

High-pressure phases and structural bonding of Ge_3N_4

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(Received 18 January 2000)

The spinel structure of Ge_3N_4 is compared with that of $\beta\text{-Ge}_3\text{N}_4$ and a cubic defect zinc-blende structure recently considered possible for C_3N_4 . The β phase is suggested to be a possible precursor phase to the spinel structure. Electronic structure calculations reveal that the spinel structure is a subtle extension of the defect zinc-blende phase in which the Ge atoms attempt to connect into the conventional zinc-blende structure.

The continuing search for materials with refractory properties comparable or even harder than diamond has been the focus of much recent attention. Of the nitrides, Si_3N_4 has now proven itself to be much used as an engineering ceramic material where, because of its hardness and relative weight, it is an optimum replacement for some metals in uses such as machine bearings. Si_3N_4 was also the prototype material leading to the postulate that C_3N_4 may be harder than diamond^{1,2} and recently other modifications of the structure have been considered³⁻⁵ for their potentially super-hard properties.

One of the harder forms of Si_3N_4 is expected to take either the α or β hexagonal forms although recently another still higher-density structure has been identified⁶ that has a cubic spinel structure. It would appear that the structure needs a pressure of over 15 GPa for its synthesis making it lie outside a pressure region normally accessible for present industrial synthesis. Despite this, the structure is the first in which Si is surrounded by a Group-V atom—here N—in a sixfold co-ordination, and recent calculations indicate that it could have quite an appreciable bulk modulus.⁷ More recently a similar spinel structure has been observed for a binary Ge_3N_4 system⁸ again in which the Ge atom is surrounded by six N atoms. This structure could possibly be easier to synthesize because of the larger volumes encountered. Accordingly, details of this material—especially its electronic structure—will help to elucidate its properties and relate it to other structural forms of the material.

The chemistry of nitrogen in germanium has recently been reviewed by Chambouleyron and Zanatta⁹ where it has been pointed out that many aspects of the structure of Ge-N alloys are not well understood. Here again electronic structure calculations can provide much insight into both existing and possibly new structures.

It is tempting to compare Ge_3N_4 with C_3N_4 and Si_3N_4 or even diamond. Several structures of C_3N_4 have now been considered recently¹⁰ as possible super-hard materials. One of these is a defect zinc-blende phase that essentially is the conventional zinc-blende lattice with an empty vacant site to preserve the C_3N_4 stoichiometry. As with Si_3N_4 , this structure has an energy lying well above that of the β structure. It is very likely that the Ge_3N_4 alloy will have similar features. The structure of the defect zinc-blende and β structures, considered recently as possible phases of carbon nitride, are shown in Fig. 1. The defect zinc-blende structure has $P43m$ symmetry and essentially can be viewed as a conventional zinc-blende lattice but containing vacant sites to allow for the chemical stoichiometry of the material. This structure has not been identified in the case of either Ge_3N_4 or Si_3N_4 , to our knowledge. On the other hand Ge_3N_4 , as with Si_3N_4 , has been observed in both α and β form. The β structure, which is not too different from the α structure, is hexagonal with a $P6_3/m$ space group¹¹ and has tentatively been synthesized in crystalline form as phenacite from Ge interacting with NH_3 or $\text{Ge}(\text{NH})_2$.^{12,9,13} More recently a spinel structure $Fd3m$ has only recently been synthesized⁸ and has a higher density than the other phases of Ge_3N_4 . It would appear that the synthesis method used by Serghiou *et al.*, leading to the spinel structure, did not involve the presence of H. The atoms of the spinel structure are located at positions $\text{Ge}(1):(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and $\text{N}(x, x, x)$ with $x = 0.25 + \delta$. As pointed out by Serghiou *et al.*,⁸ the Ge-N distances for the tetrahedrally and octahedrally coordinated Ge atoms are the same when $\delta = 0.0125$. This structure is shown in Fig. 2.

The relation of the various phases as well as their elastic properties will be now investigated using techniques of *ab initio* molecular dynamics. Soft Troullier-Martin¹⁴ nonspin-

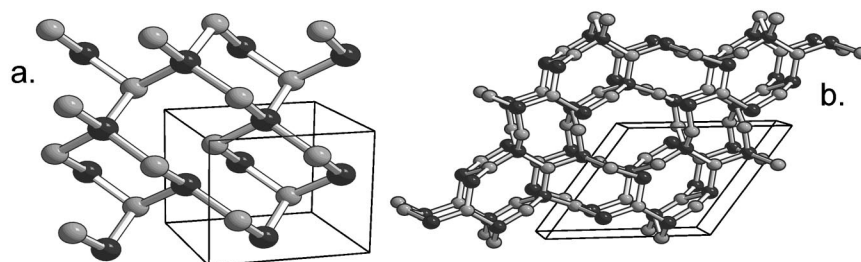
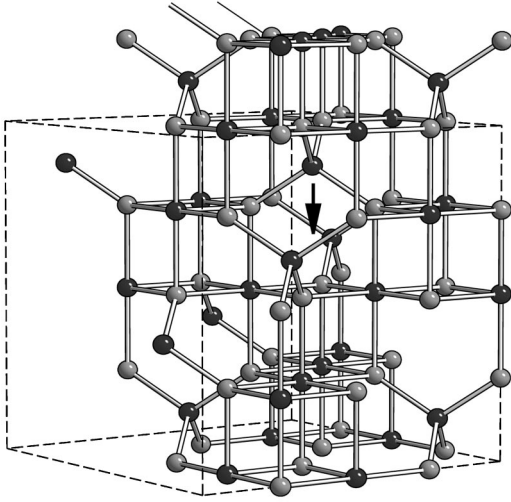
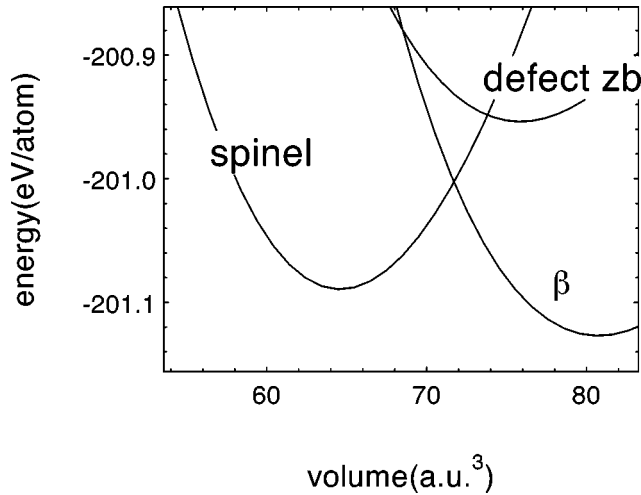
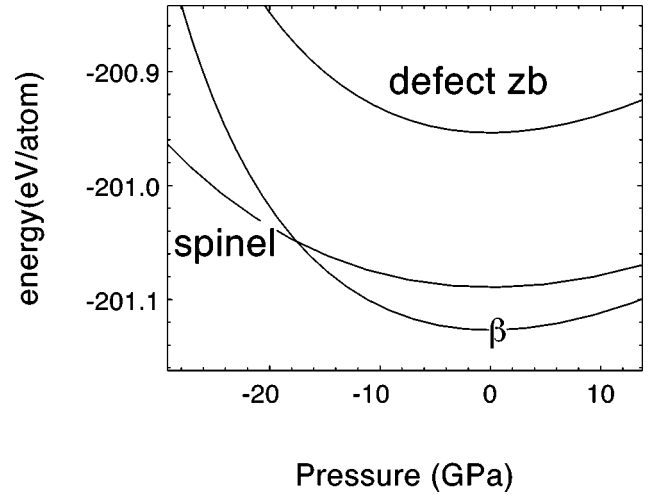


FIG. 1. The defect zinc-blende (a) and beta phase (b) of Ge_3N_4 . Dark spheres represent Ge atoms.

FIG. 2. Unit cell of the spinel structure of Ge_3N_4 .FIG. 3. Relative energies of some phases of Ge_3N_4 .FIG. 4. Transition pressure of the Ge_3N_4 phases—negative pressure indicates compression.

polarized pseudopotentials with plane waves of 64 Ry were used throughout with a k -point sampling using a [444] Monkhorst-Pack grid.¹⁵ Energy-volume relations were calculated using a plane wave algorithm¹⁶ for each structure and the results fitted to a standard equation of state¹⁷ from which an estimate of the bulk modulus can be obtained. Each structure was optimized for a specified cell geometry with lattice relaxation of all atoms included in each case. This procedure is proving to be quite reliable in the computational design of advanced materials.

In Figs. 3 and 4 we show the calculated energies and pressures—as calculated from the common-slope method—for each of the three phases, with the calculated structures and equation-of-state parameters such as the bulk modulus given in Table I. The relative ordering in energies of the phases strongly suggest that lower energy β phase would be a precursor phase of the spinel phase with a transition pressure of 19 GPa being predicted for the transition to the spinel phase. The transition pressure of 14 GPa reported recently for the synthesis of the spinel structure is not too far from this value and would strongly imply that the β phase is also formed in the synthesis procedure. As far as the spinel phase is concerned, the calculated value of $\delta=0.0078$ shows that the Ge-N distances are slightly different for the tetrahedrally and octahedrally coordinated Ge atoms being 1.87 Å and 1.97 Å, respectively.

TABLE I. Calculated properties of Ge_3N_4 . Z is the number of formula units per unit cell.

Phase	Z	Lattice (Å)	Density (g/cm ³)	B (GPa)	B'	Relative energy (eV/atom)
Defect zinc-blende ($P43m$)	1	$a=4.31$	4.92	193	3.32	0.173
Spinel ($Fd3m$)	8	$a=8.12$ $\delta=0.0078$	6.16(6.36, ^a Ref. 8)	266	1.91	0.037
$\beta(P6_3/m)$	2	$a=7.40, c=3.20$ C: (0.1735,0.7696) N: (0.3320,0.0348)	5.24(5.25–5.28, ^a Refs. 9 and 11)	214	4.41	0.000

^aDenotes experimental values.

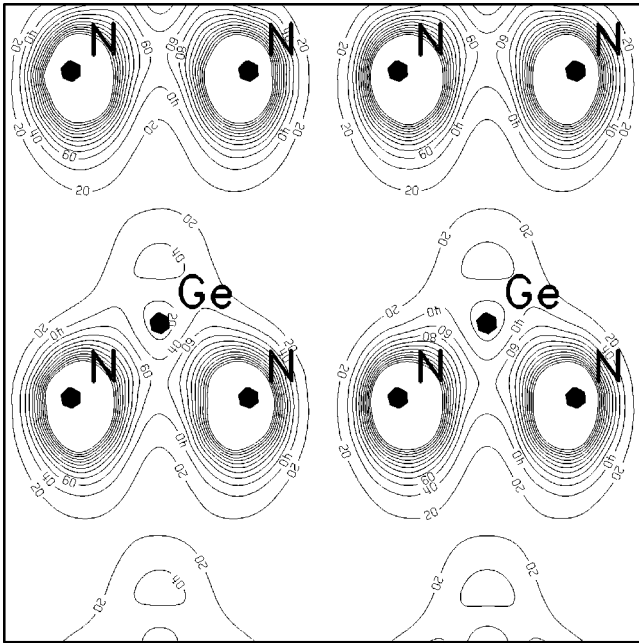


FIG. 5. Charge contour of the defect zinc-blende structure in the $[110]$ plane (top) and the beta structure in a plane perpendicular to the hexagonal c axis of Ge_3N_4 . Contours are in units of milli electron/(bohr³).

Quite clearly, from the energy-volume phase diagram of Fig. 3, the defect zinc-blende phases are highly metastable and unlikely to be realized as they are far higher in energy than either of the other two phases. In itself the defect zinc-blende phase can be viewed as being a conventional zinc-blende lattice with a missing Ge atom needed for the Ge_3N_4

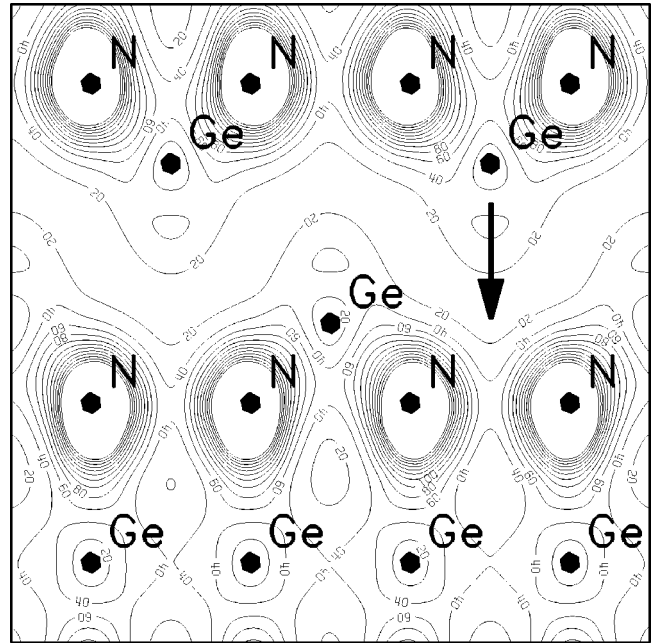


FIG. 6. Charge contour of the spinel structure of Ge_3N_4 in the $[110]$ plane. The arrow points to the site that, if occupied, would be occupied by a Ge atom in the zinc-blende structure.

stoichiometry. The absence of this atom does not seem to affect the directionality of the Ge-N bond, which is compared with that of the β -phase in Fig. 5. As expected there is very little charge located around the Ge atom relative to the N atom. If we compare the charge density of these structures with that of spinel Ge_3N_4 —which is now shown in Fig. 6—once again we see a very similar directionality of Ge-N bonding. The tetrahedral Ge-N bond appears to be slightly harder than the Ge-N octahedral bond at least as suggested from the magnitude of the charge density along the bond. One point also emerges—in Fig. 1 we indicated by an arrow how a Ge atom if displaced would occupy a site of the conventional zinc-blende structure. The arrow in Fig. 6 does likewise. If we compare the charge density with that in Fig. 4 then we see there is an attempt in the spinel structure for the Ge atoms in adjacent tetrahedra to achieve the defect zinc-blende charge distribution—in fact this is the reason for the difference between the tetrahedral and octahedral Ge-N bond distances as reflected in the nonzero value of the parameter δ describing the spinel cellular structure and the slightly larger Ge-N bond in the octahedral coordination.

In summary, we have investigated the relative energetics of some possible phases of Ge_3N_4 deducing their elastic properties and possible transition pressures. The β phase is suggested as being a likely precursor phase to the recently found spinel phase.

The NRF (S.A.) is thanked for supporting this work. Dr. G. Serghiou is thanked for a generous correspondence.

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