# Metastability of atomic phases of nitrogen

## T. W. Barbee III

L-299, Lawrence Livermore National Laboratory, P.O. Box 808, Livermore, California 94551

(Received 21 May 1993)

The metastability of a recently proposed candidate for a polymeric structure for nitrogen is examined using linear response theory to calculate the phonon dispersion throughout the Brillouin zone. It is found that the structure is mechanically stable at pressures below 360 GPa. In contrast, nitrogen in the simple cubic structure is found to be unstable over the same pressure range. Calculations of Raman- and infrared-active phonon frequencies are presented for the metastable phase.

#### INTRODUCTION

At ambient pressure and low temperature, nitrogen freezes into a diatomic solid where strongly covalent (N=N) N<sub>2</sub> molecules are weakly (van der Waals) bonded to each other.<sup>1</sup> At high pressures, theory predicts dissociation of the molecule and formation of monatomic phases similar to those observed in other group-V elements, i.e., phosphorus and arsenic. At extremely high pressures, nitrogen is predicted to occur in the simple cubic structure.<sup>2</sup> Two calculations<sup>3,4</sup> of the transition pressure for the dissociation of the N<sub>2</sub> molecule yielded results below 100 GPa (1 Mbar). However, diamond anvil cell experiments at pressures up to 180 GPa found only modest changes in the frequency of the intramolecular bondstretch mode (vibron), indicating that room-temperature nitrogen remains diatomic to these pressures.<sup>5,6</sup> However, an anomaly observed in a shock compression experiment<sup>7</sup> on fluid nitrogen above 30 GPa has been interpreted<sup>8</sup> as evidence for a transition to a denser atomic phase. These two observations can be reconciled by assuming that a large barrier between the molecular and the atomic phases results in high-pressure metastability of the diatomic phase in the room-temperature diamond anvil experiments.

Recently, an extensive theoretical study of polymeric phases of nitrogen was performed.<sup>9</sup> This study considered structures in which extended networks of singly or doubly bonded nitrogen atoms were formed. A structure with all gauche dihedral angles [the "cubic gauche" (cg) structure] was found to have the lowest total energy of all the polymeric structures considered, but was higher in energy than the molecular structure by approximately 1 eV/atom. The possibility of metastability of cg nitrogen was raised by the discovery that a substantial energy barrier existed for the transformation of cg nitrogen into molecular nitrogen at ambient pressure along a path suggested by symmetry considerations. Since only one possible transition path out of many was considered, this result suggests, but does not prove, that cg nitrogen is metastable under ambient conditions.

A stronger requirement for metastability is mechanical stability, i.e., the existence of positive restoring forces for all small motions of the atoms of a crystal about their equilibrium positions. However, mechanical stability provides no information about barrier heights and thus cannot predict the lifetime of the metastable state. An equivalent condition to mechanical stability is the statement that the phonon frequencies  $\omega_{\mathbf{q}\lambda}$  for wave vector  $\mathbf{q}$  and polarization  $\lambda$  satisfy  $\omega_{\mathbf{q}\lambda}^2 > 0$  throughout the Brillouin zone (BZ), except for the acoustic modes at the zone center.

In this paper, we present *ab initio* calculations of phonon spectra  $\omega_{q\lambda}$  for nitrogen in two atomic structures at low (0–12 GPa) and high (240–360 GPa) pressures using the linear response formalism described below and discuss the consequences for metastability. The linear response method is particularly well suited to calculations of complete phonon dispersion relations throughout the Brillouin zone. We find that nitrogen in the cubic gauche structure is mechanically stable at both low and high pressures, while nitrogen in the simple cubic structure is mechanically unstable at both pressures. In addition, we present calculations of the frequencies of the Ramanand infrared-active modes in cg nitrogen as a function of pressure to aid in the identification of the cg phase.

#### THEORETICAL METHOD

The calculations whose results are presented below employ density functional theory within the local density approximation (LDA), with the electron-ion interaction modeled by a pseudopotential. The Ceperley-Alder<sup>10</sup> exchange-correlation potential was used in the Perdew-Zunger<sup>11</sup> parametrization. The momentum-space formalism and a plane-wave basis for the wave functions are used.<sup>12</sup> A nonlocal, norm-conserving pseudopotential was generated using the scheme of Troullier and Martins,<sup>13</sup> and the separable form of Kleinman and Bylander<sup>14</sup> was used in the calculations.

Since the nitrogen atom contains only one core orbital  $(1s^2)$ , there are no p or d states in the core and the corresponding components of the pseudopotential will be very attractive, requiring a large kinetic energy cutoff for the plane wave expansion of the wave functions. We employ

the same pseudopotential that was used in Ref. 9. The calculations reported below were performed using a cutoff of 70 Ry. The Brillouin zone integrals were calculated using sets of 2 and 8 special  $\mathbf{k}$  points<sup>15</sup> in the cg structure and 20 special  $\mathbf{k}$  points in the simple cubic structure.

The linear response (LR) method for calculating phonon frequencies has been described in detail elsewhere,<sup>16-18</sup> and so only a brief review will be given here, following the formulation of Gonze and Vigneron.<sup>17</sup> The starting point of the LR method is a self-consistent calculation of the electronic wave functions in the unperturbed crystal. The crystal is then distorted according to the phonon mode under consideration, and the Hamiltonian H, wave functions  $|\Psi_j\rangle$ , external (i.e., unscreened electron-ion) potential  $V_{\text{ext}}$ , and total energy  $E_{\text{tot}}$  are expanded in a perturbation series using the amplitude of the phonon distortion as a small parameter  $\alpha$ :

$$H = H^{(0)} + \alpha H^{(1)} + \alpha^2 H^{(2)} + \cdots, \qquad (1)$$

$$|\Psi_j\rangle = |\Psi_j^{(0)}\rangle + \alpha |\Psi_j^{(1)}\rangle + \cdots, \qquad (2)$$

$$V_{\text{ext}} = V_{\text{ext}}^{(0)} + \alpha V_{\text{ext}}^{(1)} + \alpha^2 V_{\text{ext}}^{(2)} + \cdots,$$
(3)

$$E_{\rm tot} = E_{\rm tot}^{(0)} + \alpha E_{\rm tot}^{(1)} + \alpha^2 E_{\rm tot}^{(2)} + \cdots .$$
 (4)

The first-order perturbed wave functions  $|\Psi_{j}^{(1)}\rangle$  are obtained from

$$(H - \varepsilon)^{(0)} |\Psi_j^{(1)}\rangle = -H^{(1)} |\Psi_j^{(0)}\rangle,$$
 (5)

where  $\varepsilon$  is the energy eigenvalue. Since the perturbed Hamiltonian depends on the perturbed wave functions through the charge density, this equation must be solved self-consistently. The primary advantage of the LR method over the frozen phonon method is that the calculations may be performed in the original unit cell rather than in a supercell; hence, the calculations are much faster for the long wavelength modes.

After self-consistency is reached, the second-order change in the total energy [and, therefore, the diagonal elements of the dynamical matrix  $D(\mathbf{q})$ ] can be found from the expression

$$E_{\text{tot}}^{(2)} = E_{\text{ion-ion}}^{(2)} + \sum_{j}^{\text{occ}} \left[ (\langle \Psi_j^{(1)} | V_{\text{ext}}^{(1)} | \Psi_j^{(0)} \rangle + \text{H.c.} \right] + 2 \langle \Psi_j^{(0)} | V_{\text{ext}}^{(2)} | \Psi_j^{(0)} \rangle \right], \quad (6)$$

where the sum runs over occupied states, and  $E_{\rm ion-ion}^{(2)}$ is the contribution from the ion-ion repulsive energy and may be easily found by Ewald techniques.<sup>18</sup> In this expression, only first-order quantities must be determined self-consistently, since it is the unscreened electron-ion interaction which appears in second order. The off-diagonal elements of the dynamical matrix can be obtained<sup>17</sup> from an expression similar to Eq. (6). Once the dynamical matrix  $D(\mathbf{q})$  is determined, it can be diagonalized to find the harmonic phonon frequencies  $\omega_{\mathbf{q}\lambda}$ and polarizations  $\hat{\epsilon}_{\mathbf{q}\lambda}$  for all modes  $\lambda$  at wave vector  $\mathbf{q}$ .

### **RESULTS AND DISCUSSION**

The first structure considered was the simple cubic structure for nitrogen, which was recently  $predicted^2$  to



FIG. 1. Phonon dispersion for nitrogen in the simple cubic structure at ambient pressure. The squares of the phonon frequencies  $\omega^2$  are plotted versus wave vector  $\mathbf{q}$ , and the wave vector labels are defined in Table I. The structure is mechanically unstable, as shown by the existence of phonon modes with  $\omega_{\mathbf{q}\lambda}^2 < 0$ .

be stable for pressures above 1500 GPa, but is expected to be unstable in the pressure range considered here. Figure 1 shows the squares of the phonon frequencies  $\omega^2$  for nitrogen in the simple cubic structure at zero pressure plotted as a function of wave vector along high-symmetry paths in the BZ. The labels are defined in Table I. Since the squared phonon frequency  $\omega^2$  is negative for at least one mode, the structure is mechanically unstable.

The phonon instabilities at certain high-symmetry points in the BZ indicate possibly more stable structures. The distortion that takes the simple cubic structure into the arsenic (A7) structure is related to the Rpoint phonon, the transformation to the black phosphorus structure is related to the X-point phonon, and the distortion that transforms simple cubic to cg is related to the M-point phonon. If only one phonon mode were unstable, it might indicate a barrierless path to a particular more stable structure. Since many modes are unstable for simple cubic nitrogen at zero pressure, Fig. 1 provides no clear insight into what structure simple cubic nitrogen would spontaneously transform into.

The phonon dispersion relation for simple cubic nitrogen at 240 GPa is shown in Fig. 2. Once again, the squares of the frequencies  $\omega^2$  are plotted, and unstable modes are found near the R and X points. These instabilities suggest barrierless paths from simple cubic to the arsenic (A7) and black phosphorus structures, respectively, at ~ 240 GPa. While the *M*-point frequency is real, a previous study<sup>9</sup> found that the cg structure was more stable (i.e., lower in energy) than A7 at these pressures, which is consistent with an extremely small barrier

TABLE I. High-symmetry points for the simple cubic Brillouin zone. The wave vector  $\mathbf{q}$  is given in Cartesian coordinates in terms of the lattice constant a of the real space lattice.

Label	q	
Γ	0	
X	$\frac{\pi}{a}(1,0,0)$	
M	$\frac{\pi}{2}(1,1,0)$	
<i>R</i>	$\frac{\frac{a}{\pi}}{a}(1,1,1)$	



FIG. 2. Phonon dispersion for nitrogen in the simple cubic structure at high pressure (240 GPa). The squares of the phonon frequencies  $\omega^2$  are plotted versus wave vector  $\mathbf{q}$ , and the labels are the same as in Fig. 1. The structure is mechanically unstable, as shown by the existence of phonon modes with  $\omega_{\mathbf{q}\lambda}^2 < 0$  near the R and X points of the Brillouin zone.

from simple cubic to cg which we found in frozen phonon calculations.

The primary result of this paper is the metastability of nitrogen in the cubic gauche structure over a pressure range from 12 to 360 GPa, and we expect that metastability will persist down to atmospheric pressure. The cubic gauche structure consists of a body centered cubic Bravais lattice with a four-atom basis at (x, x, x), (0.5 - x, -x, 0.5 + x), (-x, 0.5 + x, 0.5 - x), and (0.5 + x, 0.5 - x, -x) in Cartesian coordinates. The structure is completely determined by specifying the lattice constant a and the internal parameter x. When x = 0, the cg structure becomes simple cubic with lattice constant a/2.

As a first step, the total energy was minimized as a function of x for cg nitrogen at volumes of 108 and 170 bohr<sup>3</sup>/(primitive cell), corresponding to pressures of 360 and 12 GPa, respectively. The optimal values of x were found to be 0.0624 and 0.0862, respectively.

The phonon dispersion relation for cubic gauche nitrogen at 12 GPa is shown in Fig. 3. The labels are defined in Table II. All phonon modes have positive frequency and no modes appear to be soft, indicating that this structure is mechanically stable.

Figure 4 shows the phonon dispersion relation for cg



FIG. 3. Phonon dispersion  $\omega(\mathbf{q}\lambda)$  for nitrogen in the cubic gauche structure at low pressure (12 GPa). All phonon modes have real and positive frequency, indicating that the structure is mechanically stable; however, no information about the barrier heights is given (see text).



FIG. 4. Phonon dispersion  $\omega(\mathbf{q}\lambda)$  for nitrogen in the cubic gauche structure at high pressure (360 GPa). All phonon modes have real and positive frequency, indicating mechanical stability, although a soft mode is developing at the N and H points.

nitrogen at 360 GPa. All phonon modes are still of positive frequency, indicating mechanical stability, although a soft mode is developing at the N and H points, suggesting instability at higher pressures. From Figs. 3 and 4, we conclude that cg nitrogen is metastable at and below 360 GPa.

Since the linear response method provides only the curvature of the energy versus displacement curve (i.e., the harmonic phonon frequency), we cannot estimate the lifetime of the metastable state since no estimate of the barrier height is available from linear response. A previous calculation of barrier heights<sup>9</sup> found a barrier of approximately 0.86 eV/atom for the transformation of cg nitrogen into the molecular  $\beta$ -O<sub>2</sub> structure at ambient pressure. For comparison, the barrier to graphitization of diamond is only about 0.3 eV/atom.<sup>19</sup> To determine whether cg nitrogen could be experimentally observed at ambient pressure, the effects of defects and/or surfaces on the metastability should be considered. These could be treated within a supercell, but are probably more amenable to treatment via molecular dynamics using simple interatomic potentials.

Since the most likely route to synthesis of cg nitrogen



FIG. 5. Frequencies of zone-center phonon modes in cubic gauche nitrogen as a function of pressure. Lines are a guide to the eye. In this structure, all zone-center modes are either Raman or infrared active, or both.

TABLE II. High-symmetry points for the Brillouin zone of the cubic gauche structure. The wave vector  $\mathbf{q}$  is given in Cartesian coordinates in terms of the lattice constant a of the bcc real space lattice.

q	
0	
$\frac{2\pi}{a}(1,0,0)$	
$\frac{\pi}{a}(1,1,0)$	
$rac{ ilde{\pi}}{a}(1,1,1)$	
	$\begin{array}{c} \mathbf{q} \\ 0 \\ \frac{2\pi}{a}(1,0,0) \\ \frac{\pi}{a}(1,1,0) \\ \frac{\pi}{a}(1,1,1) \end{array}$

will take place in a diamond anvil cell at high pressure and temperature, knowledge of the optical response of cg nitrogen will be necessary to confirm its creation. The cg structure has nine zone-center optical modes which occur as two triply degenerate modes, a doubly degenerate mode, and one nondegenerate mode. All of these are Raman active, and the triply degenerate modes are also infrared active. The calculated frequencies of zone-center modes versus pressure are plotted in Fig. 5. The appearance of these modes, together with the disappearance of the molecular vibron, would signal the transformation into the cg structure. Since the vibron lies at much higher frequency (~  $2300 - 2500 \text{ cm}^{-1}$ , depending on pressure), the dissociation of the molecular phase should be clearly observable. The multiply degenerate modes in Fig. 5 may split under nonhydrostatic conditions, and so more than four lines may be observed for cg nitrogen.

- <sup>1</sup> D. A. Young, *Phase Diagrams of the Elements* (University of California Press, Berkeley, 1991).
- <sup>2</sup> S. P. Lewis and M. L. Cohen, Phys. Rev. B **46**, 11117 (1992).
- <sup>3</sup> A. K. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985).
- <sup>4</sup> R. M. Martin and R. J. Needs, Phys. Rev. B **34**, 5082 (1986).
- <sup>5</sup> R. Reichlin *et al.*, Phys. Rev. Lett. **55**, 1464 (1985).
- <sup>6</sup> P. M. Bell and H. K. Mao, Physica B+C **139&140B**, 16 (1986).
- <sup>7</sup> H. B. Radousky et al., Phys. Rev. Lett. 57, 2419 (1986).
- <sup>8</sup> M. Ross, J. Chem. Phys. **86**, 7110 (1987).
- <sup>9</sup> C. Mailhiot, L. H. Yang, and A. K. McMahan, Phys. Rev. B **46**, 14419 (1992).
- <sup>10</sup> D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. 45, 566 (1980).

#### SUMMARY

We have studied the possibility of metastability of nitrogen in the simple cubic and cg structures via *ab initio* full-zone phonon calculations using the linear response formalism. The simple cubic structure was found to be mechanically unstable over the entire pressure range considered, while the cg structure was found to be metastable over a wide pressure range up to 360 GPa. Since the predicted<sup>9</sup> transition pressure ( $50 \pm 15$  GPa) for the formation of polymeric cg nitrogen from molecular nitrogen falls within the region of metastability, it can be hoped that cg nitrogen will persist after cooling to low temperature under pressure and perhaps also at low pressure. The calculated optical mode frequencies presented here should aid in the identification of the cg structure.

#### ACKNOWLEDGMENTS

I gratefully acknowledge conversations with A. McMahan, C. Mailhiot, and H. Lorenzana. This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48, and has been supported in part by the Joint DoD/DOE Munitions Technology Development Program.

- <sup>11</sup> J. Perdew and A. Zunger, Phys. Rev. B 23, 5048 (1981).
- <sup>12</sup> J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979); **13**, 3095(E) (1980).
- <sup>13</sup> N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).
- <sup>14</sup> L. Kleinman and D. M. Bylander, Phys. Rev. Lett. 48, 1425 (1982).
- <sup>15</sup> D. J. Chadi and M. L. Cohen, Phys. Rev. B 8, 5747 (1973).
- <sup>16</sup> S. Baroni, P. Giannozzi, and A. Testa, Phys. Rev. Lett. 58, 1851 (1987); 59, 2662 (1987).
- <sup>17</sup> X. Gonze and J. P. Vigneron, Phys. Rev. B **39**, 13120 (1989); **44**, 3494(E) (1991).
- <sup>18</sup> P. Giannozzi, S. Degironcoli, P. Pavone, and S. Baroni, Phys. Rev. B **43**, 7231 (1991).
- <sup>19</sup> S. Fahy, S. G. Louie, and M. L. Cohen, Phys. Rev. B **34**, 1191 (1986); **35**, 7623 (1987).