

First-principles calculations on solid nitrogen: A comparative study of high-pressure phases

J. Kotakoski^{1,2} and K. Albe²

¹*University of Helsinki, Accelerator Laboratory, P.O. Box 43, Helsinki FI-00014, Finland*

²*Institut für Materialwissenschaft, Technische Universität Darmstadt, Petersenstraße 23, D-64287 Darmstadt, Germany*

(Received 7 January 2008; revised manuscript received 7 March 2008; published 10 April 2008)

There is experimental evidence that nitrogen forms a polymeric solid under pressure. In this study, we compare various solid nitrogen phases by means of *ab initio* calculations based on density-functional theory to describe solid nitrogen at different pressures. We show that two phases with covalent bonds in all three dimensions are energetically the most favored at pressures of 50–200 GPa and that the layered *black phosphorus* phase becomes lower in enthalpy at pressures exceeding 200 GPa, at least at low temperatures. However, according to our results, black phosphorus is unstable at pressures close to 200 GPa. We further present band structure and density of states calculations for the relevant known phases at several pressures and show that black phosphorus is metallic when metastable, whereas the lower-pressure phases remain dielectric with pressure-dependent band gaps. Also the questionable experimental relevance of several of the previously proposed structures is addressed.

DOI: [10.1103/PhysRevB.77.144109](https://doi.org/10.1103/PhysRevB.77.144109)

PACS number(s): 71.15.Mb, 81.40.Vw, 71.20.Mq

I. INTRODUCTION

Nitrogen is usually considered as chemically inert due to the strong $\text{N}\equiv\text{N}$ triple bond in the N_2 dimer, which form molecular solids at low temperatures. However, a search for a single-bonded nonmolecular form of nitrogen was launched in 1985, when its existence was first proposed by McMahan and LeSar.¹ The sixfold energy difference between the $\text{N}\equiv\text{N}$ bond and the $\text{N}-\text{N}$ single bond gives this material an energy density much higher than that of the best energetic materials known today. Hence, it would serve as an ideal environmentally clean high-energy-density material with applications such as energy storage, propellants, and explosives. In 1992, Mailhot *et al.*² were able to predict the atomic structure of this solid, labeled *cubic gauche* (cg), based purely on theoretical considerations and *first-principles* calculations. This stiff dielectric material is often referred to as *polymeric nitrogen* because of its resemblance with carbon diamond. The interest on this material further increased in 1993, when Barbee showed that cg-nitrogen is at least metastable at ambient conditions.³

The synthesis of cg-nitrogen has been proven to be extremely difficult. In recent years, different experimental groups have reported evidence on nonmolecular amorphous solid nitrogen,^{4–6} and Eremets *et al.*⁵ even succeeded in bringing the material to ambient pressures at low temperatures. However, no signs of ordered polymeric structures were seen before 2004, when Eremets *et al.* made a second breakthrough and finally successfully synthesized a crystalline single-bonded cg-nitrogen structure at high pressures (>110 GPa) and temperatures (2000 K).⁷

Meanwhile, theoreticians were identifying other single-bonded nitrogen phases that could even be more stable or easier to synthesize. Several candidates have been introduced ranging from metallic chainlike phases^{8,9} and layered structures^{2,10} to truly three-dimensional phases with some resemblance with cg.^{11–13} While the work has been mainly concentrated on predicting other structures, a consistent comparison reviewing all the suggested phases is still lack-

ing. Hence, obtaining a coherent picture on the thermodynamical stability of the different nitrogen phases from the literature has remained extremely difficult. Also, improving on interaction models for molecular dynamics simulations on nonmolecular solid nitrogen, such as presented by Nordlund *et al.*,¹⁴ is currently nearly impossible based on these data.

In this study, we use *ab initio* calculations based on density-functional theory (DFT) to study the different proposed nitrogen phases. We show that many of the phases are most likely of no relevance, and compare the relevant phases to sketch a consistent picture that can be used to analyze the experimental data. Our results simplify the overview on the nonmolecular solid nitrogen in general and may shed some light on the experimentally observed amorphous structures. The calculations may further assist in designing the optimum conditions for obtaining the N-cg structure experimentally. We also present a comparison between a recently found phase¹¹ (labeled *pN* in the text) and other proposed nitrogen phases. We further present the electronic band structure of the relevant phases and describe the pressure dependence of their electronic density of states.

II. METHODS

We have employed DFT calculations as implemented in the plane wave basis set VASP code¹⁵ with the general gradient approximation (GGA) exchange-correlation functional by Perdew *et al.*¹⁶ GGA has been found^{9,10,17} to give a better description of nitrogen than the local density approximation used in several previous studies.^{2,3,8} The core ($1s^2$) electrons were described with a projector augmented wave pseudopotential.^{18,19} As has been noted before,³ nitrogen requires a high kinetic energy cutoff because it has no *p* or *d* states in the core. Therefore, a cutoff of 1200 eV (88.2 Ry) was used in all relaxation calculations. This was found to result in smooth energy-volume curves for the studied phases. Brillouin zone sampling was performed using the *k*-point sampling scheme of Monkhorst–Pack²⁰ (including the Γ point). Because of the relatively low symmetry of some

TABLE I. Different solid nitrogen phases considered in this work. D is the number of dimensions over which the structure is periodic in terms of continuous bonding.

Phase	D	Ref.	Phase	D	Ref.		
Cubic <i>gauche</i>	cg	3	2	Layered boat	lb	2	10
Chaired web	cw	3	13	Phosphorus-like	BP	2	2
<i>poly</i> -N	<i>pN</i>	3	11	Zigzag chain	zz ^a	1	9
Simple cubic	sc	3		Molecular 1	α -N ₂	0	2
Arsenic-like	A7	2	2	Molecular 2	ε -N ₂	0	2

^aSeveral chainlike phases have been proposed for nitrogen. We always refer to the phase presented by Mattson *et al.* (Ref. 9).

of the phases, for consistency, a $13 \times 13 \times 13$ k -point mesh was used for all the relaxation simulations. Further densifying the mesh was found to alter the results for the lattice constant by less than 1% and by less than 0.5% for the minimum energies of different phases. For calculations with larger supercells, the number of k points was decreased.

Relaxation simulations for calculating the equation of state (EOS) were started by searching for the volume and structural parameters yielding the minimum energy E_0 for each structure. After finding the minimum energy structure, the EOS curve was produced, whenever possible, by relaxing both the simulation cell and ion positions simultaneously for the volume range of interest. Constant volume was used in all our calculations.

To estimate the stability of some of the phases, we calculated the phonon dispersion relation following the scheme proposed by Kunc and Martin.²¹ Within this method, a supercell of sufficient size to limit the forces inside the cell is first created, and all irreducible directions within the cell are searched for. After this, each plane of atoms perpendicular to each direction is displaced along the 3 degrees of freedom to calculate the forces exerted on all atoms by the displacement. The force constant matrix is then constructed and used to calculate the dynamical matrix $\Phi_{\mathbf{k}}$ for the primitive cell for different \mathbf{k} vectors along the high symmetry axes. The square roots of the eigenvalues, $\omega_i(\mathbf{k})$, of $\Phi_{\mathbf{k}}$ give the frequencies of the phonon modes for each k . Imaginary frequencies correspond to directions of barrierless phase transitions indicating instability of the phase.

III. SIMULATIONS AND RESULTS

The solid nitrogen phases included in this work are listed in Table I, and the most important ones are presented in Fig. 1. To connect our study to the previous works, we started by searching for agreement with the published data. We first calculated the EOS (energy vs volume) for the different phases. The data obtained were then fitted to the Birch–Murnaghan equation of state.²² The fits are presented in Fig. 2. The EOS results for sc, cg, and molecular phases agree well with those presented by Mailhiot *et al.*² For layered A7 and BP structures, we were able to get qualitative agreement only with a fixed cell. When also relaxing the lattice vectors, we found (similar to graphite) that it is energetically more

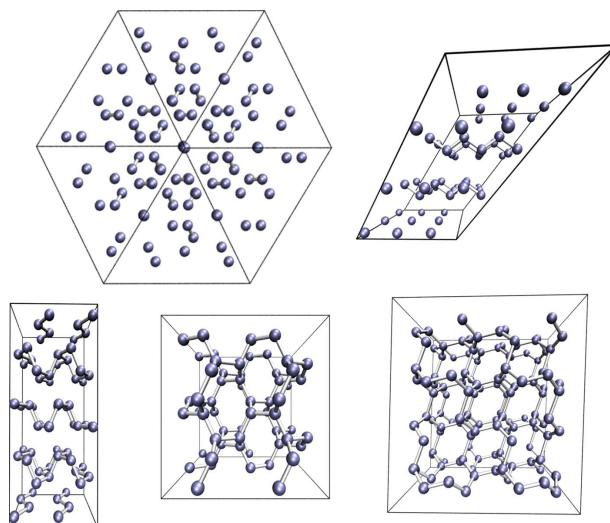


FIG. 1. (Color online) Atomic illustrations of the most relevant solid nitrogen phases. From left to right and top to bottom: ε -N₂ (this cell is built from $2 \times 2 \times 2$ primitive cells, 8×16 atoms), zz [$(3 \times 3 \times 3) \times 2$ atoms], BP [$(2 \times 2 \times 2) \times 4$ atoms], cg [$(2 \times 2 \times 2) \times 4$ atoms] and *pN* [$(2 \times 2 \times 2) \times 16$ atoms]. The ε -N₂ cell is displayed in an orthographic view perpendicular to the [111] direction, other structures are presented in perspective view.

favorable to separate the layers than to expand the structure in all three dimensions, leading to a flat tail for the EOS curve. This holds also for the lb phase and the chainlike phases (when expansion is allowed in two dimensions). Also, for BP, we obtained approximately 0.3 eV/atom lower energy when the structure was relaxed in the (eight-atom) cubic

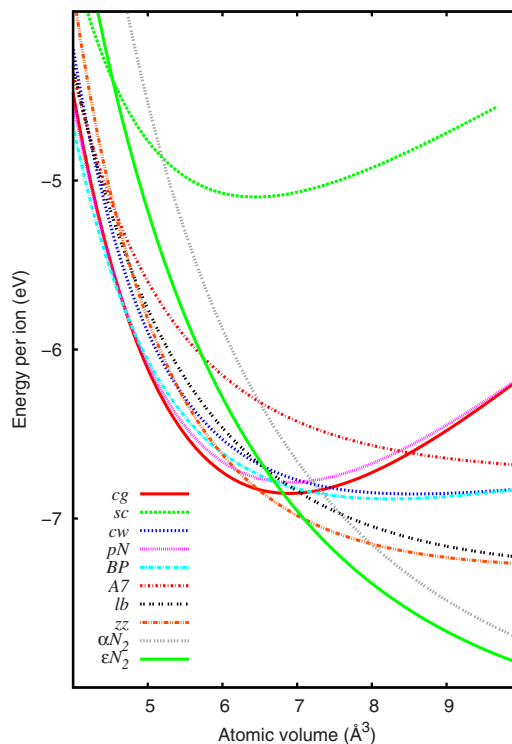


FIG. 2. (Color online) The equation of state $E(V)$ for different solid nitrogen phases.

TABLE II. Structural parameters for the relevant structures. N_{prim} is the number of atoms in the primitive cell. For cg, pN, zz, and BP, the calculations were performed with both the primitive cell and the cubic unit cell ($N_{cubic}=2N_{prim}$).

Phase	Space group	a (Å)		Sites	x, y, z	N_{prim}
		b/a	c/a			
ϵ -N ₂ ^a	$R\bar{3}c$ (167)	7.707		12c	$z_c=0.051$	16
				36f	$x_f=-0.339$	
		1.415			$y_f=-0.135$ $z_f=0.047$	
cg	$I2_13$ (199)	3.805		8a	$x=0.082$	4
pN ^b	$C2/c$ (15)	5.490		8f	$x_1=0.373$	8
		3.945			$y_1=-0.054$	
		5.515			$z_1=0.284$	
		$\beta=87.68^\circ$			$x_2=0.300$	
					$y_2=0.273$ $z_2=0.370$	
BP ^a	$Cmca$ (64)	2.186		8f	$y=0.094$	4
		3.360			$z=0.121$	
		1.446				
zz ^a	$Cmcm$ (63)	3.040		4c	$y=0.061$	2
		1.965				
		0.870				

^aValues for ϵ -N₂ are given at a pressure of about 13 GPa (dimer length $d=1.107$ Å), for BP at about 50 GPa, and for zz at about 10 GPa.

^bNote that a two atom unit occupies each site for pN. The lattice vectors of pN are distorted for the y axis by 0.091 Å toward the z axis, and for the z axis by 0.027 Å toward the y axis. All structural parameters are given according to Ref. 23.

cell instead of the (four-atom) primitive cell. With this cell, the structure was unstable at $P < 25$ GPa, breaking into separated zigzag chains.

The atomic volume V_0 obtained for cg (6.89 Å³) agrees well with the experimental value (6.59 Å³) and previous calculations [6.67 Å³ (Ref. 2) and 7.08 Å³ (Ref. 17)], as does the bulk modulus $B_0=268$ GPa [298 GPa (Ref. 7)]. For pN, we got values of $V_0=7.02$ Å³ and $B_0=210$ GPa. The minimum energy E_0 for cg is about 70 meV lower than that for pN. The structural parameters for the relevant phases are listed in Table II.

To compare the different phases, we also calculated enthalpies at $T=0$ K:

$$H = E - PV, \quad (1)$$

where E is energy, P is pressure, and V is atomic volume. The enthalpy difference of each phase to that of cg at a given pressure ($H-H_{cg}$) is presented in Fig. 3. The molecular phases are found to be the most stable at pressures lower

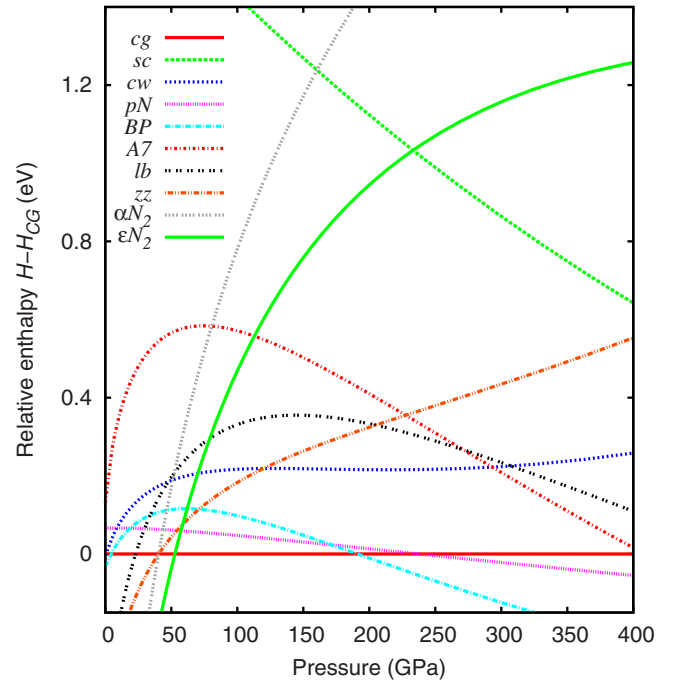


FIG. 3. (Color online) Enthalpy difference between the various nitrogen phases and cg at pressures $P \in [0, 400]$ GPa. Note that the enthalpy lines are shown also for the parts where the structures are unstable (see text) to ease the interpretation of the figure.

than 40 GPa, after which molecular phases, cg and zz are all close to each other in enthalpy. The cg phase is the most stable at $P \in [40, 200]$ GPa. At higher pressures, it is replaced by BP, which then remains as the lowest-enthalpy structure at least up to 400 GPa. However, BP is unstable at these pressures (discussed in detail below). The transition pressures and relative order for the higher-enthalpy phases agree mostly with the previous calculations.^{2,8–10} Interestingly, the pN phase remains very close (within ~ 0.1 eV) to cg at all pressures.

When performing the above-described calculations, we saw indications of instabilities for some of the structures, such as relaxing into another phase or demands for several subsequent relaxation calculations before converging. To estimate the stability of the different phases, we calculated the phonon dispersion for the relevant cases. We tested our method with cg and sc phases, and were able to reproduce the main features of the low-pressure dispersion curves presented by Barbee,³ showing also the imaginary frequencies for the unstable sc. For cg, the phonon frequencies remained real throughout the Brillouin zone.

One of the phases causing us much trouble at low pressures was BP. We found that at $P < 50$ GPa, the phonon modes of BP have imaginary frequencies toward breaking the weakest bonds (the bonds between zigzag chains, see Fig. 1; these bonds are $< 40\%$ covalent) in the BP layer, suggesting instability of the structure by separating the chains. This finding is in perfect agreement with the results by Alemany and Martins⁸ who found BP to break into zigzag chains in molecular dynamics simulations. Part of the lowest-frequency band of the phonon dispersion of BP at several pressures is presented in Fig. 4. We also saw the

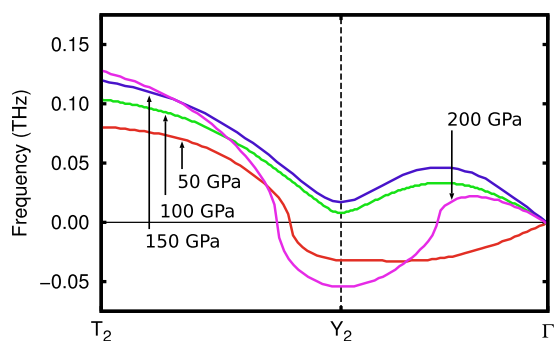


FIG. 4. (Color online) Lowest-frequency band of phonon dispersion relation for BP nitrogen at several pressures between certain symmetry points (see Ref. 23). Imaginary frequencies are plotted with negative values. Y_2 corresponds to the $(-\frac{1}{2}, \frac{1}{2}, 0)$ direction.

breakage of BP into a chainlike structure at 10 GPa within the EOS calculations with an eight-atom cubic cell. However, in our simulations, zz was always favored over other chainlike phases like the one found by Alemany and Martins.⁸ According to our results, the BP phase becomes metastable with increasing pressure as the imaginary part of the frequencies vanishes before 100 GPa and develops into a soft mode. Curiously, at about 200 GPa, the branch becomes imaginary again at Y_2 . At higher pressures, we were only able to relax the structure with a supercell containing 64 atoms, which allowed for displacing the atoms and, hence, distorting the original structure. Therefore, we conclude that BP is metastable only at a pressure range of 100–150 GPa and unstable at other pressures, at least up to 250 GPa.

Phonon dispersion for BP has also been studied (among other phases) by Zahariev *et al.*¹² They reported the instability of the BP phase for all P , but saw curiously no imaginary phonon frequencies. As also the enthalpies they reported differ both from studies made by others,⁸ and from a previous work of the same group,¹⁰ these discrepancies may be caused by the low kinetic energy cutoff (39 Ry) used in the work.¹²

The phonon calculations allowed us to estimate the entropy contribution to the Gibb’s free energy of the structures. The results suggest that the reason for the BP remaining hidden from the experimentalists is not a temperature effect; at least when calculated for the low pressure structures, the entropy of BP remains always higher than that of cg , thus increasing the difference in Gibb’s free energies at higher temperatures. Instead, this is most likely due to the instability of the BP at pressures other than $100 < P < 150$ GPa.

After studying the enthalpies and stability of the various phases, we moved on to look at their electronic properties at increasing pressures. In Fig. 5, the electronic bands are presented for the relevant phases along with the densities of states at different pressures. According to the results, cg remains dielectric at pressures up to at least 200 GPa. The band gap increases with increasing pressure by 16% before 100 GPa, but starts to decrease after this and reaches 86% at 200 GPa. For pN , the band gap is at ambient pressure 28% smaller than that of cg and decreases with increasing pressure, reaching 69% of the original band gap at $P=400$ GPa. For BP, the bands cross near S soon after pressure exceeds 50 GPa. This means that the BP structure is metallic at all

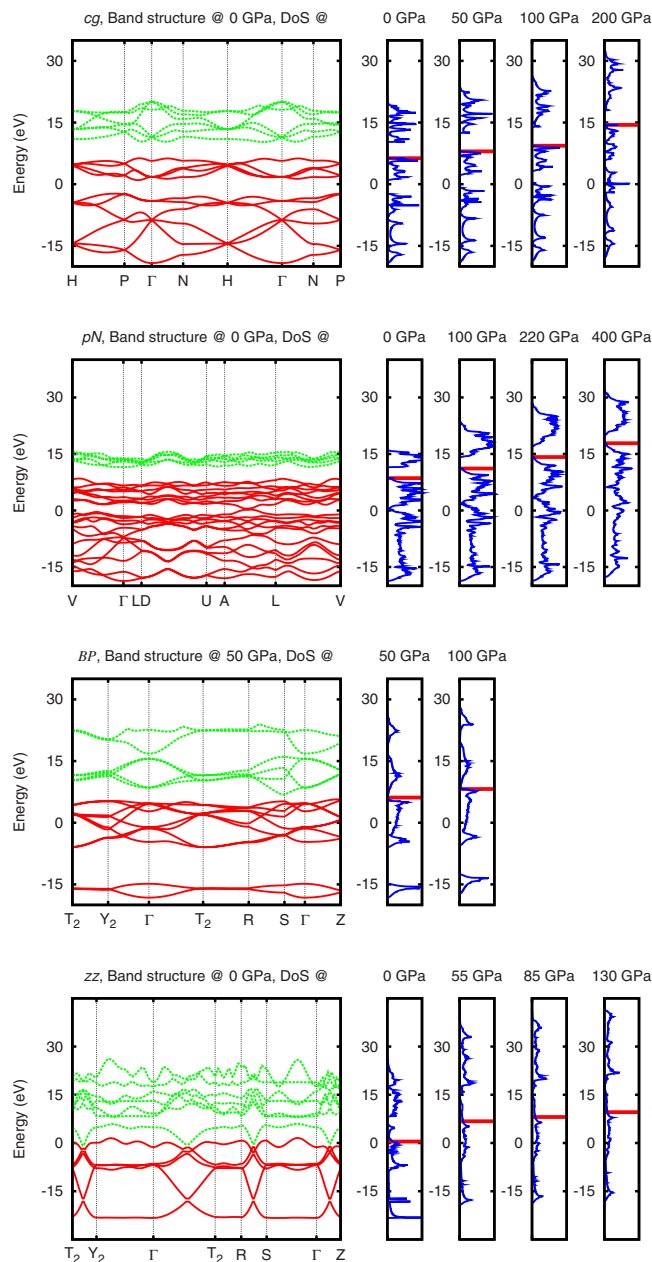


FIG. 5. (Color online) Electronic band structures between selected symmetry points for the cg , pN , BP, and zz phases (from top to bottom) and densities of states (DOS) at different pressures. The solid band lines correspond to the occupied bands. Fermi energy is marked with a solid horizontal line each DOS graph. High symmetry points are from Ref. 23. The zero point of the y axis is arbitrary.

pressures where it is metastable. As expected, zz is metallic at all studied pressures. The band structure for cg perfectly agrees with the quantum Monte Carlo results by Mitas and Martin,²⁴ except for the underestimated band gap which is a characteristic feature of the DFT method.

IV. DISCUSSION AND CONCLUSIONS

One significant aspect to note is that the layered lb and $A7$ are clearly higher in enthalpy than BP for all relevant pres-

tures ($P \in [50, 400 \text{ GPa}]$). As all of these phases consist of connected zigzag chains, they can be thought of as high-pressure forms of *zz*. From the results of the present study and those by Alemany and Martins,⁸ it is clear that the layered phases do not exist at pressures $P < 50 \text{ GPa}$, and they seem to be unstable also at higher pressures (150–200 GPa). The $zz \leftrightarrow \text{BP}$ transition pressure, as indicated by Fig. 3, is about 70 GPa, but may, in reality, be higher due to a transition barrier. Also, the fact that BP has never been seen in experiments indicates either a high transition barrier or an unknown high-pressure phase for nitrogen, which is more stable than BP. The latter is further supported by the instability of the BP phase at a pressure of 200 GPa.

Of the different chainlike phases, we have only presented results for *zz*, because we found it to be lower in energy as, for example, the chainlike phase presented by Alemany and Martins.⁸ Due to the weakness of the interchain interactions (less than 5% covalent), the chains can relatively easily slide with respect to one another, and the other phases consisting of zigzag chains may exist as transition phases between, for example, the molecular phases and *zz* or for the $zz \leftrightarrow \text{BP}$ transition.

The $\varepsilon\text{-N}_2 \leftrightarrow \text{cg}$ transition pressure is about 50 GPa (see Fig. 3). The *cw* phase, as also noted in the original work by Zahariev *et al.*,¹³ is lower in enthalpy than *cg* at ambient pressure. However, we found this structure to gain in energy at low pressures by breaking the weakest bonds in the structure and by flattening the six-membered N rings. Hence, it is not even metastable at 0 GPa, and at higher pressures, it is not thermodynamically favored. Also, the transition pressure for $\varepsilon\text{-N}_2 \leftrightarrow \text{cw}$ is higher than that for *cg*. The third three-dimensional phase (*pN*), on the contrary, is very close (within 0.1 eV) in enthalpy to *cg* at all pressures, and they may well coexist. The *sc* phase is highly unstable at low pressures, but will become thermodynamically favored at ultimate pressures. We even saw transitions to *sc* within EOS calculations of different phases at very high pressures. Estimating the transition pressures, however, is difficult because of the sensitiveness of the EOS fit at $P \geq 500 \text{ GPa}$.

Our results indicate that at pressures lower than 50 GPa, the molecular phases remain as the lowest-enthalpy structures for solid nitrogen. After this, *cg* is favored up to about 200 GPa, where BP becomes lower in enthalpy. However, BP is unstable at this pressure. The recently found¹¹ *pN* is comparable to *cg* at all pressures. Layered structures other than BP (i.e., *A7* and *lb*) are highly unlikely to be found

within experiments, as is the three-dimensional *cw* because they are all thermodynamically unfavored. However, they may contribute to the experimentally observed amorphous structures. As our results are for the zero-temperature case, it should be remembered that temperature can also affect the transition pressures of Fig. 3.

The *cg* phase was found to remain dielectric up to pressures above 200 GPa. Although DFT is known to underestimate the band gap energy of semiconducting and dielectric materials, it usually correctly describes the pressure effect. Interestingly, the band gap increases with increasing pressure up to at least 100 GPa, but starts to decrease already below 200 GPa. For the other three-dimensionally bonded phase (*pN*), the band gap decreases always with increasing pressure. Also, this phase remains dielectric at least up to 400 GPa. The layered BP phase was found to be metallic at all pressures where it is at least metastable ($50 < P < 150 \text{ GPa}$). At highest pressures, all structures become metallic because of the overlap of electronic bands.

Our results indicate that several of the previously suggested nitrogen phases (such as chaired web, layered boat, and arsenic-7) are most likely of no relevance to the experiments. The remaining relevant ones (in addition to the molecular phases) are cubic gauche² and the polymeric phase presented by Oganov and Glass¹¹ at intermediate pressures (50–200 GPa) and possibly zigzag chains⁹ at pressures near 50 GPa. The high-pressure phase remains unknown as the black phosphorus, which has the lowest enthalpy of the compared phases at high pressures and is unstable at 200 GPa. Of these phases, zigzag chains and black phosphorus are metallic at all relevant pressures, and the others remain dielectric with pressure-dependent band gaps up to very high pressures.

ACKNOWLEDGMENTS

We thank M. Eremets, S. Medvedev, and I. Trojan for useful discussions. Grants of computer time from the Center of Scientific Computing in Espoo, Finland, Jülich Supercomputing Centre in Jülich, Germany, and the Center for Scientific Computing of the Johann Wolfgang Goethe-University, Frankfurt, Germany, are gratefully acknowledged. This work has been supported by Deutsche Forschungsgemeinschaft through Project No. AL 578/3-1. We also acknowledge financial support through a program funded by the German foreign exchange server (DAAD) and the Academy of Finland.

¹A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).

²C. Mailhot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).

³T. W. Barbee III, Phys. Rev. B **48**, 9327 (1993).

⁴A. F. Goncharov, E. Gregoryanz, H. K. Mao, Z. Liu, and R. J. Hemley, Phys. Rev. Lett. **85**, 1262 (2000).

⁵M. I. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, Nature (London) **411**, 170 (2001).

⁶E. Gregoryanz, A. F. Goncharov, R. J. Hemley, and H. K. Mao, Phys. Rev. B **66**, 224108 (2002).

⁷M. I. Eremets and V. V. Gavriluk, Nat. Mater. **3**, 558 (2004).

⁸M. M. G. Alemany and J. L. Martins, Phys. Rev. B **68**, 024110 (2003).

⁹W. D. Mattson, D. Sanchez-Portal, S. Chiesa, and R. M. Martin, Phys. Rev. Lett. **93**, 125501 (2004).

¹⁰F. Zahariev, A. Hu, J. Hooper, F. Zhang, and T. Woo, Phys. Rev.

- B **72**, 214108 (2005).
- ¹¹A. R. Oganov and C. W. Glass, *J. Chem. Phys.* **124**, 244704 (2006).
- ¹²F. Zahariev, S. V. Dudiy, J. Hooper, F. Zhang, and T. K. Woo, *Phys. Rev. Lett.* **97**, 155503 (2006).
- ¹³F. Zahariev, J. Hooper, S. Alavi, F. Zhang, and T. K. Woo, *Phys. Rev. B* **75**, 140101(R) (2007).
- ¹⁴K. Nordlund, A. Krasheninnikov, N. Juslin, J. Nord, and K. Albe, *Europhys. Lett.* **65**, 400 (2004).
- ¹⁵G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ¹⁶J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **80**, 891 (1998), and references therein.
- ¹⁷T. Zhang, S. Zhang, Q. Chen, and L.-M. Peng, *Phys. Rev. B* **73**, 094105 (2006).
- ¹⁸G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- ¹⁹P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ²⁰H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ²¹K. Kunc and R. M. Martin, *Phys. Rev. Lett.* **48**, 406 (1982).
- ²²F. Birch, *Phys. Rev.* **71**, 809 (1947).
- ²³Bilbao Crystallographic Server, <http://www.cryst.ehu.es/>
- ²⁴L. Mitas and R. M. Martin, *Phys. Rev. Lett.* **72**, 2438 (1994).