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Density-functional study of nonmolecular phases of nitrogen: Metastable phase at low pressure

M. M. G. Alemany*
Instituto de Engenharia de Sistemas e Computadores, Rua Alves Redol 9, 1000-029 Lisboa, Portugal

José Luís Martins
Instituto de Engenharia de Sistemas e Computadores, Rua Alves Redol 9, 1000-029 Lisboa, Portugal
and Departamento de Física, Instituto Superior Técnico, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

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In first-principles variable-cell-shape molecular dynamics simulations and structural optimizations of nitrogen at pressures of 0–500 GPa, the phase with lowest enthalpy at high pressures, BP, was found to transform at low pressures into a new, metastable, metallic phase with a chainlike structure. The latter may possibly be related to a metastable nonmolecular phase that was recently observed experimentally at low temperatures and pressures.

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I. INTRODUCTION

The pressure-induced transformation of molecular crystals into nonmolecular states, with the possibility of a concomitant insulator-to-metal transition, is a phenomenon of considerable interest for condensed-matter physics. Nitrogen has been extensively studied in this regard. At low temperatures and pressures nitrogen consists of very stable diatomic molecules that interact via weak van der Waals forces, constituting an insulator with a large band gap. Theory predicts that raising the pressure destabilizes the triple molecular bond and leads to the formation of a nonmolecular structure in which each atom is bound by single bonds to three neighbors.[1–3] The high-pressure phase of nitrogen has been characterized experimentally as a largely amorphous, narrow-gap semiconductor[4]; in particular, its infrared absorption spectrum is similar to what one would expect for an amorphous phase in which the atoms have a coordination number of about 2.5 (Ref. 5).

The pressure-induced molecular-to-nonmolecular transformation of nitrogen has been observed experimentally at around 30 GPa and 6000 K in a shock-wave compression experiment.[6] Density-functional calculations predict that at low temperatures it should occur in the 30–70-GPa range,[1–3] but it has in fact not been observed below 150 GPa in low-temperature experiments.[7] The hypothesis[3] that this discrepancy is due to the molecular-nonmolecular transition being subject to a large degree of hysteresis associated with the large volume discontinuity between the molecular and high-pressure phases has recently been supported by optical and electrical measurements, which likewise confirmed its slow kinetics.[8] A particularly exciting result of these recent experiments was the survival of a nonmolecular phase at ambient pressure and temperatures of up to 100 K.

Here we report results obtained in an extensive first-principles study of the pressure dependence of several phases of nitrogen. Structures were initially taken from the literature or sought by high-temperature constant-applied-pressure variable-cell-shape molecular dynamics simulations; were then optimized at pressures from 0 to 500 GPa; and the stability of these structures was confirmed by further variable-cell-shape simulations. Particular attention was paid to the phase with lowest enthalpy at high pressures, BP, which at pressures below about 20 GPa was found to transform into a metastable, metallic phase with a chainlike structure.

II. METHODS

All calculations were based on density-functional computation of the total energy using the local density approximation with Ceperley-Alder[9] exchange and correlation as parametrized by Perdew and Zunger.[10] The core electrons were represented by norm-conserving nonrelativistic s and p pseudopotentials[11] generated for the reference ground state configuration $[\mathrm{He}]2s^2 2p^3$ with radial cutoffs of 1.0 a.u.; this small pseudopotential radius is appropriate for situations in which a short triple bond may appear. The nitrogen potential was made separable by the procedure of Kleinman and Bylander[12] using the s pseudopotential as the local potential. Besides the total energy, we also calculated the forces on the atoms and the stress tensor of the cell.

The parameters calculated as described above were used in variable-cell-shape constant-temperature constant-pressure (VCS-NPT) molecular dynamics simulations and to optimize the geometry by a minimization of the enthalpy by a Hessian method[13] (unlike previous theoretical studies, we optimized unit cell parameters and atomic positions simultaneously). The plane-wave energy cutoff used was 110 Ry for the molecular dynamics simulations, and 140 Ry for optimization; these large values are due to the small core radii and because a well-converged pressure is desirable in both VCS-NPT molecular dynamics and optimization. In the molecular dynamics simulations the Brillouin zone was integrated employing 32 special points.[14] For crystalline structures we used a mesh of special points with similar densities (see below).

Using the above plane-wave pseudopotential method, we first calculated, for pressures of interest, the enthalpies, relative to that of the simple cubic (sc) structure, of the three-coordinated nitrogen structures that have been described as possible lowest-energy phases at high pressure: namely, the cubic *gauche* (cg) distortion of sc; the α-arsenic structure $A7$, a rhombohedral distortion of sc; and the black phos-

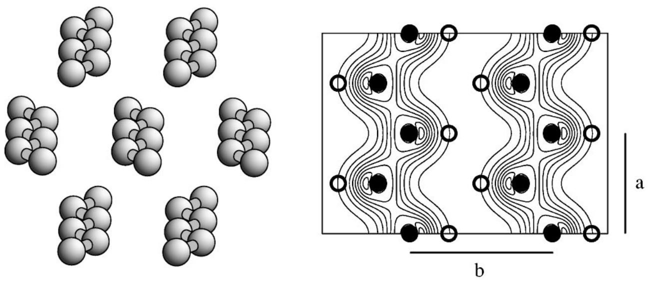

FIG. 1. The structure of ch nitrogen at zero pressure (the unit cell parameters are $a=2.175$, $b=3.099$, $c=5.452$ Å, and $u=0.363$). Left panel: three-dimensional plot showing three planes of coplanar chains. Right panel: valence electron density in a plane containing zig-zag chains of atoms shown as solid circles (contours are drawn at intervals of 10 electrons per unit cell); open circles indicate atoms lying in the layers that are $c/2$ above and below the plane of those indicated by solid circles.

phorus structure BP, an orthorhombic distortion of sc (see Ref. 3 for the structural characterization of these phases). Starting from an eight-atom sc cell, we then searched for other possible high-pressure phases by performing VCS-NPT molecular dynamics simulations at 165 GPa and 300 K, a point of the phase diagram that lies outside the experimentally determined hysteresis loop[8]; sc was chosen as the starting structure because *ab initio* calculations of phonon spectra for sc nitrogen using the linear response formalism have shown that it is mechanically unstable at pressures below 360 GPa.[15] As expected, this structure was quickly lost in our simulations, the system evolving to forms with lower enthalpy. Finally, all structures of interest, including cg, $A7$, BP, and the diatomic N_2 phase β-O_2 (for which previous theoretical results are available for comparison) were optimized over as much of the range 0–500 GPa as was possible or of interest, and the local stability of the optimized structures at 300 K was confirmed by VCS-NPT molecular dynamics simulations.

III. RESULTS AND DISCUSSION

The most interesting of the structures identified in our molecular dynamics simulations, other than cg, $A7$, and BP, is a zigzag chainlike arrangement that is metastable at low pressure (see below) and can be reduced to a body-centered-orthorhombic Bravais lattice with a two-atom basis at $\pm(0.25+u,0.25,0.5+u)$ with respect to primitive lattice vectors with Cartesian coordinates $\frac{1}{2}\{(-a,b,c),(a,-b,c),(a,b,-c)\}$ (Fig. 1). As far as we know, this structure, which we denote ch, has not been reported or considered previously. The nearest neighbors of each atom in ch are its neighbors in the chain to which it belongs, which at zero pressure lie 1.29 Å away[16] [cf. 1.25 Å (Ref. 17) for the double bond of difluorodiazine, F−N=N−F, and 1.10 Å (Ref. 17) for the triple bond of N_2]; thus ch is partially polymeric and each atom has a coordination number of two. The zigzag structure of each chain is flat, and the planes containing coplanar chains are equidistant from one another. It is noteworthy that this phase is metastable at low pressure (see below) and is metallic, as can be seen in a plot of band structure at zero pressure (Fig. 2). Besides the presence of partly filled bands in this figure, it is also worth noting that the band structure is not one dimensional, in spite of charge density being clustered mostly along the atom chains: there is dispersion in π bands along the Y-Γ and T-Z symmetry lines (both of which are parallel to y and perpendicular to the chains), i.e., there is a non-negligible interaction between layers of zigzag chains. The density of states at the Fermi level has a value of $N(E_F)=0.118$ states/(atom eV spin).

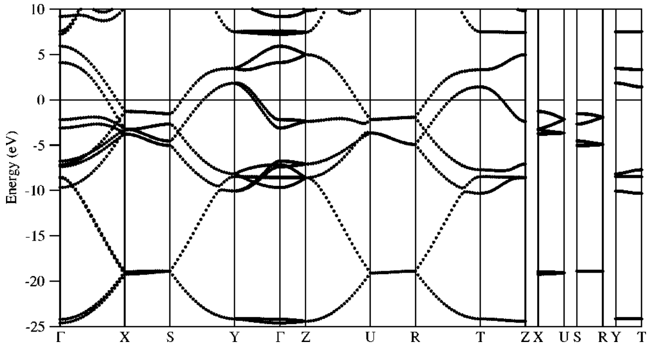

FIG. 2. The electronic band structure of ch nitrogen at zero pressure along the symmetry lines of the conventional orthorhombic Brillouin zone. The Fermi level is set to zero.

Figure 3 shows, as functions of pressure, the calculated enthalpies $H=E+PV$ per atom of cg, $A7$, BP, β-O_2, and ch relative to that of sc (all structures were optimized at each pressure). The number of **k** points used in these calculations was 220 for sc, 60 for cg, 110 for $A7$, 80 for BP, 110 for β-O_2, and 100 for ch. With these sample densities and the energy cutoff mentioned above (140 Ry), the error in the

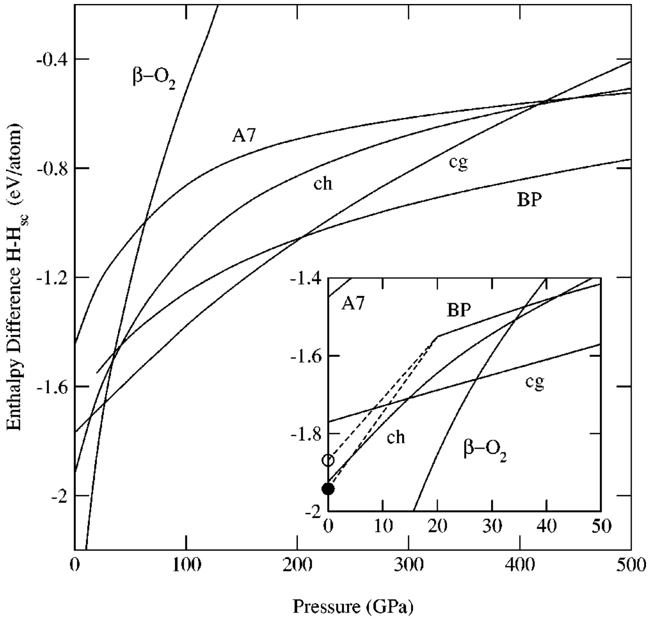

FIG. 3. Calculated enthalpies of the theoretical phases of nitrogen considered in this work, plotted as functions of pressure relative to that of the sc structure. The numerical errors are estimated to be about 0.5 mRy/atom (≈7 meV/atom). The inset shows an enlargement of the low pressure region.

calculated enthalpies is estimated to be no more than 7 meV/atom. As expected, at ambient pressure the molecular phase has the lowest energy. Although β-O_2 is not the experimentally observed ground phase of nitrogen at this pressure, *ab initio* total-energy calculations have shown previously that in this region it differs little in energy from more complex structures such as α-N_2 and ε-N_2.[3] The value we obtained for the molecular bond length, 1.10 Å, is identical to that calculated by Martin and Needs[2] and to the experimentally observed value.[17] Of the nonmolecular phases identified, that of lowest enthalpy at pressures less than 15 GPa is ch (it is possible, of course, though perhaps unlikely, that there may be high-pressure phases of nitrogen that we missed because their structures cannot be attained in a simulation with just eight atoms).

Figure 3 predicts that the molecular phase β-O_2 transforms into the nonmolecular phase cg at 27 GPa.[18] As pressure rises, the cg structure remains that of lowest enthalpy until a transition to the BP form is predicted at 205 GPa, close to the experimentally determined upper limit of the hysteresis loop for nitrogen at 0 K, ≈ 210 GPa.[8] Of the structures identified, $A7$ is the highest-enthalpy nonmolecular structure at all pressures below 400 GPa. When differences in the procedure and/or system are taken into account, these results are supported by the similarities between our prediction for the β-O_2-to-cg transition and the prediction of Mailhiot *et al.* of an ε-N_2-to-cg transition at 33 GPa,[3] and between our prediction for a hypothetical β-O_2-to-$A7$ transition (that would take place at 64 GPa and involve a volume jump of 23%) and that of Martin and Needs[2] (that would occur at approximately 70 GPa and involve a volume jump of approximately 25%).

At high pressures, where it is the lowest-enthalpy phase, BP is a semiconductor with a narrow energy gap (0.75 eV at 500 GPa). As pressure falls the gap narrows further: at 240 GPa it is 0.19 eV, which is to within experimental error the same as the optical band gap of 0.25 ± 0.10 eV reported in Fig. 3 of Ref. 4 for a pressure of 230 ± 5 GPa, and at about 160 GPa it vanishes, making BP a semimetal.[20] As pressure continues to fall the value of $N(E_F)$ increases until at 20 GPa it is 0.012 states/(atom eV spin). This band gap trend is the opposite of the trend obtained experimentally for high-pressure nonmolecular nitrogen by extrapolation of optical absorption spectra after removal of the Urbach tail[4]; however, since the experimentally observed phase is largely amorphous, this discrepancy does not prevent the agreement between the orders of magnitude of the calculated and observed gaps from suggesting that the local order of the amorphous phase may be related to the BP structure (by contrast, according to our calculations cg nitrogen is an insulator with an energy gap of 3.75 eV at 240 GPa, which appears to rule out the possibility of its being in any way involved in the amorphous phase). In further support of there being a local relationship between the amorphous phase and BP, the coordination number of each atom in the latter is somewhere between two and three, two of its three nearest neighbors lying the same distance away and the third at a distance about 10% longer; as noted in Sec. I, the experimentally observed coordination numbers of the atoms of the amorphous phase are about 2.5 (Ref. 5).

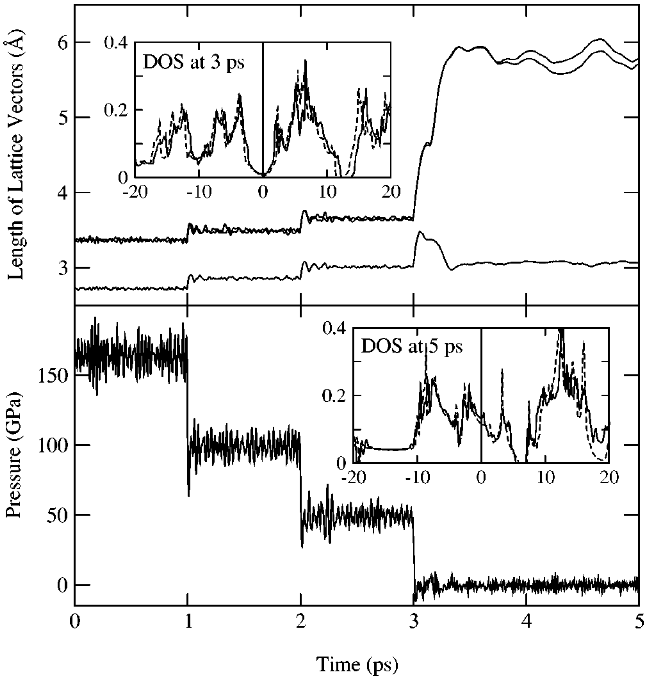

FIG. 4. Lattice vector lengths (upper panel) and pressures (lower panel) in a VCS-NPT molecular dynamics simulation in which, starting at 165 GPa with the BP structure as optimized at this pressure, the pressure was successively reduced to 100, 50, and 0 GPa while temperature was kept at 300 K. The inset of the upper panel compares the density of states distribution calculated for the configuration attained after 3 ps (solid line) with that obtained for ideal undistorted BP at 50 GPa (dashed line); and that of the lower panel compares the density of states distribution calculated at the end of the simulation (solid line) with that of undistorted ch at 0 GPa (dashed line). Densities of states in states/(atom eV spin), energies in eV. Fermi levels are set at zero.

We found that at zero pressure BP was unstable in the sense that the ratios of the lattice constants took values differing greatly from those found at high pressure. Furthermore, even very slight differences between starting structures led to different optimized geometries (see the circles in the inset of Fig. 3). However, at zero pressure all these forms had enthalpies close to that of ch. In fact, we were able to observe a BP-to-ch transformation in room temperature molecular dynamics simulations in which the pressure was successively decremented. Specifically, starting from the BP structure as optimized at 165 GPa, we performed a four-atom VCS-NPT molecular dynamics simulation in which the temperature remained constant at 300 K while the pressure, initially 165 GPa, was successively reduced to 100, 50, and 0 GPa, each of these pressures being maintained for at least 1 ps (see Fig. 4). At 165, 100, and 50 GPa the BP structure was conserved: after a transient period lasting just a small fraction of a ps, the lengths of the lattice vectors oscillated around the values obtained by enthalpy minimization for the pressure in question. Also, the density of states distribution calculated after 1 ps at 50 GPa was very similar to that obtained for the ideal undistorted BP structure at this pressure.

At ambient pressure, however, the BP structure was disrupted, the system finally stabilizing as ch after about 1 ps (Ref. 21); 1 ps after becoming stable, its density of states distribution was similar to that obtained for undistorted ch at zero pressure. Incidentally, the observation of this transition corroborates the relative stabilities of BP and ch at low pressure.

IV. CONCLUSIONS

In an extensive study of theoretical phases of nitrogen up to 500 GPa, the stable crystalline phase at pressures higher than about 205 GPa proved to be the black phosphorus structure BP, and the stable crystalline phase at pressures between 27 and 205 GPa the cubic *gauche* structure; below 27 GPa, molecular diatomic nitrogen was stable. At pressures below about 20 GPa BP underwent a transformation to a hitherto unreported metallic form of nitrogen, ch, that at ambient pressure is the most stable nonmolecular form hitherto detected. The electronic and structural characteristics of BP suggest that it may influence the local order of the amorphous nonmolecular form of nitrogen that is observed experimentally at high pressure; and it seems possible that ch may similarly be related to a metastable nonmolecular form recently observed at ambient pressure.

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*Present address: Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455 and Minnesota Supercomputing Institute, University of Minnesota, Minneapolis, Minnesota 55455, USA.

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[20] It is well known that the local density approximation usually gives band gaps 30%–50% smaller than experiment. In particular, Mitáš and Martin have estimated the discrepancy to be about 30% for compressed atomic nitrogen (Ref. 19). Applying a correction of this magnitude to our calculated band gap for BP at 240 GPa improves its agreement with experiment.

[21] The lattice vectors in the four-atom VCS-NPT simulation, initially those of the ideal BP structure, evolved to those of a nonstandard lattice for ch, specifically the set with Cartesian coordinates $\{(a,0,c),(0,b,0),(0,0,c)\}$, where a, b, and c are as defined in Fig. 1. Note that the volume of the cell obtained at the end of the simulation differs only by 1.45% from that of the optimized structure of ch.