

Pressure Dissociation of Solid Nitrogen under 1 Mbar

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The zero-temperature transition pressure from molecular to monatomic nitrogen is predicted to be less than about 1 Mbar, and should be observable in diamond-anvil cells. This estimate is obtained from total-energy calculations in which compressed molecular nitrogen is found to dissociate into a simple cubic monatomic structure, slight distortions of which are common to other group-V elements. The calculated 35% volume change raises the possibility of a large barrier to dissociation and extensive regions of metastability.

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Recent shock-wave experiments by Nellis *et al.*¹ show that fluid nitrogen undergoes a transition at modest pressures (300 kbar) and high temperatures (6000 K) that appears to be dissociation of the N₂ molecules to form a monatomic fluid. It is known that nitrogen remains in its molecular form in the solid at room temperature to pressures over 500 kbar,² so that the observed transition is likely driven by the high temperatures. However, the relatively low transition pressure suggests that the monatomic state may be much more favorable than expected considering the strong N₂ molecular bond. If so, then nitrogen may have a diatomic to monatomic transition at pressures low enough to be seen in static experiments. The present paper reports calculations which support this possibility, and predict an extraordinary stability for the simple cubic (sc) structure of monatomic nitrogen. This puts nitrogen in line with other group-V elements where an arseniclike *A7* distortion of sc is common,³ and the sc structure itself has been observed.^{3a}

Total-energy calculations in this paper were carried out with use of the linear muffin-tin orbitals (LMTO) method⁴ for possible monatomic structures of nitrogen, and a recently reported method^{5,6} based on the Gordon-Kim electron-gas model,⁷ for the diatomic structures. The first method has been amply proven in previous structural calculations for monatomic solids^{8,9}; the second, for diatomic and other molecular solids.^{5,6} To our knowledge, no *single* technique has as yet been demonstrated to provide results of comparable accuracy in both limits.¹⁰

Care has been taken to minimize possible errors in the separation between monatomic- and diatomic-phase total energies which might arise from the different approximations made by the two techniques used here. Specifically, the monatomic- and diatomic-phase total energies were determined *relative* to isolated atoms and molecules, respectively, and the experimental N₂ dissociation energy used to fix the energy separation between isolated atoms and molecules. As in routine cohesive-energy calculations, a consistent

treatment was used for both the monatomic solid and isolated atom; and similarly, for the diatomic solid and isolated molecule. By this procedure, any errors in the separation between monatomic and diatomic total energies will arise from the familiar uncertainties of zero-pressure cohesive-energy calculations, and from those in the volume dependence of the individual curves. Both sources of error are considered in the discussion below.

Calculations for five monatomic¹¹ nitrogen structures, sc, diamond, bcc, (ideal) hcp, and fcc, were carried out by use of the LMTO method.⁴ The calculations were nonrelativistic, used the von Barth and Hedin exchange-correlation potential,¹² and treated all electrons self-consistently, with the outer five treated in a band mode. Brillouin-zone sampling was sufficient to yield total energies accurate to within 0.0001 hartree/atom.

The one-electron potential was taken to be spherically symmetric within atom-centered spheres for the bcc, hcp, and fcc structures as is customary in LMTO calculations⁴; however, additional interstitial spheres were needed in the case of the more open sc and diamond structures. This, and inclusion of the Ewald (or muffin-tin) correction¹³ to the electrostatic energy, are essential to get accurate energy differences between the open-packed sc or diamond structures and the more close-packed bcc, hcp, and fcc structures. Successful application and testing of this procedure for the structural energy differences in C and Si have already been reported.⁹

The total energies, relative to the ⁴S_{3/2} ground state of the isolated N atom, for the five solid N structures are presented in Fig. 1 as a function of volume per atom. The isolated-atom energy was taken to be -54.2557 hartrees/atom, obtained with use of the same von Barth-Hedin exchange-correlation potential as for the N solid. A spin-polarized calculation was used for the atom, in which all three 2*p* electron spins were taken parallel, as it is well known that accurate cohesive energies require such treatment of the atom

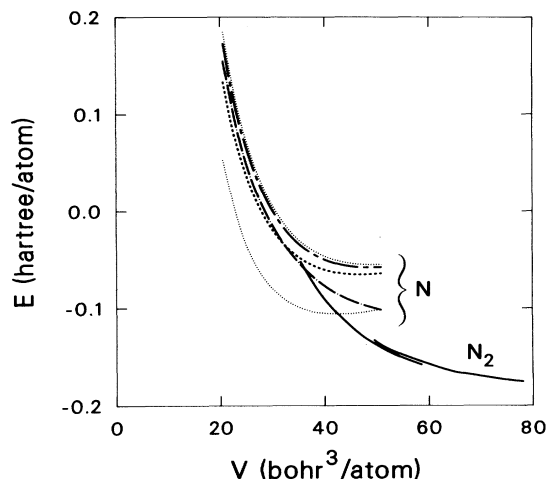


FIG. 1. Total energy vs volume for various phases of solid diatomic ($R\bar{3}c$ structure, labeled N_2) and monatomic (labeled N) nitrogen at $T=0$. The structures corresponding to the monatomic curves are as follows: simple cubic (lower dotted curve); diamond (chain-dotted); bcc (dashed); hcp (chain-dashed); and fcc (upper dotted curve). The two solid curves for N_2 differ in treatment of the dispersion energy, as described in the text.

when it has unpaired electrons.¹⁴ This procedure yields a cohesive energy of 0.11 hartree/atom for sc N at a zero-pressure volume of 41.4 bohr³/atom.

Given the success of similar LMTO calculations⁹ for C and Si, in regard to volume dependence and separation between different monatomic curves, the largest uncertainty in the five monatomic curves in Fig. 1 is likely the possibility of an overall constant error in total energy. Since our zero of energy is the isolated-atom ground state, such an uncertainty is just that routinely encountered in calculating zero-pressure cohesive energies, where the present theory is generally within about 10% of experiment. For the important sc case, with calculated cohesive energy of 0.11 hartree/atom, this suggests an uncertainty of about ± 0.01 hartree/atom. About the same uncertainty is estimated by considering the effect of using an alternative exchange-correlation potential.¹⁵

The structural properties and total energy of solid N_2 were obtained, as noted earlier, by use of a method^{5,6} based on the Gordon-Kim electron-gas model⁷ for calculating the short-range interactions between closed-shell atoms and molecules. This method involves no adjustable parameters, with the exception of a damping function for the dispersion energy which is discussed below. It yields results for the zero-temperature properties of a number of molecular solids in good agreement with experiment. For nitrogen, it gives the zero-pressure lattice constant and cohesive energy within 0.1% and 7% (or only 0.0002 hartree/molecule), respectively, of experiment.⁶

In these calculations the electronic distribution of the nitrogen molecule is assumed to remain unchanged from the gas-phase distribution, even in the high-pressure solid. A recent test of this approximation for solid Ar found that the changes induced in the electronic distributions of the Ar atoms by the high-pressure environment were reasonably small, lowering the calculated total free energy by only 0.006 hartree/atom at 750 kbar.¹⁶ While solid N_2 is likely to experience a somewhat larger pressure effect, the change in bond length has been estimated² from Raman spectra to be only about 0.02 bohr at 374 kbar, and thus should not affect the energy greatly. This is consistent with solid I_2 , where the I_2 bond length is known to remain constant to within 2% all the way up to 210 kbar where dissociation occurs.¹⁷

At low temperatures, the structure of solid N_2 above 20 kbar is thought to be of rhombohedral symmetry with eight molecules per primitive cell and space group $R\bar{3}c$.¹⁸ Changes in the phonon spectrum indicate a transition¹⁸ at about 200 kbar, possibly to $R3c$. Since theoretical calculations exceeding 750 kbar continue to find the $R\bar{3}c$ structure to be the most stable among those considered (including $R3c$),^{6a} we assume the $R\bar{3}c$ structure for all N_2 calculations. Note that in the volume regime considered below for the dissociation of the N_2 lattice, the N-N separation between molecules is more than twice the N_2 bond length, and differences in energy between plausible structures for the molecular phase are small compared to the scale of the N to N_2 differences. We subtract the molecular dissociation energy ($D_e=0.3640$ hartree/molecule)¹⁹ from the molecular total energies (calculated relative to the $^1\Sigma_g^+$ ground state of the free molecule), and divide by 2 to obtain the N_2 results in Fig. 1 relative to the $^4S_{3/2}$ atomic ground state.

The two curves for N_2 in Fig. 1 correspond to different choices of a parameter in a function used to damp the dispersion energy at small separations.^{6b} The curve at larger volumes used a value chosen to yield good agreement with the low-pressure phase diagram, but the resulting pressure-volume curve at 100 kbar was slightly too stiff. We choose^{6a} a value for the set of calculations at smaller volumes which gave agreement with the experimental volume²⁰ at 100 kbar. While the latter curve was used below in our estimates of the dissociation pressure, the energies obtained from these two sets of N_2 calculations do not differ greatly. An earlier calculation, with a different description of the dispersion energies, gave results almost identical with the curve at small volumes.^{5b} With these and the above-mentioned uncertainties, we estimate the error in the diatomic curves in Fig. 1 to be roughly 0.01 hartree/molecule in the volume regime considered below for dissociation of the N_2 lattice. The error is negligible at the zero-pressure volume

(not shown) of the diatomic solid, by virtue of the accurate, zero-pressure, calculated diatomic cohesive energy mentioned above.

A common-tangent construction between the molecular and monatomic curves in Fig. 1 indicates a zero-temperature transition from solid N_2 to a sc phase of N at about 770 kbar. Previously mentioned uncertainties for both N- and N_2 -phase energies, as well as an estimate of the zero-point energy difference between phases,²¹ could raise this pressure to about 940 kbar. The volume change for the transition is quite large, about 35%. A transition to the diamond structure would take place at about 2 Mbar with a volume change of about 17%, and to the fcc structure at about 3 Mbar with a 16% volume change.

Some insight into the stability of a sc (or distorted sc) N phase is gained by considering calculations on the group-IV elements.^{9,22} Diamond-phase N has a large gap between bonding and antibonding hybrid- sp^3 levels which is comparable to that of C. However, the additional valence electron possessed by N must go above this gap, destroying the highly favored status of the diamond structure. In contrast, the sc structure has only a dip in the density of states near the Fermi level, which is sufficiently broad to favor this phase over such structures as bcc and fcc; regardless of whether there are four (C) or five (N) valence electrons. The $A7$ distortion of sc apparently deepens this dip at the five-electron Fermi level to the point of semimetallic behavior by providing greater separation between bonding and antibonding p^3 levels, with both bonding and antibonding s levels being occupied.²³ In P and As the resultant lowering of the band-structure energy is gradually surpassed under pressure by the lower electrostatic Madelung energy of the more symmetric sc phase,²⁴ so that the $A7$ structure is observed³ to deform towards sc under pressure.

While it is likely that nitrogen, like phosphorous, will eventually reach the sc structure, phases not considered here may well intervene. Thus our calculations suggest an upper bound to the transition pressure. The threefold coordinated, rhombohedral $A7$ structure is one obvious candidate for an intermediate phase. We attempted LMTO calculations for this structure, and did obtain lower energies than sc. Unfortunately, increasing distortion away from sc brings the $A7$ structure, even with interstitial spheres, rapidly into a region of low-packing fraction and low symmetry where the LMTO method as used here becomes unreliable.⁹ The even lower symmetry, threefold coordinated, orthorhombic, black-phosphorous structure²⁵ is another possibility. With weak van der Waals interactions between sets of strongly bonded double layers,²⁵ such a phase might well permit destruction of the diatomic bond in nitrogen without requiring the immense volume change seen here.

In summary, our calculations suggest that solid N_2 will undergo dissociation to a monatomic lattice below 1 Mbar, which is within the reach of static high-pressure experiments. We also predict, for the first time, that nitrogen will behave like other group-V elements in showing a tendency to assume the sc structure under pressure. Intervening phases may well result in dissociation at lower pressures with a far smaller volume change than the 35% seen here; however, the possibility of a large volume change cannot be ruled out. Indeed, a transition from the N_2 molecular phase (each atom triply bonded to its sole near neighbor) to either of the $A7$ distorted sc or the black-phosphorous structure (each atom singly bonded to three near neighbors) is suggestive of a polymerization transition where large volume changes are not uncommon. Furthermore, there may be a large barrier to dissociation due to the energy necessary to break the strong triple bond in the N_2 molecule, raising intriguing kinematic questions, and the possibility of considerable hysteresis in actually making the dissociated phase. The reverse argument suggests a low-pressure region of metastable monatomic phase, which would make monatomic nitrogen an exceedingly interesting material.

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