PHYSICAL REVIEW B VOLUME 46, NUMBER 17 1 NOVEMBER 1992-I

Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

High-pressure atomic phases of solid nitrogen

Steven P. Lewis and Marvin L. Cohen
Department of Physics, University of California, Berkeley, California 94720
and Materials Sciences Division, Lawrence Berkeley Laboratory, Berkeley, California 94720
(Received 22 April 1992)

Several candidate atomic phases for solid nitrogen at high pressures have been studied theoretically. The semimetallic *A*7 (α-arsenic) phase is found to be the most energetically favored of the atomic phases studied which agrees with previous calculations. At extremely high pressures, this phase is found to deform continuously into the metallic simple cubic structure which is unstable at lower pressures. The possibility that a metallic simple tetragonal phase is metastable at lower pressures is discussed.

Elemental nitrogen exists in nature as a small, very stable diatomic molecule.[1] At low pressures, the molecular nature of nitrogen persists in the solid state which forms at low temperatures via weak intermolecular interactions. A variety of stable molecular phases of solid nitrogen, all of which are insulators, are found to exist at low[2] and moderate[3] pressures. However, as nitrogen is further compressed and the intermolecular distance becomes comparable to the molecular bond length, these molecular phases are expected to become unstable with respect to more highly coordinated atomic phases. While this molecular-to-nonmolecular transition has not as yet been observed in nitrogen up to 130 GPa,[3] it has been predicted theoretically.[4,5]

Martin and Needs[5] further predict that the stable high-pressure atomic phase is the rhombohedral *A*7 (α-arsenic) structure. All other elements in group V exist in this semimetallic, threefold-coordinated structure,[2,6] which is a slight distortion of the simple cubic (sc) structure.[7] It has been shown[8–12] in P, As, and Sb that pressure diminishes the distortion from sc, and ultimately removes it through a weakly first-order structural phase transition. Because of the odd number of electrons per cell, the group-V elements in the sc structure are metals.

This paper reports on a first-principles investigation of the structural and electronic properties of several candidate atomic phases of solid nitrogen at high pressures. These candidate phases include the sc structure plus three structures which are distortions of sc: the *A*7 structure and two simple tetragonal (st) structures. The results agree with previous work[5] in that the *A*7 phase is found to be the lowest-energy nonmolecular phase of nitrogen within the manifold of structures considered in the present and previous investigations. A recent theoretical study[13] predicts, however, that a candidate polymeric phase of nitrogen is of even lower energy than the *A*7 phase and may be the first nonmolecular phase of nitrogen. Since the present study does not investigate the molecular-to-nonmolecular phase transition, the absence of the polymeric phase from consideration does not significantly alter the present conclusions.

The present study also agrees with previous authors[5] that the sc structure is unstable with respect to the *A*7 phase. However, we find that both st structures studied are stable with respect to sc, and therefore possibly metastable with respect to the *A*7 structure. This is of particular interest because a st form of nitrogen would necessarily be metallic. At extremely high pressures, the distortions from sc in the *A*7 and st structures are found to diminish to zero, leaving sc as the stable structure.

The calculations for nitrogen were performed using the *ab initio* pseudopotential total energy method.[14] The electron-ion interaction was treated using a nonlocal, norm-conserving pseudopotential,[15] the electronic exchange and correlation energies were treated within the local-density approximation[16] (LDA) using a standard form for the exchange-correlation potential,[17] and zero temperature was assumed.

Because nitrogen cores lack *p* states, *p*-like valence electrons are not effectively excluded from the core region. Hence the $l = 1$ component of the pseudopotential is relatively deep in the core region, and plane-wave expansions of the wave functions require a very high kinetic energy cutoff for good convergence. In the present work, plane waves of up to 60 Ry in energy are used in the expansion. The relative total energies between different structures calculated using this energy cutoff were converged to within a few mRy. The irreducible part of the Brillouin zone of the various structures studied was sampled at 110–150 special points,[18] depending on the structure. Total energies calculated using this degree of sampling were converged to within a mRy.

The two families of structures studied here, $A7$ and st, are both slight distortions of the sc structure. If sc is viewed as two interpenetrating fcc sublattices (i.e., the rocksalt structure with one atomic species), then the $A7$ structure is obtained from sc by a relative displacement of the two sublattices along the [111] direction, accompanied by a rhombohedral shear strain of the cubic cell. These distortions of the metallic sc structure double the unit cell, suggesting a Peierls-like effect. The resulting crystal structure[7] has lattice vectors $\mathbf{a}_1 = (a/\sqrt{3}, 0, c/3)$, $\mathbf{a}_2 = (-a/2\sqrt{3}, -a/2, c/3)$, and $\mathbf{a}_3 = (-a/2\sqrt{3}, a/2, c/3)$, and basis vectors $\tau_\pm = \pm(0,0,uc) = \pm u(\mathbf{a}_1 + \mathbf{a}_2 + \mathbf{a}_3)$. Thus, at each volume the $A7$ structure depends on two parameters — the fractional displacement u of the fcc sublattices, and the c/a ratio of the rhombohedral unit cell. For the sc structure, $u = 0.25$ and $c/a = \sqrt{6}$.

The st structure is obtained from sc by either shortening or extending the cubic cell along one of the cubic axes. The lattice vectors of the st structure are $\mathbf{a}_1 = (a,0,0)$, $\mathbf{a}_2 = (0,a,0)$, and $\mathbf{a}_3 = (0,0,c)$, where $c = a$ for the sc structure.

For both the $A7$ and st structures, the respective structural parameters were first relaxed by a coarse sampling of parameter space followed by a finer sampling near the minimum. This method resulted in a discrepancy with a previous calculation[5] in the relaxed $A7$ structural parameters at the reference volume 5 Å^3. In the previous work, the calculations were performed using a 50 Ry plane-wave energy cutoff and an irreducible Brillouin zone sampling of ten special points. The optimal parameters ($u = 0.217$ and $c/a = 2.643$) were found by relaxing each parameter one at a time in an alternating fashion for two iterations. In the present work, a broad, deep minimum in the total energy was found at $u = 0.205$ and $c/a = 3.453$ using the uniform parameter-relaxation technique described above. No minimum was found at the previously predicted parameters until the k-point sampling and plane-wave energy cutoff were reduced to the previous work's values, whereupon a small minimum appeared. This spurious minimum apparently resulted from an inadequate sampling of the Brillouin zone and an insufficient number of plane waves.

Because of nitrogen's small mass, zero-point motion of the ion cores becomes a significant effect. However, the present computational method treats the ion cores as fixed. Therefore, an estimate of the zero-point energy is added to the total energy as a correction. A Debye model is used for this correction:

$$E_{\mathrm{ZPM}} = \tfrac{9}{8}\hbar\omega_D = \tfrac{9}{8}\hbar q_D v_s = \tfrac{9}{8}\hbar q_D\sqrt{B/\rho}, \qquad (1)$$

where ω_D is the Debye frequency, v_s is the speed of sound, B is the bulk modulus, ρ is the mass density, and q_D is the Debye wave vector.

We first present calculations of the relative stability of the various structures studied. Figure 1 shows the relative energy of nitrogen in st as a function of c/a at two volumes: uncompressed [Fig. 1(a)] and compressed [Fig. 1(b)]. In general, three local minima were found — one at $c/a \approx 1$, corresponding to sc; one at $c/a < 1$, referred to as oblate st; and one at $c/a > 1$, referred to as prolate st.

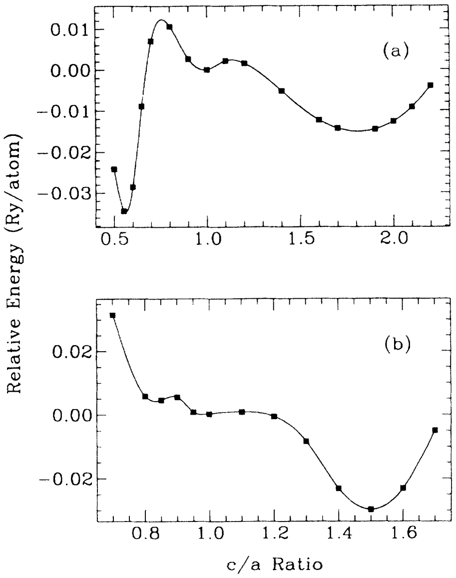

FIG. 1. Relative energy vs c/a ratio for nitrogen in the simple tetragonal structure at (a) an uncompressed volume (44 a.u./atom, which is the calculated equilibrium volume of nitrogen in sc) and (b) a compressed volume (26 a.u./atom). At both volumes, three distinct minima are present, one for $c/a < 1$, one for $c/a \approx 1$, and one for $c/a > 1$. The filled squares are calculated data points, which are connected by a solid curve to guide the eye.

At the uncompressed volume, the energetically favored st structure is the oblate st structure. It has an activation barrier of 47 mRy/atom to the other st structures. Both the sc and prolate st minima are metastable with respect to oblate st, and have activation barriers of 11 and 28 mRy/atom, respectively. The sc structure is the least favored minimum with a barrier to the prolate st structure of 3 mRy/atom. At the compressed volume, the prolate st structure becomes energetically favored over the sc and oblate st structures by 30 and 35 mRy/atom, respectively. The other two minima are marginally metastable, with the sc structure slightly more favored than the oblate st structure.

Upon compression, the optimum c/a ratio of both the oblate st and prolate st structures approaches the sc value of 1. Therefore, even though sc is never favored over prolate st when both minima exist distinctly, at very high pressure the optimal st structure is sc.

In Ref. 5, the sc phase is found to be unstable with respect to variations of the $A7$ parameters u and c/a. This instability of sc with respect to $A7$ distortions is also evident in the present work. However, the optimal $A7$ parameters are found to approach the ideal sc parameters (see above) continuously upon compression. At a volume of 15 a.u./atom, the optimal $A7$ structure is indistinguishable from sc to within the accuracy of the calculations. This corresponds to a pressure of about 15 Mbar. Therefore, at very high pressure the optimal $A7$ structure is sc.

The equations of state for the four structures, $A7$, sc, prolate st, and oblate st, are shown in Fig. 2. The computed data points (dots) are fitted, for each structure, to a Murnaghan equation of state[19] (solid lines). The parameters of the fit are shown in Table I.

The $A7$ structure is energetically favored within this set of structures, in agreement with previous work.[5] At low pressure, sc is the least energetically favored. At moderate pressure, oblate st becomes slightly higher in energy. At very high pressure, all of the curves merge, because all of the structural parameters tend toward their sc values. This tendency toward sc can be understood in terms of a preference for more highly coordinated compact structures at high pressures where the Madelung energy begins to dominate. The sc structure is more highly coordinated (sixfold) than the oblate st (twofold), $A7$ (threefold), and prolate st (fourfold) structures.

Several other simple structures have been shown not to be viable candidates for high-pressure phases of nitrogen. We have studied nitrogen in a simple hexagonal structure with an optimized c/a ratio. This phase is higher in energy than the $A7$ phase at all pressures, and higher than the sc phase at all but the lowest pressures. A previous theoretical investigation[4] has shown (for atomic volumes down to 20 a.u./atom) that diamond, bcc, hcp, and fcc phases of nitrogen would all be higher in energy than the sc phase.

The nature of the filled electronic states of nitrogen will depend on the crystal structure and pressure. Because nitrogen has five valence electrons, it will necessarily be metallic in any structure with one atom per cell, such as the sc or st structures. Since the $A7$ structure has a two-atom unit cell, nitrogen in $A7$ can be either insulating, semiconducting, or semimetallic.

The density of states at the Fermi level [$N(E_F)$] of nitrogen in the $A7$, sc, and prolate st structures is tabulated in Table II for two volumes; one uncompressed and one compressed. The values of $N(E_F)$ for the oblate st structure have not been calculated because it is the less likely of the two st structures to form. This will be discussed below. As expected, the sc and prolate st structures are metallic with fairly large $N(E_F)$, even at low pressures. Upon compression, the $N(E_F)$ of these structures decreases. This behavior is consistent with a free-electron-like picture, in which $N(E_F) \sim V^{2/3}$.

TABLE I. Best-fit parameters to the Murnaghan equation of state (Ref. 19) for nitrogen in the four phases studied. The parameters are the equilibrium volume V_0, and the bulk modulus B_0 and its pressure derivative B_0' at this volume.

Structure	V_0 (a.u./atom)	B_0 (GPa)	B_0'
$A7$	48.8	192	2.69
sc	44.4	206	2.83
Oblate st	111.4	9	3.11
Prolate st	47.4	92	4.20

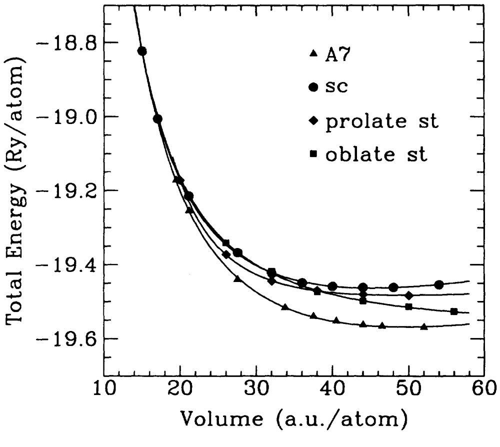

FIG. 2. Total energy vs volume, fitted to the Murnaghan equation of state (Ref. 19) (see Table I), for nitrogen in the four phases studied. For the $A7$ and the two st phases, all structural parameters have been relaxed at each volume. At very high pressures, these parameters all approach their sc structure limiting values. The zero-point energy correction has been included using a Debye model.

Since the $A7$ structure is a Peierls-like distortion of sc, a gap at the Fermi level is expected. This is seen in the vanishing of $N(E_F)$ at the uncompressed volume. However, since the $A7$ structure approaches the sc limit upon compression, the $N(E_F)$ of the $A7$ phase is expected to become nonzero and approach that of the sc phase. The existence of a finite $N(E_F)$ is indeed found for the compressed $A7$ phase, however the value is still quite small ($\sim$ 50% of the sc and prolate st values at this volume).

As shown above, the $A7$ structure is the lowest-energy atomic form of solid nitrogen of the structures studied. This phase is nonmetallic or semimetallic at all but the very highest pressures ($\sim$15 Mbar) where it becomes sc. In contrast, the sc phase is a metal with a large $N(E_F)$ at all pressures. However, the sc phase is unstable with respect to the $A7$ phase at all pressures for which the two are distinct. The $\sim$15 Mbar of pressure required to stabilize the metallic sc phase are, at present, unachievable for static experimental conditions.

The question of the existence of a stable or metastable metallic form of solid nitrogen is of particular interest because of the possibility of superconductivity at a high transition temperature (T_c) in such a phase. This possibility is suggested both by the small mass and by the large valence of nitrogen. The small mass of nitrogen implies a large Debye temperature, and the large number of valence electrons of nitrogen implies a large carrier density in a metallic phase. Both of these properties will tend to enhance T_c.

TABLE II. Density of states at the Fermi level [$N(E_F)$] for nitrogen in three of the phases studied. Values are given for two volumes — uncompressed (44 a.u./atom) and compressed (21 a.u./atom). The estimated numerical error is $\sim$ 10%.

Structure	$N(E_F)$ (states/Ry atom)	
	V=44 a.u./atom	V=21 a.u./atom
$A7$	0.00	0.91
sc	4.06	1.82
Prolate st	3.61	2.06

The two st structures studied here, both of which are stable with respect to sc, are candidates for a metastable metallic phase. It is important to point out, however, that the metastability of a st phase of nitrogen with respect to the $A7$ phase has not been proven here. Indeed, the only path connecting the two structures that has been considered is st → sc → $A7$. The st structure might be unstable with respect to distortions analogous to the $A7$ distortions of sc. Such considerations are beyond the scope of the present work.

Assuming the st structures are metastable, one possible mechanism for achieving such a phase would be to compress a sample in the $A7$ phase to sc, and then quench it into a st phase on releasing the pressure. Such a procedure would likely favor the prolate st structure, even though the oblate st structure has a lower energy at low pressures. This can be seen in Fig. 1(b). A sample prepared in the sc structure is more apt to "find" the prolate st minimum than the oblate st minimum as the pressure is released. The sample is then likely to remain in the prolate st minimum due to the large activation barrier to the oblate st minimum.

We would like to thank Dr. A. Y. Liu for her invaluable assistance and advice in the early stages of this work. This research was supported by the National Science Foundation (Grant No. FD91-20269), and by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy (Contract No. DE-AC03-76SF00098). Computer time was provided by the National Science Foundation at the National Center for Supercomputing Applications. S.P.L. acknowledges support from the National Science Foundation and the U.S. Department of Defense. M.L.C. acknowledges support from the J. S. Guggenheim Foundation.

---

[1] B. H. Mahan, *University Chemistry* (Addison-Wesley, Reading, 1965), pp. 392–395.

[2] J. Donohue, *The Structures of the Elements* (Wiley, New York, 1974).

[3] R. Reichlin, D. Schiferl, S. Martin, C. Vanderborgh, and R. L. Mills, Phys. Rev. Lett. **55**, 1464 (1985).

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

[5] R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).

[6] T. Kikegawa and H. Iwasaki, Acta Crystallogr. B **39**, 158 (1983).

[7] For a thorough discussion of the $A7$ structure see, for example, the Appendix of R. J. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **33**, 3778 (1986).

[8] K. J. Chang and M. L. Cohen, Phys. Rev. B **33**, 7371 (1986); **33**, 6177 (1986).

[9] T. Sasaki, K. Shindo, and K. Niizeki, Solid State Commun. **67**, 569 (1988).

[10] I. Shirotani, K. Tsuji, M. Imai, H. Kawamura, O. Shimomura, T. Kikegawa, and T. Nakijima, Phys. Lett. A **144**, 102 (1990).

[11] H. J. Beister, K. Strössner, and K. Syassen, Phys. Rev. B **41**, 5535 (1990), and references therein.

[12] Anthony L. Chen, Stephen P. Lewis, Zhenpeng Su, Peter Y. Yu, and Marvin L. Cohen, Phys. Rev. B **46**, 5523 (1992).

[13] C. Mailhiot (private communication).

[14] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4401 (1979); M. L. Cohen, Phys. Scr. **T1**, 5 (1982).

[15] D. R. Hamann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979). The nitrogen pseudopotential used here is the one suggested by G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[16] See, for example, *Theory of the Inhomogeneous Electron Gas*, edited by N. H. March and S. Lundquist (Plenum, New York, 1983).

[17] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[18] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **16**, 1748 (1977).

[19] F. D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).