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# Theoretical study of the molecular-to-nonmolecular transformation of nitrogen at high pressures

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We report calculations of the electronic charge density and the total energy of nitrogen as a function of volume in both molecular and nonmolecular crystal structures, using the local-density-functional method with an *ab initio* pseudopotential. At low pressures the molecular bond length is found to be 1.10 Å, in good agreement with experiment. At high pressures we find a stable distorted arseniclike structure, which is semimetallic with a very small Fermi surface and is lower in energy than simple cubic and all other simple metallic structures considered previously by McMahan and LeSar. To investigate the transition under pressure we have carried out calculations for a number of structures which are on a path that connects continuously the molecular $\beta$-$O_2$, diamond, graphitic, arseniclike, and simple-cubic structures. The calculated transition occurs at a pressure of approximately 700 kbar, with a large barrier of approximately 1 eV/atom along this path. One signature of the transition is a large decrease of the highest phonon frequency. Although there is some uncertainty in our calculated pressure, we conclude that our results predict a transition to a nonmolecular structure at experimentally accessible pressures, in apparent disagreement with recent experiments in which no such transition was found up to a reported pressure of 1.3 Mbar.

## I. INTRODUCTION

Nitrogen has a special place among the elements since $N_2$ has the greatest binding energy of all the elemental diatomic molecules and, except for $H_2$, the shortest bond length.[1] Because of the great stability of the molecule, all solid phases of nitrogen at ordinary pressures are composed of weakly interacting molecules, which leads to a plethora of stable molecular crystal phases as a function of temperature and pressure.[2] Of course, all these phases are insulators with large band gaps.[3] However, at very high pressures the properties of nitrogen must be completely different because the molecular solid must become unstable relative to more closely-packed phases. Such a molecular-to-nonmolecular transition is one of the fundamental transitions in condensed matter physics, which has been the object of much recent work.[4] The purposes of the present work are to investigate theoretically the nature of the high-pressure phase(s) of nitrogen, to calculate the pressures and volumes for the molecular-to-nonmolecular transition, and, together with our previous work[5] on arsenic and phosphorus, to make a more unified picture of the properties of group-V elements. We use the local-density functional method with *ab initio* pseudopotentials, which has been shown to predict accurately the structural properties of a great number of solids.[5-8]

The heavier group-V elements typically occur in threefold-coordinated structures, which may be viewed as small distortions of the simple-cubic metallic structure[2,9] and which are narrow gap insulators or semimetals. Under pressure the structures approach more closely to simple cubic,[10] which has been reported to occur for *P* at approximately 110 kbar.[11] However, As does not exist in the simple-cubic structure[2] and reports of simple cubic Sb at approximately 70 kbar (Ref. 12) have not been reproduced in more recent work.[12] The distortion from the simple cubic is important because a group-V element is necessarily a metal in the simple-cubic structure, whereas in the arseniclike structure it may be insulating, semimetallic, or zero-band-gap-semiconductor, depending on the topology of the band structure. Furthermore, it has a Raman active phonon which can serve as a signature. In our previous work[5] for those elements we found structures in good agreement with experiment; for example, we have found that P is stable in the simple-cubic structure at moderate pressures, whereas As is predicted not to be stable in this structure of any moderate pressure.

The primary purpose of the present work is to investigate the stability and properties of N in compressed nonmolecular phases. Our experience for P and As gives us confidence that the theoretical methods are sufficiently accurate to predict these properties. In addition, however, we want to predict the pressures and volumes at which the nonmolecular phases of N are stable, which requires calculation of the relative stability of molecular and nonmolecular phases. This is a more severe test of the theoretical methods because of the great differences between these types of structures. The accuracy of this part of our work depends upon the extent to which the local-density approximation (LDA) (Refs. 13 and 14) describes solids which range from well-separated, strongly bound molecules to simple monoatomic metals. Although there have been many calculations of either molecules[15] or simple solids,[6-8,14] to the knowledge of the authors, only for hydrogen[16] have previous calculations been carried out with sufficient precision to give accurate LDA predictions for the transition pressures and volumes. In the present paper we present results of calculations done in a consistent way for molecular crystals, simple nonmolecular crystals, and a range of distorted structures which connect continuously these two types of crystals.

Our work was stimulated by the recent prediction of McMahan and LeSar[17] (ML) that the pressure required to cause the phase transition in nitrogen is less than 1 Mbar. Since this is an accessible range for pressures in a diamond anvil cell,[4] their prediction has stimulated interest that it may be possible to realize a new metallic structure among the first row elements. Their conclusions are derived from calculations which used the Gordon-Kim method[18] for the molecular phase and self-consistent linear muffin-tin orbital (LMTO) density-functional method[19] for a number of simple metallic structures. They found that the simple-cubic structure is much more favorable than all the other simple metallic structures considered, in agreement with the properties of the other group-V elements. The possibility of N occurring in distorted arseniclike structures was foreseen by ML,[17] who recognized that a transition to such a structure would occur at a pressure below that for the simple cubic. However, ML did not carry out calculations for any distorted structures.

There is evidence from shock-wave data for a transition in fluid nitrogen around 300 kbar and 6000 K, which has been ascribed to molecular dissociation.[20] However, little is known about the properties of any such high-pressure phase, especially at low temperatures. Thus the prediction of ML has stimulated new experimental studies using static pressure techniques. Recently, two groups[21,22] have carried out new experiments in the diamond cell going to pressures reported to be approximately 1.3 and 1.8 Mbar to test the predictions. The experiments have found a decrease of the band gap, so that the solid appears colored, and small changes in the molecular Raman frequencies—both of which are the expected precursors to the transition—but *the experiments found no evidence for any transition to a nonmolecular phase at these pressures.* Since our work supports the general conclusions of ML concerning the existence of the transition, there is an apparent discrepancy between these experiments and our theoretical calculations. It is not possible at the present time to draw definitive conclusions from this apparent difference, because it is not feasible for us to consider all possible structures of the molecular phases(s). In particular, we have *not* considered the complex distorted molecular phases discovered in the recent high-pressure experiments.[21] We comment on the relation to experiment in the discussion section at the end of the paper.

The present paper is organized as follows: In Sec. II we describe the structures with $A7$ symmetry, which we will explicitly consider, and the relation to other possible interesting structures. The calculational methods are described in Sec. III. In Sec. IV we present the results for the structures in the family with $A7$ symmetry, the phase transition under pressure, and the properties of the predicted phases—charge densities, electronic structure, and phonon frequencies. In Sec. V we briefly describe results for other molecular structures, $\alpha$ and $\gamma$ nitrogen, and in Sec. VI we discuss the cohesive energy relative to the atom. Finally, in Sec. VII we discuss our results with emphasis upon the role of the local-density approximation and the relation to experiments.

## II. DESCRIPTION OF STRUCTURES

The structures which we will consider for N are grouped into molecular (coordination 1), arseniclike (coordination 3), and simple cubic (coordination 6). It is well known that the arsenic $A7$ structure may be described as distorted simple cubic, in which there is an internal displacement of the two fcc sublattices along the [111] direction.[2,5,9] The resulting structure has trigonal symmetry and there are two degrees of freedom in addition to the volume. One is the internal parameter $u$ which is defined so that $u=\frac{1}{4}$ denotes the simple cubic. The arsenic structure with $u$ slightly less than $\frac{1}{4}$ is shown in Fig. 1(a). (We need consider only $u<\frac{1}{4}$ since the structures are identical for $u>\frac{1}{4}$.) The other degree of freedom of the structure is the $c/a$ ratio, where $a\,(c)$ is the translation length in (perpendicular to) the basal plane, as is illustrated in Fig. 1. For cubic structures the $c/a$ ratio is fixed by symmetry to be $6^{1/2}$, and for the distorted structures[2,5,9] it tends to be greater than $6^{1/2}$. It follows that we may treat $A7$ and simple cubic as one family of structures in which simple cubic is a special case.

In addition, this family of structures varies continuously to a well-known molecular structure, the $\beta$-oxygen structure,[2] and we will use this fact to carry out calculations for N in all three types of structures within a single symmetry class. Within the family of structures defined above, if $u$ is decreased continuously toward 0 one finds an interesting sequence shown in Fig. 1. At $u=\frac{1}{6}$, [Fig. 1(b)] the two planes of atoms coalesce into a single plane, which has the honeycomb structure of the planes in graphite, with the plane stacked exactly as in the rhombohedral phase of graphite,[2] i.e., with each atom having a single second neighbor either directly above or below it in the $c$ direction. If $u$ is decreased further to $u=\frac{1}{8}$ [Fig. 1(c)], then a new bond is made so that each atom has four equivalent neighbors. For $c/a=6^{1/2}$ this is the cubic diamond structure. Finally, if $u<\frac{1}{8}$, then each atom has only one nearest neighbor and the structure is the $\beta$-oxygen molecular structure [Fig. 1(d)]. This is one of the simplest possible molecular structures since it contains only one molecule per primitive cell. It may be viewed as close-packed hexagonal planes of molecules, with the molecular axes perpendicular to the planes, and with the planes stacked in the same $ABC$ sequence as in fcc. It may be noted that this sequence is essentially the same as was considered by Froyen and Cohen.[23] They carried out calculations along a path from rock salt to zinc-blende structures, which is the ionic analogue of our path from simple cubic to diamond. However, in their cases the molecular structure played no important role.

It should be pointed out that, although our primary calculations on molecular N are for the $\beta$-oxygen structure, there is no evidence that N actually exists in this structure

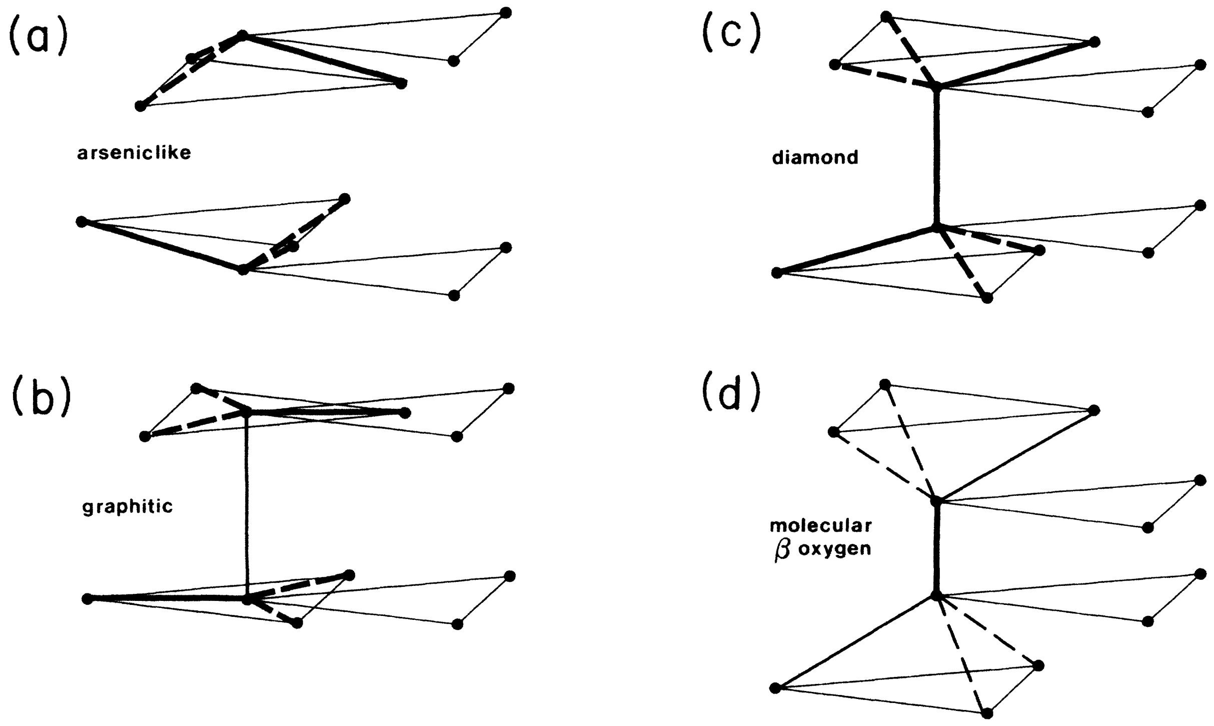

FIG. 1. Sequence of structures with $A7$ symmetry. Each structure can be viewed as consisting of close-packed planes of atoms, with atoms in the same plane connected by triangles. There are two translationally-inequivalent planes and the sequence is generated by vertical displacement of the inequivalent planes. The case in which the planes merge is the rhombohedral graphite structure (see Ref. 2). Bonds are indicated by heavier lines—solid lines for bonds in the plane of the paper and dotted lines for bonds at an angle to the plane.

and the only structures known experimentally for N are more complex.[2,18,21] For our purposes, consideration of only the simpler $\beta$-oxygen structure is sufficient at large volumes, where the molecules interact weakly and there are only small energy differences between different molecular structures. At small volumes, however, the arrangement of the molecules becomes more important. To test the effects we have also done limited calculations on the more complex $\alpha$- and $\gamma$-nitrogen structures, which have, respectively, four and two molecules per cell and are described by Donahue.[2] Although we cannot carry out full minimizations of these structures, in Sec. V we present results which indicate the energy differences between various molecular structures at compressed volumes and the effects upon the phase transition.

There are also two other classes of structures which must be considered in an exhaustive study for N. One class is the set of simple metallic structures, such as fcc, hcp, etc., compared to simple cubic. This need not be done here because ML (Ref. 17) have already made these comparisons and they have shown convincingly that all such structures are much higher in energy than simple cubic in the volume range considered here. Finally, one should consider other threefold coordinated structures, such as those which occur naturally for P.[2] None of these structures are considered here, or in our related work,[5] because of their complexity. Because we cannot examine all possible structures, we must temper all conclusions concerning the high-pressure phases of N with the recognition that we are predicting the relative stability only within the chosen set of phases—there may always be some other phase which is in fact more stable.

## III. METHOD OF CALCULATION

In the present study calculations of the total energy, forces, and stresses were performed within the self-consistent local-density approximation (LDA) (Refs. 13 and 14) using *ab initio* norm-conserving pseudopotentials[24] and a plane-wave basis set. The detailed equations for all quantities are given in Ref. 8 and the implementation of the method has been presented by us in calculations on structural stability and phase transitions under pressure in Si,[25] C,[26] As,[5] and P,[5] as well as applications to many other diverse problems.[27] The essential point is that the LDA equations are completely specified by the choice of the potential and the form of the LDA function. These are solved essentially exactly within two limitations: the number of plane waves in the basis set is cut off at a maximum kinetic energy and the number of points used to carry out the integrations over the Brillouin zone is finite. The details of our calculations are thus specified by giving this information.

All calculations described here are done with the Ceperley-Alder LDA form[28] as parametrized by Perdew and Zunger.[29] The N ionic pseudopotential is chosen to be that given by Bachelet *et al.*,[24] in which we have taken the $l=2$ component to be the local potential (i.e., it applies to all $l>2$). It may be noted that the $l=0$ and $l=1$ potentials are very different, as they must be for first row atoms that do not contain a $p$ core. We expect that this strong nonlocality plus the fact that all components of the potential are quite strong, leads to the differences in the behavior of the first row from that of the heavier elements. This reasoning has been used by Yin and Cohen in their work on carbon.[30] The resulting Schrödinger equation was solved self-consistently in momentum space at 20 (84 in tests) special points in the irreducible part of the Brillouin zone for simple cubic and 10 (20 in tests) points for the $A7$ symmetry structures. Plane waves of up to 50 Ry in energy ($\sim 200$ plane waves/atom) were included in the basis set used for the results reported. The only exceptions to these choices are for the molecular structures at large volumes ($V>5$ Å$^3$) and the more complex $\alpha$ structure, which were done with the waves from 30 to 50 Ry included in second-order Löwdin perturbation.[31] Also smaller $k$ point sets were used for the $\alpha$ and $\gamma$ structures and for the $\beta$-oxygen structure at the largest volume ($V=10$ Å$^3$).

To confirm that the results given are not greatly dependent upon these choices, we carried out calculations with additional plane waves from 50 to 80 Ry included in second-order Löwdin perturbation and with the larger $k$ point sets. There were only small changes in the energy differences; for example, the energy difference of 0.52 eV/atom between simple cubic and an arsenic structure near equilibrium at $V=5$ Å$^3$ increased by 0.07 eV/atom with the increased cutoff and by 0.06 eV/atom when the larger $k$ point sets were used. Although such changes could increase the value of the stabilization energy of the arsenic structure by $\sim 25\%$, clearly they would not modify our conclusions concerning the relative ordering of any of the phases considered here.

Because only relative energies enter into the question of stability, we present our results as the energy relative to the (arbitrarily chosen) energy of the simple-cubic phase at the volume of 5 Å$^3$. Since the calculated energy depends upon the cutoffs on the plane waves, in each case the relative energy is calculated as the difference between the given structure and the simple cubic calculated with the same energy cutoffs for the plane waves treated exactly and in perturbation theory. We compare with ML by also referring their results to this energy. In Sec. VI we will discuss our results for the cohesive energy relative to the atom. Calculation of this quantity is more difficult for numerical reasons and, more important, it is known that the greatest errors in the cohesive energy come from the errors in the LDA applied to the atom.[32] Thus we emphasize that this number is not essential for any of our conclusions and we relegate it to a separate section.

## IV. RESULTS

### A. Stability of structures

We first present calculations done at a single volume which demonstrate the results for the different structures. We have chosen the volume of 5 Å$^3$ because it is near the point where the phase transition is predicted to occur, both by ML and as found in the present work. Our primary results are the charge densities, which are shown in Fig. 2 for four representative cases corresponding to the structures shown schematically in Fig. 1, and the total energies, given for a number of structures in Fig. 3.

We have initially carried out calculations for structures along the path illustrated in Fig. 1, where the $u$ parameter is varied keeping the $c/a$ ratio fixed at the fcc value of $6^{1/2}$. The calculated total energies are shown as the points enclosed by circles in Fig. 3, with a continuous line drawn through the points as a guide to the eye. This curve shows immediately the most important result: none of the high-symmetry structures are stable. In particular, simple cubic is unstable to the internal distortion, i.e., it has an imaginary frequency for the zone-boundary phonon that doubles the unit cell and generates the $A7$ structure. This has been checked by calculating the force at very small displacements at this and other volumes, from which it was found that *simple cubic is unstable to infinitesimal displacements at all volumes considered.* In addition, the only other cubic structure, diamond at $u=\frac{1}{8}$, is also a maximum in the total energy, not a minimum. The planar rhombohedral graphite structure ($u=\frac{1}{6}$) is not a point of high symmetry along this curve, as may be verified by reference to Fig. 1, which shows that inequivalence of positive and negative changes in $u$ around the value $u=\frac{1}{6}$. The only stable minima are the two structures which are, respectively, arseniclike, $u\sim 0.22$, and $\beta$-oxygen-like, $u<0.1$. Within this family of structures the only possible phase transition is between these two minima. The transition will be discussed after the following considerations.

Before one can find the true minima for these structures, one must also minimize the energy with respect to the $c/a$ ratio, which is an additional degree of freedom for all the noncubic structures. For this the use of the stress theorem[8] is extremely useful. Because of the trigonal symmetry of the crystal, the only nonzero components of the stress tensor are diagonal $\sigma_{zz}$ and $\sigma_{xx}=\sigma_{yy}$ where $z$ is oriented along the $c$ axis. The trace of this tensor is $3P=\sigma_{zz}+2\sigma_{xx}$ and the difference $\sigma_{zz}-\sigma_{xx}$ is the shear stress. For a given structure the shear stress is the linear derivative of the energy with respect to the shear of the cell, and the equilibrium value of the $c/a$ ratio is that which yields zero shear stress. At $u=0.21$ we have minimized the energy with respect to the shear strain $\varepsilon$, using the stress theorem, and we have found $\varepsilon=0.05$ (or $c/a=2.643$ using the relation given in Ref. 5). The points and curve for $\varepsilon=0.05$ are shown in Fig. 3, which is adequate to establish the arseniclike minimum to be $u=0.217$ and $\varepsilon=0.05$, with $E_{\text{tot}}=0.56$ eV/atom below that for simple cubic. (It may be noted that these are quite similar to those in As where $u=0.23$ and $\varepsilon=0.08$ experimentally,[2] compared to $u=0.23$ and $\varepsilon=0.06$ calculated using exactly the same methods as here.[5])

For the $\beta$-oxygen-like minimum, we have followed a similar procedure, first minimizing with respect to $u$, then $\varepsilon$, followed by a calculation at the predicted minimum to demonstrate that the forces and shear stresses are essentially zero, i.e., that the structure is near the minimum. In

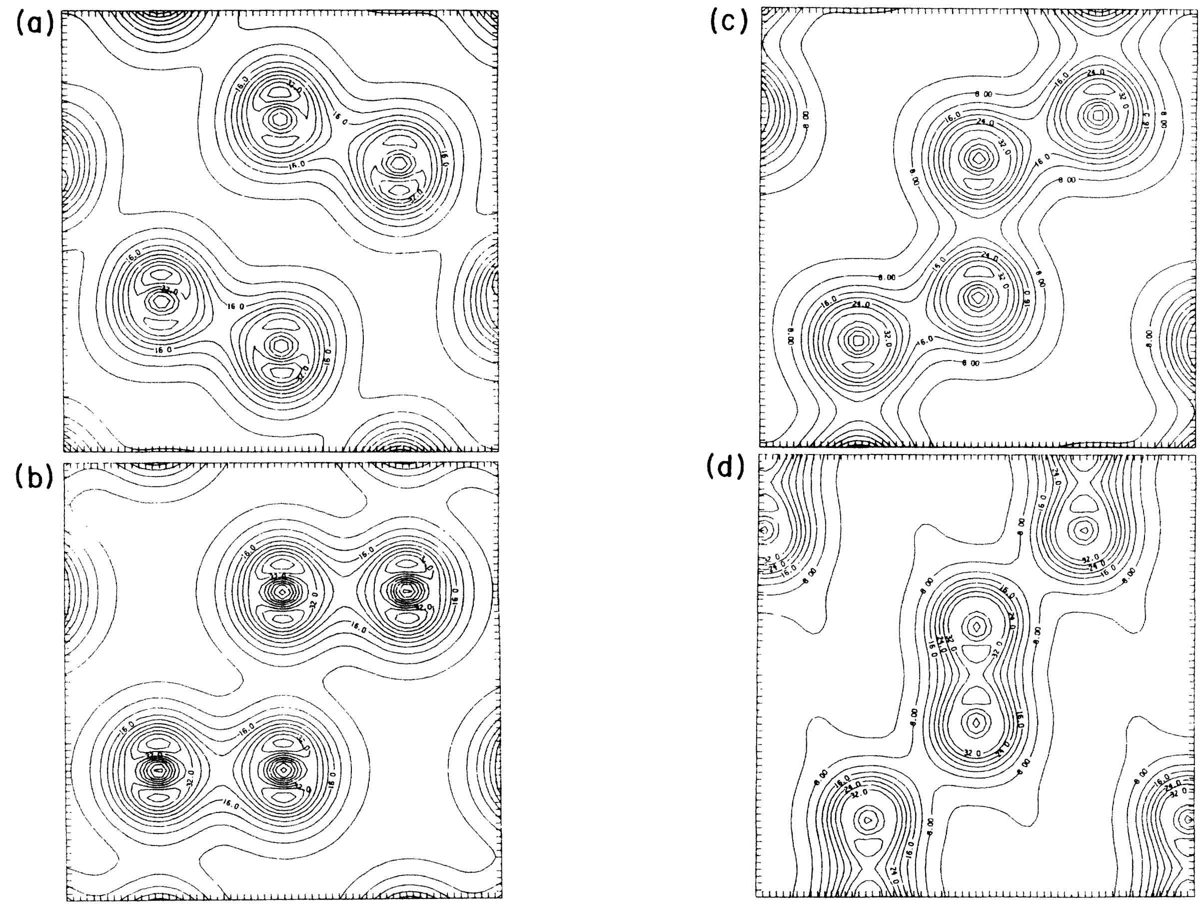

FIG. 2. Charge-density contours for structures along the path shown schematically in Fig. 1. The plane chosen is the same as in Fig. 1 containing the bonds shown as heavy lines. The increased magnitude of the bonding charge in (d) indicates the strength of the intramolecular bond in the $\beta$-oxygen structure. (The reason the two bonds about each atom in the diamond structure are not identical is that diamond was treated as trigonal $A7$, just like the other cases. The extent to which the results approach cubic symmetry is a test of the accuracy of our calculations.)

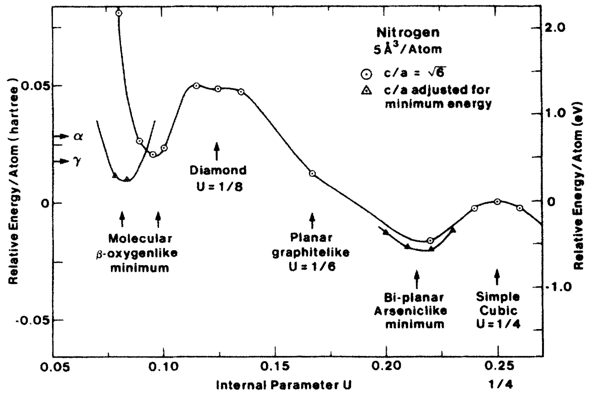

FIG. 3. Energy of nitrogen at constant volume $=5$ Å$^3$/atom as a function of the sublattice displacement $u$, which spans the structures illustrated in Fig. 1. Note that both simple cubic and diamond are maxima and the two stable minima are for distorted structures. The circles show the results for the "ideal" $c/a=6^{1/2}$ and triangles, the results for the $c/a$ ratio which minimize the energy: $c/a=3.10$ for $\beta$-oxygen-like and $c/a=2.643$ for arseniclike. The parabola at the left is derived from the calculated forces. Its curvature indicates the high-phonon frequency in comparison with the curvature at the arseniclike minimum.

this case the predicted $c/a$ ratio is 3.1, quite different from the ideal, and the triangles in Fig. 3 show the behavior near the predicted minimum. The parabola drawn through the two points was calculated from the energies and forces at these points. Note that the large change in $u$ between the two minima shown in Fig. 3 is almost entirely due to the change in $c$, with the bond length ($r=2uc$) remaining constant to within the accuracy we could determine. One result is that the molecular bond length $r=1.15$ Å is found to be slightly greater than that at low pressures. (At low pressures we find $r=1.10$ Å, as discussed later, in excellent agreement with the known bond length in the molecule.) Although this structure is clearly very molecular in character, the results described below show the extent to which the properties of this phase are modified by the volume compression.

The electronic charge densities for the various structures along the path given in Fig. 1 show the changes in the bonding as the coordination and geometries are changed. The calculated densities for the two stable structures are shown in Figs. 2(a) and 2(d). In the arseniclike structure at the top each atom has three bonds to nearest neighbors: one is shown in the plane and corresponds to the solid bold lines in Fig. 1(a); the other two equivalent bonds are, respectively, above and below the plane. In the $\beta$-oxygen molecular structure at the bottom, each atom has only one near neighbor and the strong molecular bond is shown in the plane. The charge density for intermediate structures between these phases is shown in the middle figures: the flattening of the arsenic pyramids into planar threefold coordinated structure of rhombohedral graphite in Fig. 2(b); and the formation of a new bond perpendicular to the planes to make the fourfold coordinated diamond structure of Fig. 2(c). It is this new fourth bond in the diamond structure which becomes the single molecular bond for each atom in the $\beta$-oxygen structure in Fig. 2(d).

In the molecule the nearest-neighbor distance is much shorter than in the other structures and the strength of the molecular bond is shown by the greater charge density in the bonds, 38 electrons/cell compared to 20 in the arsenic structure at the bond centers. Also the shapes of the charge densities are different, reflecting the different linear combination of the $s$ and $p$ states involved in each bond. In this molecular structure each atom has three second neighbors on different molecules, one of which is shown in the plane. Although this is clearly a molecular solid, the second-neighbor interactions are sufficiently important at this density to cause the distortions of the molecular density shown in Fig. 2(d) and to other effects. In particular, in our calculations the intermolecular interactions at this volume are so large that the system is metallic. The properties of these phases will be considered further below.

The charge densities for the unstable intermediate structures, rhombohedral graphite and diamond, are shown in Figs. 2(b) and 2(c), respectively. Since the bond contours are not markedly different than those for the arsenic structure, the reason for the higher energy is not immediately apparent. It is more revealing to examine the band structures and the filling of states, which favor threefold coordination or a single triple bond for group-V elements, and do not favor structures such as the diamond structure where electrons are forced into the conduction band above a band gap. This has been described by ML.

### B. Transition under pressure

In order to calculate the pressures and volumes at which there can be a phase transition between the two minima, we must determine the total energy of the solids at each minima as a function of volume. The transition will occur as a function of pressure when the relative enthalpies $(H=E+PV)$ of the two minima change sign, which can be determined by constructing the tangent between the two curves for $E(V)$. Figure 4 shows the results of our calculations at different volumes, all referred to the energy of the simple cubic at $V=5$ Å$^3$.

For the distorted structures we have only roughly minimized the energy with respect to all parameters at each volume. For the determination of the energy alone, it is not essential to find the structure accurately because the error in the energy is quadratic in any structural deviations. For the arseniclike minimum we have kept $u$ and $\varepsilon$ fixed. For the $\beta$-oxygen-like minimum, we show points calculated with a simple prescription that $r$ be the free molecule length and the $c/a$ ratio be that derived by requiring the shortest distance between atoms on different molecular planes to be equal to that $(=a)$ between atoms on different molecules in the same molecular plane. This is quite good as may be seen by the fact that the energies of structures with optimized $c/a$ ratios (triangles) are only slightly lower. Also the results shown in Fig. 3, as well as the force constants discussed below, are sufficient to show that the energy is lowered by less than approximately $\sim 0.05$ eV/atom by relaxing the bond length.

The transition pressure which we find from the tangent construction is approximately 700 kbar, and the transition occurs between phases with atomic volumes of approximately 7.2 and 5.5 Å$^3$/atom, i.e, a rather large volume jump of approximately 25%. The present result for the transition is only slightly smaller than that found by ML of approximately 770 kbars. This close similarity of the numerical values is a coincidence because, as ML pointed out, their pressure should have been increased to compensate for differences in the two methods they used, respectively, for the molecular and nonmolecular phases. ML estimated the increase to be approximately 220 kbars so that their estimated pressure for the transition to simple cubic was approximately 1 Mbar. (Even though we find simple cubic not to be stable, we can compare with ML by constructing the tangent between the molecular and simple-cubic curves. From Fig. 4 one can find the pressure for this transition to be approximately 1.1 Mbars in good agreement with the best estimates of ML.) Thus our result is indeed a lower transition pressure than that of

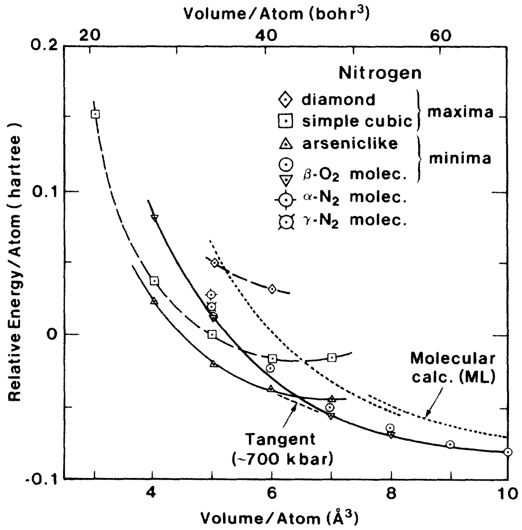

FIG. 4. Energy as a function of the volume for several different structures relative to simple cubic at $V=5$ Å$^3$. The calculation transition occurs at the pressure of approximately 700 kbar, given by the slope of the tangent shown. The curve for simple cubic is close to that of ML (Ref. 17) and the dashed line is the molecular calculation of ML. The shift in the latter above our results is not relevant to our calculation of energy differences between the phases but it does show the error in our LDA calculation of the binding relative to the atom (see the text).

ML, caused by the lower energy of the arsenic structure relative to the simple cubic. This is also evident from the difference in the transition volumes. We find a smaller volume jump (~25% compared to 33%) because the shape of $E(V)$ For the arsenic structure is more similar to that for the molecular phase than is $E(V)$ for the simple cubic.

One important result is that the energies for simple cubic and diamond agree well with the LMTO results of ML; this may be seen by comparing Fig. 4 with Fig. 1 of ML and, in addition, the energy relative to the atom is in good agreement, as discussed in Sec. VI. Also our calculated $E(V)$ for the $\beta$-$O_2$ structure is quite similar to that found by ML and shown as dashed lines in Fig. 4. That curve is actually for the $R3c$ ($C_{3v}^6$) structure and was found using the Gordon-Kim (GK) method.[18] If we ignore for the moment the shift in energy between the curves (which is discussed in Sec. VI) the variation with volume is similar except that ours does not increase as rapidly at smaller volumes. This difference is understandable in terms of the dispersion in the bands which we find at small volumes. Our energy is lowered by hybridization of the bands (and by transfer of electrons when they overlap to form a metal for volumes below ~6 Å$^3$/atom). On the other hand, the GK method[18] is an approximation to the LDA designed work for closed-shell atoms and molecules which does not include these effects.

### C. Properties of the phases at high pressure

#### *1. Electronic states*

Perhaps the most important property to consider is the effect of the structure upon the electronic bands at high pressure. If the simple-cubic structure were stable, it would of course be metallic since it would have an odd number of electrons per cell. On the other hand, the $A7$ symmetry structures with two atoms per cell can be insulating, zero-gap semiconducting, or semimetallic. The nature of the Fermi surface (if any) is one of the goals of this work since it will be critical for whether or not metallic nitrogen could be a superconductor. This is of particular interest in N since electron-phonon interactions should be large in this element, as in other first row elements. On the one hand the electron-phonon interaction is responsible for the instability of the simple cubic; on the other hand, if the stable structure is metallic, then the electron-phonon interaction could lead to a high superconducting transition temperature $T_c$. Thus N can be an example of the competition between high $T_c$ and structural instabilities.[33]

In Fig. 5 we show the band structure for the predicted stable arseniclike structure at $V=6$ Å$^3$/atom. The calculated bands show semimetallic character not unlike those found for As. The Fermi surface is small which indicates that superconductivity is not favored. However, at smaller volumes, the density of states at the Fermi surfaces which might be more favorable for superconductivity. The greatest difference from As, other than the greater bandwidth, is that the N bands cross the Fermi energy $E_F$ in only one region of the Brillouin zone (BZ) near the $T$ point (the top center of the hexagonal BZ), whereas in As there are also pieces of the Fermi surface near point $L$. This has interesting possible consequences for N, if we imagine small variations around the structure shown in Fig. 5 (due either to physical variations like pressure or to corrections to the present theoretical calculation). First, symmetry analysis of the bands shows that the doubly degenerate bands near $E_F$ at the $T$ point must connect to the band well below $E_F$ at $W$ and to one well above $E_F$ at $\Gamma$. Any band structure with this topology must have at least one band crossing the Fermi energy, so that there can be no finite gap. However, if the bands cross only at the one point (and others related by symmetry) required by the topology, the Fermi surface may consist only of points, i.e., a zero-band-gap semiconductor. Our calculations indicate that this would actually happen at a slightly larger volume so that the predicted nonmolecular phase of N is near a transition from zero-band-gap to semimetallic bands.

It is clear in Fig. 5 that there is a gap well above the Fermi energy between the $2s$-$2p$ bands and all other bands. This can happen in the light elements where $3s$, $3p$, and $3d$ are well separated in energy, whereas there is no such gap in the heavier elements like As (see Ref. 5).

Our calculations also lead to results for the band gap in the molecular phase and its variation with pressure. Although we will give representative results here, we want to emphasize that the calculated gaps for the molecular phases depend sensitively upon the $c/a$ ratio. Because we did not judge it worthwhile to go to great lengths to determine the $c/a$ ratio accurately (since it makes only very minor differences in the total energy), any comparison with experiment must be considered very qualitative. Also we expect the calculated gap to be less than the true

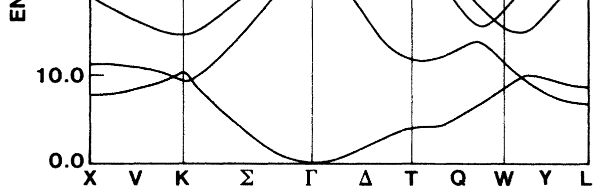

FIG. 5. Electronic band structure of nitrogen in the arseniclike structure at $V=6$ Å$^3$/atom. The most significant feature is the set of bands crossing the Fermi surface near $T$. As discussed in the text, this means that at this volume $N$ is near the transition between a zero-band-gap semiconductor and semimetal with a small Fermi surface. Note that there is a gap above the Fermi energy separating the 8 $s$-$p$ bands per cell from the higher bands.

gap, as in other LDA calculations.[14] Our most quantitative results are for $V=7$ Å$^3$, near the predicted transition, and 5 Å$^3$, for which our most extensive calculations were done. At $V=5$ Å$^3$ the molecular structures were found to be metallic for all values of the $c/a$ ratio tested on both sides on the minimum $c/a=3.1$. At $V=7$ Å$^3$ the bands are slightly metallic for $c/a=2.67$ (the case indicated by the circle in Fig. 3), but for $c/a=3.4$ (near the minimum) the lowest gap is $\sim 2.7$ eV. This gap is indirect and the minimum direct gap is $\sim 5$ eV. Such a minimum gap is consistent with the data of Ref. 21, where it was found that N becomes colored under pressure. Thus we find that the molecular phase remains insulating up to the transition, unlike the conclusion of Min *et al.*[16] for hydrogen, where it was predicted to be metallic in the molecular phase.

### 2. Phonons

One of the most accessible signatures, distinguishing the $A7$ structure from simple cubic, is the existence of Raman active phonon modes. We have calculated frequencies of these modes in three cases, the molecular $\beta$-oxygen phase at $V=5$ and 8 Å$^3$/atom and the arseniclike phase at $V=5$. We have determined the frequencies by calculating the force at two different values of the internal parameter $u$. From this one can find a force constant and a harmonic frequency. For $V=5$ the $u$ values are the ones shown in Fig. 3 closest to the minima, and as we have already noted, the parabola drawn in Fig. 3 for the stable molecular structure is derived from the forces. Although we have not tried to find accurate values of the phonon frequencies (which would require extensive tests with larger $k$ point sets, energy cutoffs, and different displacements to extract the anharmonic terms, as was done in our previous work[5,8]), we believe that the results show the important features.

Our results are that the frequency at the largest volume, i.e., lowest pressure, is 2780 cm$^{-1}$, which is to be compared to the experimental value of 2359 cm$^{-1}$ for the isolated molecule and the Raman active modes of the crystal, approximately 2400–2470 cm$^{-1}$, observed by Reichlin *et al.*[21] in the pressure range approximately 0.5–1.0 Mbars. Secondly, there is a large decrease at $V=5$ (where the theoretical pressure is approximately 1.9 Mbars) to 1820 cm$^{-1}$. This large decrease illustrates the extent to which the molecules are interacting in the highly compressed molecular structure. The lower frequency is also presumably related to overlap of bands and metallic character of the bands. We would expect only a moderate decrease in the frequency so long as the band structure is insulating; thus we conclude that the frequency is not greatly changed from the molecule at the calculated transition volume of $\sim 7.2$ Å$^3$/atom and pressure of approximately 700 kbars.

Probably the most important point is that the frequency in the arseniclike structure is much lower, 960 cm$^{-1}$. We consider this large difference (a factor of 2 in the frequency means a factor of 4 in the force constant) to show that the phonon frequencies in any reasonable nonmolecular structure are greatly reduced compared to those in any reasonable molecular structure. If that is so, then the Raman frequency is a clear indicator of the molecular-to-nonmolecular transition. Since the recent experimental results[21,22] report that there are no great reductions in the intramolecular phonon frequencies even at the highest pressures of 1.4–1.8 Mbars, our results support the interpretation that N has remained in a molecular structure in these experiments.

## V. OTHER STRUCTURES

Because one cannot examine all structures, it is essential to consider candidates likely to be low in energy. This is particularly relevant for the present work, since nitrogen forms molecular structures at high pressure[2,21] which are more complex than any which we are able to consider here. To try to quantify the effects of different structures, we have done calculations at one volume ($V=5$ Å$^3$) for the two actual structures observed for N at low pressures: $\alpha$-N$_2$ [cubic $Pa3$ ($T_h^6$), 4 molecules/cell] and $\gamma$-N$_2$ (tetragonal, 2 molecules/cell).[2] We have chosen the bond length to be the molecular value,[2] which leads to energies only slightly above the minimum ($\sim 0.05$ eV/atom as was discussed in the preceding section). This is the only free parameter for $\alpha$-N$_2$. For $\gamma$-N$_2$ we have also chosen $c/a=1.1$, close to the experimental value at low pressure.[2] As shown in Figs. 3 and 4, we find that each of these is *higher* in energy than $\beta$-O$_2$ by approximately 0.25–0.5 eV/atom. Thus we have not found any structure lower than $\beta$-O$_2$ in our tests.

It would certainly be unwarranted to conclude that all other molecular structures will also be higher in energy. Perhaps it would be appropriate to consider the difference of $\sim 0.5$ eV to be representative of the variations among different molecular structures. If some other molecular structure were *lower* in energy than $\beta$-O$_2$ by approximately 0.5 eV at $V=5$ Å$^3$/atom, it would still be above the arseniclike structure. The transition would still occur but nearer this volume. Changing the transition volume from 5.5 (as in Fig. 4) to 5 Å$^3$/atom would change the transition pressure from approximately 0.7 to 1.2 Mbar as may be found from the tangents to the $E(V)$ curve given in Fig. 4. This illustrates the extreme sensitivity of the transition pressure to the exact form of $E(V)$ for the true molecular phase. The values of the transition volumes are not so sensitive; thus it would be extremely useful if experimental measurements of the volume were made as a function of pressure.

We can also comment that if some other nonmolecular phase were low in energy, e.g., the known complex structures of P,[2] then this would always lead to a lower transition pressure. Also they could have major effects upon the bands of N in the compressed phases. Just as P changes from semimetallic in the arsenic structure to semiconducting in the more complex phorphorus structures, so it is reasonable to conclude that N would do the same. Since we have not treated any of these phases, we cannot comment further on their stability.

## VI. BINDING ENERGY OF THE MOLECULE

The binding energy relative to the atom is of intrinsic interest even though it is irrelevant for the transitions discussed above. Since the binding energy is a small difference between the total energies of the molecule and two separated atoms, it is essential to calculate each individual energy in such a way that errors will cancel. In all the calculations done here, the most significant error in the absolute value of the total energy is due the finite number of plane waves used in our basis set. Thus it is essential to calculate the energies of the atom and molecule using exactly the same cutoff on the plane waves, as was also done by Northrup and Cohen[34] in their calculations for Si and Ge molecules. We have done this by making a periodic structure of atoms with the same volume per cell as that (i.e., the volume per molecule) in the calculations for the $\beta$-$O_2$ structure. Since the energy cutoffs are the same, this means that the basis sets are the same. At the volume of 20 Å$^3$ per cell, with a 50 Ry cutoff, we find an energy difference of $266.378-258.309=8.069$ eV/atom. Four corrections to this number are needed: The major correction is for the fact that we have not properly treated the lowest-energy spin state of the atom. A better value is obtained by lowering the atomic energy by 2.924 eV, as found by spin-polarized LDA calculations.[35] Secondly, as a computational point for our "atomic" calculation, the cell of 20 Å$^3$ is not sufficiently large for the atomic case because of the effects of having partially filled bands for the "atom." Calculations on large cells (up to 60 Å$^3$) with reduced cutoffs shows that the correction is a lowering of the atomic energy by 0.272 eV. This gives a binding of

$$8.069-2.924-0.272=4.873 \text{ eV/atom}$$

for the static solid at this density. For the molecule we should also consider the zero-point motion which adds an energy of $\frac{1}{2}$ the phonon energy, 0.146 eV/molecule, to the energy of the molecule. Finally, we add a correction for the energy of the molecule relative to the crystal. We take this from ML since the GK method is accurate for this difference. Using the results given ML (Ref. 17) this is a lowering of the energy of the isolated molecule by 0.386 eV/atom compared to that at the compressed volume of 8 Å$^3$/atom. Thus our calculated binding of the molecule is

$$4.873-0.146/2+0.386=5.186 \text{ eV/atom}$$

or 10.372 eV/molecule. This may be compared with the experimental binding of 9.90 eV/molecule, a CI calculation of 9.96,[36] and other LDA calculated values of 7.8 (LMTO),[37] 11.34 (Gaussian basis),[38] and 9.97 (improved LMTO).[39] The fact that our value is larger than experiment is in accord with other LDA calculations, and the agreement with experiment is comparable to that found for diamond carbon, which is 7.58 compared to the experimental value of 7.37 eV/atom.[30]

The qualitative aspects of our binding-energy calculation may already be seen in Fig. 4 in the comparison with the molecular calculation of ML, shown as dotted lines. The energy for the molecule has been placed on the graph by ML using the atomic energies as the reference energies. Since the correct experimental binding energy of the molecule is assumed in the GK method, that curve at large volume can be regarded as the correct energy of the molecular solid. Our result is below the dotted curve by approximately 0.3 eV or 0.001 hartree/atom in agreement with the value of the binding energy given in the preceding paragraph.

The zero of energy used in the present work relative to the atom can be determined in the same way. Using our value of 264.210 eV/atom for simple cubic at $V=5$ Å$^3$/atom and 50 Ry cutoff, we find the energy to be $-2.71$ eV (0.099 hartree) relative to the atom. This is slightly larger binding energy than the value of $-2.57$ eV from Fig. 1 of ML, who also used the local-density approximation. Considering the differences in the form of the LDA (ML used the von Barth-Hedin form), the use of *ab initio* pseudopotentials and a finite number of plane waves in the present work, and the spherical approximations in the LMTO, the agreement is very good. Indeed, the difference is less than the height of the symbols around the points in Fig. 4.

We wish to emphasize that our overestimate of the binding of the molecule is expected in the LDA, and it is not an essential point for any other aspects of this paper. For the purposes of the present work, it is much more important that we have used a single method, so that the relative energies of the different phases could be determined accurately.

## VII. DISCUSSION AND CONCLUSIONS

We believe the most important and most well-founded conclusion to be drawn from the present work is that N is predicted to occur in a distorted three-fold coordinated structure at high pressures. The simple cubic is found to be unstable to distortions that take it to the $A7$ arseniclike structure at all pressures considered, up to $\sim 10$ Mbars. We conclude that these are large electron-phonon interactions which lead to the distorted structure, removing most of the Fermi surface that would occur in the simple-cubic structure, and decreasing the prospects for superconductivity. Since the Fermi surface increases with pressure, this may suggest that superconductivity will be more likely to occur at higher pressures. The band structure is found to be near the transition point between a zero-band-gap semiconductor and a semimetal with a small Fermi surface. In either case, it has properties distinctly different from a simple-cubic metal. The phonon frequencies are predicted to decrease markedly in going from a molecular structure to the arsenic structure (by a factor of at least 2 compared to zero-pressure nitrogen). This can serve as a distinct signature in high-pressure experiments.

Thus at high pressure nitrogen is found to behave much like the other group-V elements. In the respect that it is predicted not to be stable in the simple-cubic structure, it is more like As than like P. Although this might seem counterintuitive, a possible explanation may lie in the different role of $d$ states in these elements. Whereas the $d$ states play little role in N, they are important in P where they are just above the Fermi energy and are mixed into the filled states. In As the $3d$ shell is a filled core state and the $4d$ states are less important in As than are the $3d$ states in P. This can be seen directly in the pseudopotentials, for which the $d$ part is more repulsive for As than for P. We have previously concluded from our calculations that $d$ states stabilize the simple hexagonal structure in Si and we believe the same can happen for the simple cubic. Lack of $d$ contributions was also argued by Yin and Cohen[30] to be a factor in the high energy of metallic states of C.

The results for the molecular phase are less definite because of the difficulty in establishing the lowest-energy molecular structure. We have seen that properties such as the band gap are sensitive functions of the structure, and we have not attempted to accurately predict such properties. Perhaps the most important qualitative result is that the best calculations indicated the molecular phase remains insulating up to pressures above the predicted transition pressure of $\sim 700$ kbars.

Our results for the transition pressure are most tentative because they depend upon small differences in energy between states that are very different in character. In particular, all our results depend upon the validity of the local-density approximation (LDA) for the total energy. If there is a significant difference in the accuracy with which the exchange and correlation are represented by the LDA in these very different phases of nitrogen, then our results will be affected accordingly. Previous work using the LDA has found impressive agreement with experiment; however, it should be noted that in cases where the transition is between very different phases there are deviations from experiment. For example, in silicon the transition from diamond (semiconducting, coordination 4) to $\beta$-tin (metallic, coordination $\sim 6$) is found to be at 110—125 kbars experimentally, compared to 70 kbars found by Needs and Martin[25] and 90 kbars found by Yin and Cohen,[7] in two independent, but nominally identical calculations. Such precedents show that the LDA prediction for the transformation pressure for N might also be in error by $\sim 50\%$. In this light, it is relevant to note that the transition volumes are much better determined by the theory, and it would very useful if the experimental studies could include measurements of the volume, e.g., as has been done recently for hydrogen.[40]

It is important to point out that we have not considered the complex structures which have been found recently for N at high pressures.[21] We have done calculations for the known $\alpha$ and $\gamma$ structures,[2] which we found to be higher in energy than the $\beta$-$O_2$ structure at the compressed volume of $V=5$ Å$^3$. As we discussed in Sec. V, if the spread in energies of all our molecular calculations, approximately 0.25—0.5 eV/atom, is taken to be an estimate of the uncertainty in the energy difference, then transition pressure can change by approximately 0.5 Mbar. This source of uncertainty could be reduced straightforwardly in future calculations because there is no fundamental limitation on numerical accuracy for the complex molecular structures.

Our conclusion is that the calculations indicate a transition to a nonmolecular structure at approximately 700 kbars, in apparent disagreement with recent experimental results[21,22] which have reported no transformation up to pressures above 1.3 Mbars. We conclude that either (1) there is a transition as predicted, but that it has not been observed because of a large energy barrier to the transition, or (2) the transition does not occur up to such pressures. Although the latter result would mean a significant difference from our calculated pressure of approximately 700 kbars, we cannot at this point set firm error bars on this calculated number because it may be a sensitive function of the detailed structures and the exchange-correlation energies of each phase.

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[1] See, *American Institute of Physics Handbook* (McGraw-Hill, New York, 1972), Chap. 7.

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

[3] G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules,* 2nd ed. (Van Nostrand Reinholdt, New York, 1950), p. 449.

[4] See, for example, reviews by A. Jayaraman, Rev. Mod. Phys. **55**, 65 (1983); M. Ross, Rep. Prog. Phys. **48**, 1 (1985).

[5] R. Needs, R. M. Martin, and O. H. Nielsen, Phys. Rev. B **33**, 3778 (1986).

[6] See papers, in *Electronic Structure, Dynamics, and Quantum Structural Properties of Condensed Matter,* edited by J. T. Devreese and P. T. Van Camp (Plenum, New York, 1985).

[7] M. T. Yin and M. L. Cohen, Phys. Rev. B **26**, 5668 (1982).

[8] O. H. Nielsen and R. M. Martin, Phys. Rev. B **32**, 3780 (1985); **32**, 3792 (1985).

[9] For a description of the structures and properties, see M. H. Cohen, L. M. Falicov, and S. Golin, IBM J. Res. Dev. **8**, 215 (1964).

[10] B. Morosin and J. E. Schirber, Solid State Commun. **10**, 249 (1972); Phys. Lett. **30A**, 512 (1969).

[11] J. C. Jamieson, Science **139**, 1291 (1963).

[12] A simple cubic phase of Sb was reported by T. N. Kolobyanina, S. S. Kabalkina, L. F. Vereshchagin, and L. V. Fedina, Zh. Eksp. Teor. Fiz. 32, 109 (1969) [Sov. Phys. JETP **28**, 88 (1969)]. However, later work has not found such a phase: see T. Kikegawa and H. Iwasaki, in *Solid State Physics under Pressure: Recent Advances with Anvil Devices,* edited by S. Minomura (KTK Scientific Publishing, Tokyo, 1985), p. 201

[13] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964 Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[14] A. R. Williams and A. Von Barth, in *Theory of th geneous Electron Gas,* edited by N. H. March quist (Plenum, New York, 1983), p. 189.

[15] For work on diatomic elemental molecules,

O. Gunnarsson, J. Harris, and R. O. Jones, J. Chem. Phys. **67**, 3980 (1977).

[16] B. I. Min, H. J. F. Jansen, and A. J. Freeman, Phys. Rev. B **33**, 6383 (1986).

[17] A. McMahan and R. LeSar, Phys. Rev. Lett. **54**, 1929 (1985). Referred to in the text as ML.

[18] Application of the Gordon-Kim method to $N_2$ of pressures $<100$ kbars has been described by R. LeSar, J. Chem. Phys. **81**, 5104 (1984). The method is described in M. Walsman and R. G. Gordon, J. Chem. Phys. **71**, 1325 (1979).

[19] See review by O. K. Andersen, Phys. Rev. B **12**, 3060 (1975). The LMTO method has been applied to a wide range of high-symmetry structures with great success.

[20] W. J. Nellis, N. C. Holmes, A. C. Mitchell, and M. van Thiel, Phys. Rev. Lett. **53**, 1661 (1984).

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

[22] R. J. Hemley, H. K. Mao, and P. M. Bell (private communication).

[23] S. Froyen and M. L. Cohen, Phys. Rev. B **28**, 3258 (1983).

[24] D. R. Hammann, M. Schlüter, and C. Chiang, Phys. Rev. Lett. **43**, 1494 (1979). The N pseudopotential used here is that given by G. B. Bachelet, H. S. Greenside, G. A. Baraff, and M. Schlüter, Phys. Rev. B **24**, 4745 (1981).

[25] R. J. Needs and R. M. Martin, Phys. Rev. B **30**, 5390 (1984).

[26] R. Biswas, R. M. Martin, R. J. Needs, and O. H. Nielsen, Phys. Rev. B **30**, 3210 (1984).

[27] A summary is given by R. M. Martin, in *Electron Structure, Dynamics, and Quantum Structural Properties of Condensed Matter,* Ref. 6.

[28] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).

[29] J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[30] M. T. Yin and M. L. Cohen, Phys. Rev. B **24**, 6121 (1981); Phys. Rev. Lett. **50**, 2006 (1983).

[31] H. Wendel and R. M. Martin, Phys. Rev. B **19**, 5251 (1979).

[32] U. von Barth and A. C. Pedroza (unpublished).

[33] M. L. Cohen and P. W. Anderson, in *Superconductivity in d and f band metals—1971 (Rochester),* Proceedings of the Superconductivity in *d* and *f* band metals, AIP Conf. Proc. No. 4, edited by D. H. Douglas (AIP, New York, 1972), p. 17.

[34] J. E. Northrup and M. C. Cohen, Phys. Rev. A **28**, 1945 (1983).

[35] A. K. McMahan (private communication).

[36] J. S. Wright and R. J. Buenker, J. Chem. Phys. **83**, 4059 (1982).

[37] O. Gunnarsson, J. Harris, and R. O. Jones, J. Phys. C **9**, 2739 (1976).

[38] G. S. Painter and F. W. Averill, Phys. Rev. B **26**, 1781 (1982).

[39] M. Springborg and O. K. Andersen (unpublished).

[40] R. J. Wijngaarden, A. Lagendijk, and I. F. Silvera, Phys. Rev. B **26**, 4957 (1982).