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PHONONS AND METASTABILITY IN COMPRESSED NITROGEN

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The metastability of a recently proposed candidate for a polymeric structure of nitrogen is confirmed by using linear response theory to calculate the phonon dispersion throughout the Brillouin zone. It is found that the structure is mechanically stable for pressures below at least 360 GPa. Calculations of Raman and infrared-active phonon frequencies are presented for this metastable phase, and calculations of Raman frequencies for two molecular structures are compared with experimental data.

INTRODUCTION

At ambient pressure and low temperature, nitrogen freezes into a diatomic solid where strongly covalent ($N\equiv N$) N_2 molecules are weakly (van der Waals) bonded to each other. [1] 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. [2] Two calculations [3,4] of the transition pressure for the dissociation of the N_2 molecule yielded results below 100 GPa (1 Mbar). However, diamond anvil cell experiments at pressures up to 180 GPa indicate that room-temperature nitrogen remains diatomic to these pressures. [5,6] Conversely, an anomaly observed in a shock compression experiment [7] on fluid nitrogen above 30 GPa has been interpreted [8] as evidence for a transition to a denser atomic phase. These two observations can be reconciled by assuming that a large energy 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. [9] 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 structures by approximately 1 eV/atom. The possibility of metastable *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.

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 $\omega_{q\lambda}$ for wavevector q and polarization λ satisfy $\omega_{q\lambda}^2 > 0$ 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 *cg* structure is mechanically stable at both low and high pressures, while nitrogen in the simple cubic structure is mechanically unstable below 240 GPa. In addition, we present calculations of the frequencies for zone center modes in *cg* and molecular nitrogen as a function of pressure to aid in the identification of these phases.

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. A non-local, norm-conserving pseudopotential [10] in a separable form [11] was used in the calculations.

The linear response (LR) method for calculating phonon frequencies has been described in detail elsewhere, [12] so only a brief review will be given here. The starting point of the LR method is a self-consistent calculation of the electronic wavefunctions in the unperturbed crystal. The crystal is then distorted according to the phonon mode under consideration.

In the distorted crystal, the Hamiltonian, wavefunctions, external (i.e., unscreened electron-ion) potential, and total energy are formally expanded in a perturbation series using the amplitude of the phonon distortion as a small parameter. The first order perturbed wavefunctions can then be obtained from a self-consistent calculation. The primary advantage of the LR method over the frozen phonon [13] 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 long wavelength modes or low symmetry modes.

After self-consistency is reached, the dynamical matrix $D(q)$ can be found analytically from an expression in which self-consistent quantities only appear in first order. Once the dynamical matrix $D(q)$ is determined, it can be diagonalized to find the harmonic phonon frequencies $\omega_{q\lambda}$ and polarizations $\hat{e}_{q\lambda}$ for all modes λ at wavevector q .

RESULTS AND DISCUSSION

The first structure considered was the simple cubic structure for nitrogen, which was recently predicted [2] to be stable for pressures above 1500 GPa, but is expected to be unstable at lower pressures. Figure 1 shows the squares of the phonon frequencies ω^2 for nitrogen in the simple cubic structure at 240 GPa plotted as a function of wavevector along high-symmetry lines in the BZ. Since the squared phonon frequency ω^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 R point phonon, the transformation to the black phosphorus structure is related to the

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

X point phonon, and the distortion that transforms simple cubic to *cg* is related to the M point phonon.

The instabilities near the R and X points 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 [9] 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 from simple cubic to *cg* which we found in frozen phonon calculations.

The *cg* 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 $a/2$.

The phonon dispersion relation for *cg* nitrogen at 12 GPa is shown in Fig. 2. All phonon modes have positive frequency and no modes appear to be soft, indicating that this structure is mechanically stable.

Figure 3 shows the phonon dispersion relation for *cg* 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. 2 and 3, 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

Figure 2. Phonon dispersion $\omega(q\lambda)$ 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).

Figure 3. Phonon dispersion $\omega(q\lambda)$ for nitrogen in the cubic gauche structure at high pressure (360 GPa). All phonon modes have real and positive frequency, indicating mechanical stability, although soft modes are developing at the N and H points.

response. A previous calculation of barrier heights [9] found a barrier of approximately 0.86 eV/atom for the transformation of *cg* nitrogen into the molecular β -O₂ structure at ambient pressure. For comparison, the barrier to graphitization of diamond is only about 0.3 eV/atom. [14] 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 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 existence. The *cg* structure has nine zone-center optical modes. All of these are Raman active, and the two triply degenerate modes are also infrared active. The calculated frequencies of zone-center modes versus pressure are plotted in Fig. 4. The appearance of these modes, together with the disappearance of the

Figure 4. Frequencies of zone center phonon modes in cubic gauche nitrogen as a function of pressure. The lines are guides to the eye. In this structure, all zone center modes are either Raman or infrared active, or both. The degeneracies of the modes are indicated in the legend.

molecular vibron, would signal the transformation into the *cg* structure. Since the vibron lies at much higher frequency ($\sim 2300 - 2500$ cm⁻¹, depending on pressure), the dissociation of the molecular phase should be clearly observable. The multiply degenerate modes in Fig. 4 may split under non-hydrostatic conditions, so more than four lines may be observed for *cg* nitrogen.

Calculations of the optically active modes can also help identify the structure of molecular nitrogen at high pressure. We have calculated the zone-center frequencies for two structures of molecular nitrogen: α -N₂ (space group *Pa*3) at low pressure (< 1 GPa) and ϵ -N₂ (space group *R* $\bar{3}$ c) at 49 GPa. In α -N₂, the 24 modes at the zone center were calculated using the LR method. The Raman-active frequencies are plotted in Fig. 5 as crosses at a pressure of 1 GPa. The experimental low-temperature Raman data [15] for α -N₂ are shown as small horizontal bars at the left edge of the figure. The calculated vibron frequencies for α -N₂ (near 2300 cm⁻¹) are about three percent low, while the calculated lattice modes (near 150 cm⁻¹) are nearly a factor of two too high in frequency. This could be due to the failure of LDA to describe the molecule-molecule interactions at low density or due to anharmonic effects not included in the LR method.

Our calculation of all 48 zone-center modes for ϵ -N₂ at 49 GPa is, to our knowledge, the first such calculation from first principles. The 45 optical modes all have real and positive frequency, indicating that an energy barrier exists between *R* $\bar{3}$ c and the closely related *R*3c structure, which has also been proposed

Figure 5. Frequencies of zone center phonon modes in molecular nitrogen as a function of pressure. Lines are experimental data, [15] crosses are calculated frequencies for α -N₂, and circles are calculated frequencies for ϵ -N₂.

for N₂ above 24 GPa. This is consistent with a previous calculation [16] which found $R3c$ more stable than $R3c$ up to 75 GPa.

The calculated Raman frequencies are plotted as circles in Fig. 5. Here the vibron frequencies are about seven percent too low, while the lattice modes agree extremely well with experiment, especially if one assumes that some of the calculated modes may be split due to non-hydrostatic conditions in the experiment. We note that the experimental data for $P > 4$ GPa was taken at room temperature and our calculations assume zero temperature, but the differences between experiment at 15 K and room temperature are small. [15] Except for the disagreement in the vibron frequencies, the calculated Raman frequencies for ϵ -N₂ agree very well with the experimental data, raising the possibility that ϵ -N₂ persists above 24 GPa. We are currently calculating the Raman active modes for several other candidate phases over a range of pressures in order to constrain the possible structures in the 20-100 GPa range.

SUMMARY

We have studied the possibility of metastable 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 below 240 GPa, while the cg structure was found to be metastable up to 360 GPa. Calculations of Raman modes for ϵ -N₂ indicate that this structure may persist up to pressures of 50 GPa. Further calculations of Raman

frequencies for different molecular structures will aid in the determination of the high-pressure phase diagram for nitrogen.

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