in fact, at this pressure the bcc, hcp, and bct phases have lower enthalpies than dhcp, although higher than Cmca. These results rule out the possibility of a $sh \rightarrow dhcp$ transition, which was reported to occur experimentally at a pressure of 102 ± 5 GPa [8]. We note that for Ge the bct phase is very close in enthalpy to the Cmca phase (~ 0.01 eV at 90 GPa) in the whole range of pressures investigated; the bct phase has indeed been observed to occur as a high-pressure stable phase in Sn. The calculated $V(p)$ curve for the predicted Cmca-Ge and hcp-Ge phases, which could eventually be compared with experimental data, are shown in figure 4.

Table 1. Structural parameters for the Cmca phase of Si (Si-VI) and Ge. The values pertaining to Si-VI (both calculated and experimental) correspond to a volume of $V = 11.308 \text{ \AA}^3$ per atom; the calculated values for Ge, correspond to the volume $V = 11.454 \text{ \AA}^3$ per atom.

	Calculated ^a		Experimental ^b
	Ge	Si	Si
$x(8d)$	0.218	0.216	0.218
$y(8f)$	0.172	0.173	0.172
$z(8f)$	0.323	0.326	0.328
b/a	0.5929	0.5953	0.5990
c/a	0.5922	0.5949	0.5967

^a This work.

^b Hanfland *et al* [5].

In figure 5 we show the evolution under compression of the structural parameters of Si and Ge corresponding to the fully relaxed Cmca phase subject to hydrostatic conditions. The variation of these parameters in the relevant range is comparable to the experimental uncertainty, and thus it might not be appreciated in the experiment. The structural parameters of Cmca-Si and Cmca-Ge have fairly similar absolute values which, however, show a slightly

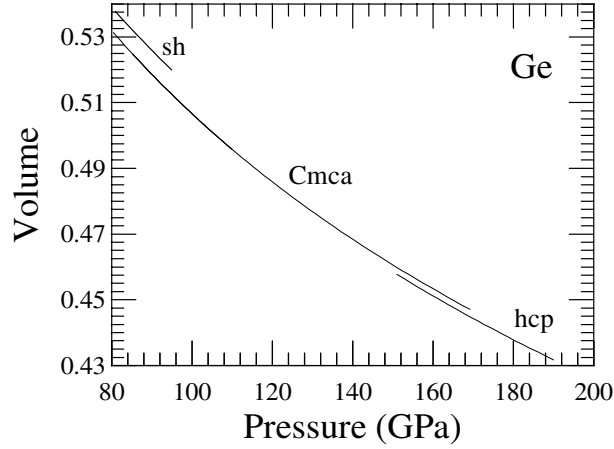


Figure 4. Predicted evolution of the volume, V , with pressure, p , for the sh, Cmca, and hcp phases of Ge. The volume is given in units of the zero-pressure volume of the diamond phase, $V_0^{cd}(\text{Ge}) = 22.64 \text{ \AA}^3$, and the pressure has been shifted by $\Delta p = 1.05 \text{ GPa}$ to take into account the usual underestimation of V_0^{cd} within the DFT-LDA formalism.

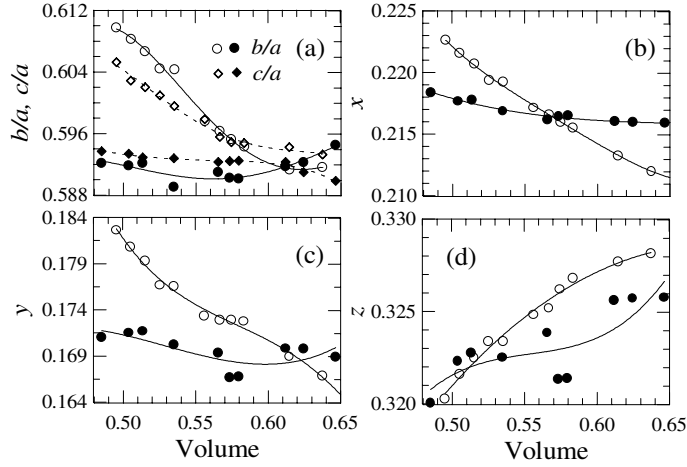


Figure 5. Evolution of the structural parameters of the Cmca phase of Si (empty symbols) and Ge (filled symbols) under compression. For each material the volume is given in units of the theoretical zero-pressure volume per atom of the diamond phase $V_0^{cd}(\text{Si}) = 19.69 \text{ \AA}^3$, $V_0^{cd}(\text{Ge}) = 22.32 \text{ \AA}^3$ (cf. the experimental values $V_0^{cd}(\text{Si}) = 20.02 \text{ \AA}^3$, $V_0^{cd}(\text{Ge}) = 22.64 \text{ \AA}^3$). The curves are guides to the eye.

different trend under compression. In table 1 we compare their calculated values at reference volumes both for Si and Ge with those obtained from experiments on Si-VI. As can be seen, the agreement between experimental and calculated values in Si is excellent. For hcp-Ge we find a c/a ratio of ~ 1.633 , which is close to the ideal value, while for sh-Ge at $p \approx 85 \text{ GPa}$ we find $c/a \approx 0.926$.

The main structural features of Cmca-Si and Cmca-Ge obtained from our calculations are the same in both cases and agree with the crystallographic description of this phase reported in Si [5]. We note in particular that there is only a very small deviation from $b/a = c/a$, and that the values of y and z are close to satisfying the condition $y+z = 0.5$, which leads to a characteristic ‘square’ shape of the octahedra of groups of atoms. However, the Cmca structure cannot sustain the tetragonal symmetry suggested by this equivalence of lattice constants, and such a relation between internal parameters is not especially favoured by symmetry considerations.

5. Summary and conclusions

In conclusion, our first-principles calculations indicate transitions from the sh phase of Ge to a Cmca phase at 91 GPa and from Cmca to hcp at 155 GPa, which contradict the previous experimental report of a sh→dhcp transition at 102 ± 5 GPa.

The similarities in the behaviour of Si and Ge under pressure extend to the existence of the Cmca and hcp phases (with similar values of the structural parameters in the case of the Cmca phases). The intervals of stability are however very different as, for example, the sh→Cmca transition in Ge occurs at pressures considerably larger than those at which the same transition occurs in Si (~ 91 GPa compared to ~ 38 GPa). This situation is similar to that found for the β -Sn→Imma→sh transitions observed in both materials and has been attributed to an effect of the d electrons of the Ge atoms [9, 10].

Acknowledgments

RJN acknowledges financial support from the Engineering and Physical Sciences Research Council (UK). The use of computer facilities at C⁴ (Centre de Computació i Comunicacions de Catalunya) is also gratefully acknowledged. AM and SR are grateful for the award of a travel grant by the Consejería de Educación del Gobierno Autónomo de Canarias (Spain).

Note added in proof. After the submission of this paper we learned of two other very recent (unpublished, at the time) studies of Ge at high pressure which report on the Cmca and hcp phases of this material. In their theoretical PWPP study, Ribeiro and Cohen [14] find a coexistence pressure for the sh→Cmca transition of 90 ± 2 GPa and of 137 ± 10 GPa for the Cmca→hcp transition (cf. our calculated values of 91 ± 2 GPa and 155 ± 5 GPa, respectively, using the same method of calculation). On the other hand, Takemura *et al* [15] report an experimental study of Ge up to ~ 190 GPa complemented by a theoretical study using the LMTO method. In their experimental study these authors find that the sh phase of Ge transforms to a Cmca phase near 100 GPa, which then transforms to the hcp phase somewhere near 160–180 GPa. The experimental values of the structural parameters of Cmca–Ge obtained by Takemura *et al* at $p \sim 135$ GPa ($V = 10.67(6) \text{ \AA}^3$) are: $b/a = 0.5904$, $c/a = 0.5899$, $x = 0.218$, $y = 0.164$, and $z = 0.313$ (cf. our calculated values at the same compression: $b/a = 0.5925$, $c/a = 0.5940$, $x = 0.218$, $y = 0.170$, and $z = 0.320$). Where comparable, our results are also in quite good agreement with the PWPP calculations of Ribeiro and Cohen although there are significant differences from the LMTO calculations of Takemura *et al*. Takemura *et al* calculate the Cmca→hcp coexistence pressure to be about 240 GPa, which is much larger than the experimental value, and they find an interval ~ 170 – 280 GPa where the bcc phase has a lower enthalpy than both the Cmca and hcp phases, which is not supported experimentally, either.

References

- [1] Nemes R J and McMahon M I 1998 *Semicond. and Semimet.* **54** 145
- [2] Olijnyk H, Sikka S K and Holzapfel W B 1984 *Phys. Lett. A* **103** 137
- [3] Duclos S J, Vohra Y K and Ruoff A L 1990 *Phys. Rev. B* **41** 12021
- [4] Degatyareva V F 2000 *Phys. Rev.* **62** 9
- [5] Hanfland M, Schwarz U, Syassen K and Takemura K 1999 *Phys. Rev. Lett.* **82** 1197
- [6] Schwarz U, Takemura K, Hanfland M and Syassen K 1998 *Phys. Rev. Lett.* **81** 2711
- [7] Schwarz U, Syassen K, Grzechnik A and Hanfland M 1999 *Solid State Commun.* **112** 319

-
- [8] Vohra Y K, Brister K E, Desgreniers S, Ruoff A L, Chang K J and Cohen M L 1986 *Phys. Rev. Lett.* **56** 1944
 - [9] Chang K J and Cohen M L 1986 *Phys. Rev. B* **34** 8581
 - [10] Lewis S P and Cohen M L 1993 *Phys. Rev. B* **48** 16144
 - [11] Needs R J and Mujica A 1995 *Phys. Rev. B* **51** 9652
 - [12] Christensen N E, Novikov D L and Methfessel M 1999 *Solid State Commun.* **110** 615
 - [13] Ahuja R, Eriksson O and Johansson B 1999 *Phys. Rev. B* **60** 14475
 - [14] Ribeiro F J and Cohen M L 2000 *Phys. Rev. B* to be published
 - [15] Takemura K *et al* 2000 *Phys. Rev. B* **62** 10603