Prediction of a new phase in solid N_2 at high pressure

Koji Kobashi, A. A. Helmy, Richard D. Etters, and Ian L. Spain
Department of Physics, Colorado State University, Fort Collins, Colorado 80523
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A pressure-induced structural phase transition from the γ structure to the $R\bar{3}m$ structure (ϵ-N_2) of solid N_2 is predicted. Lattice-energy calculations using an exp-6-1 potential form fitted to the *ab initio* results of Berns and van der Avoird show that the transition is located at $P \sim 40$ kbar at zero temperature with a volume change of 0.2 cm^3/mole. The calculated P-V relation and the lattice parameters are presented.

I. INTRODUCTION

In addition to the three well-known α, β, and γ phases of solid N_2, a new phase δ has recently been discovered above $P = 49$ kbar and room temperature.[1] The crystal structure of δ-N_2 has been determined[2] to be cubic $Pm3n$ with eight molecules per unit cell, where the molecules are orientationally disordered and occupy T_d (two molecules) and D_{2d} (six molecules) symmetry sites. This structure is identical to that of γ-O_2 and β-F_2 which exist at normal pressure. The appearance of the orientationally disordered $Pm3n$ structure, instead of the β-N_2 structure (hexagonal $P6_3/mmc$), is attributed to the small quadrupole moments of O_2 and F_2, $Q = -0.39 \times 10^{-26}$ and 0.9×10^{-26} esu cm^2, respectively.[3] By comparison, $Q = -1.4 \times 10^{-26}$ esu cm^2 for N_2.[3] The existence of the $Pm3n$, δ-N_2 structure in solid N_2 implies that the anisotropy of the electrostatic quadrupole-quadrupole (EQQ) potential is dominated by the repulsive overlap potential at high pressures. This is not surprising since the EQQ energy has a relatively weak volume dependence. The above information and a comparison of the phase diagram with those of O_2 and F_2 suggest that, in solid N_2 at low temperature and high pressure, there may exist an orientationally ordered phase whose structure is identical to one of the low-temperature phases of O_2 or F_2.[4–7] Since α-O_2 is stabilized by the magnetic interaction and α-F_2 is apparently stabilized by charge-transfer interactions, the only relevant crystal struc-

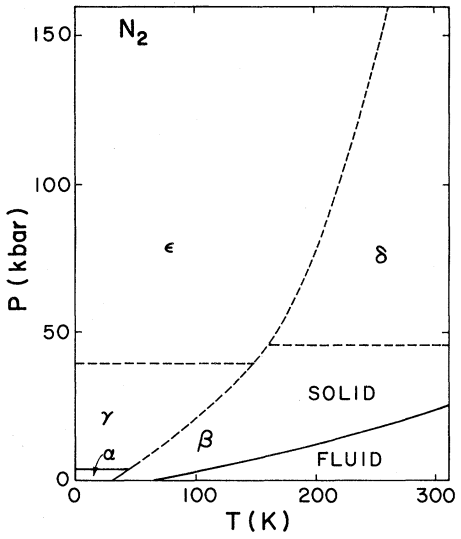

FIG. 1. Phase diagram of solid N_2. Solid curves are experimentally established and dashed curves are tentative.

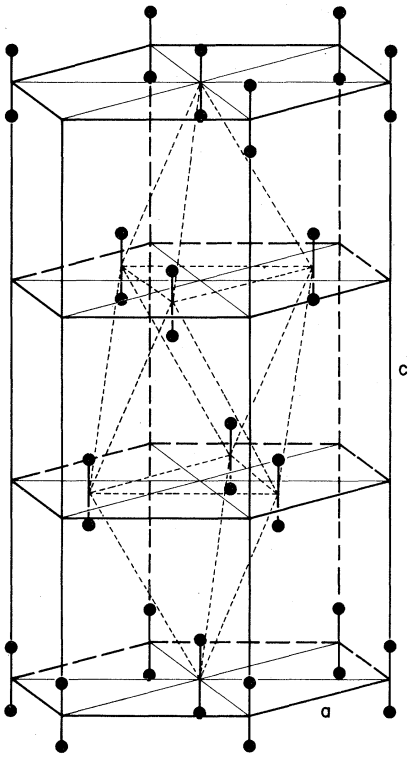

FIG. 2. $R\bar{3}m$ crystal structure proposed for ϵ-N_2.

ture for N_2 is that of β-O_2.

Based upon this information and because β-O_2 is a very closed packed structure for rodlike molecules,[4] we predict[8] that a phase transition like the β-γ transition in solid O_2 will also occur for solid N_2 at low temperature and high pressure, from δ-N_2 into an orientationally ordered state with a β-O_2 structure. We call this new phase ϵ-N_2. The purpose of this article is to show that a transition from γ-N_2 into ϵ-N_2 at high pressure and zero temperature is predicted on the basis of a simple calculation. Figure 1 shows the phase diagram of N_2 including the proposed region of stability for the new ϵ phase. The solid curves are experimentally established and the dashed curves represent tentative boundaries. The proposed β-O_2 crystal structure for ϵ-N_2 is shown in Fig. 2. It is rohombohedral $R\bar{3}m$ with one molecule per unit cell where the molecules are oriented parallel to the c axis.

II. METHOD

Lattice-energy calculations on the α, γ, and the predicted $R\bar{3}m$, ϵ-N_2 structure of solid N_2 have been made using an atom-atom exp-6-1-type representation[9] of *ab initio* molecular orbital results obtained for the interaction between a pair of N_2 molecules by Berns and van der Avoird.[10] In this model, the EQQ potential is represented by point charges distributed linearly along this molecular axis. Calculated results for the sublimation energy and lattice vibrational frequencies in α- and γ-N_2 are in good agreement with experiment,[9] considering that the potential parameters are constrained to best fit the *ab initio* data and are otherwise not adjustable. In our calculation, the lattice energy is minimized with respect to the lattice parameters and the intramolecular bond length at each volume using a pattern search optimization method that has been described elsewhere.[11] Lattice sums are taken out to 12 Å. Zero-point vibrational energies are neglected. Pressures were determined by taking the derivative of energy-volume results.

III. RESULTS AND DISCUSSION

Figure 3 shows the calculated lattice energies for γ- and ϵ-N_2 versus molar volume V. The two curves intersect at $V = 19.0$ cm^3/mole, indicating the existence of a γ-ϵ phase transition. The P-V relations for γ and ϵ-N_2 are shown in Fig. 4, and the calculated lattice parameters are plotted in Fig. 5. The γ-ϵ transition takes place at $P_t = 39.6$ kbar and the volume change associated with the transition is about 0.2 ± 0.05 cm^3/mole. The volume change obtained from the common tangent of the E-V curves and from the P-V curves agree to within 0.05 cm^3/mole.

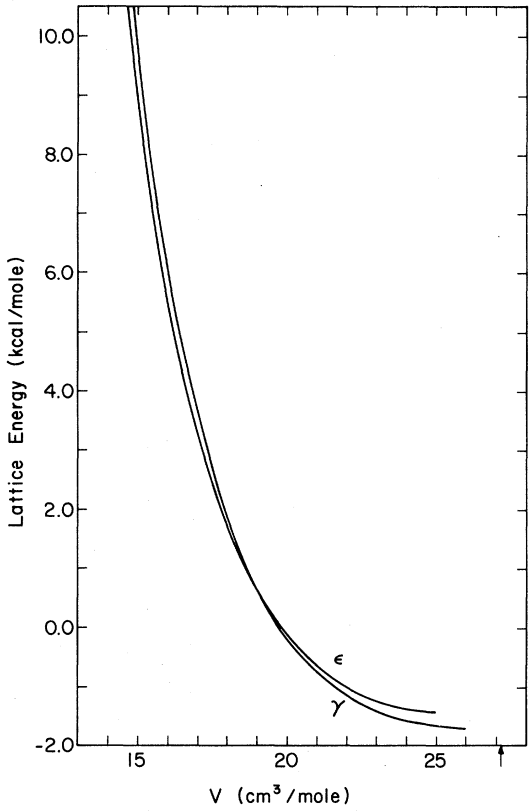

FIG. 3. Calculated static lattice energies for γ-N_2 and the $R\bar{3}m$, ϵ-N_2 structures vs molar volume. The arrow indicates the observed volume (Ref. 12) of α-N_2, 27.1 cm^3/mole, at normal pressure.

Results obtained using the empirical 6-12 + EQQ potential by Thiéry and Chandrasekharan[12] also indicate a transition at a somewhat higher pressure.

The EQQ interaction appears to be important in stabilizing α- and γ-N_2 at low temperatures. For example, at $V = 19$ cm^3/mole, the EQQ energy is -0.28 kcal/mole for both α- and γ-N_2, whereas it is about $+0.15$ kcal/mole for the $R\bar{3}m$ structure of the proposed ϵ phase. As a consequence, the ϵ phase cannot become stable until a volume is reached for which the overlap energy associated with the ϵ structure is sufficiently less repulsive than in γ-N_2 that it overcomes the unfavorable EQQ energy difference. Thus it is the repulsive interaction that destabilizes the γ phase due to compression. To support this argument, we have used the exp-6 atom-atom potential of Kuan *et al.*,[13] which does not include an EQQ interaction. In this model, the $R\bar{3}m$ ϵ-N_2 structure is more stable than both α- and γ-N_2 at all volumes considered. This is consistent with the conclusion of English and Venables.[14] These results demonstrate the importance of the EQQ interaction to the stability of α- and γ-N_2. Similar conclusions

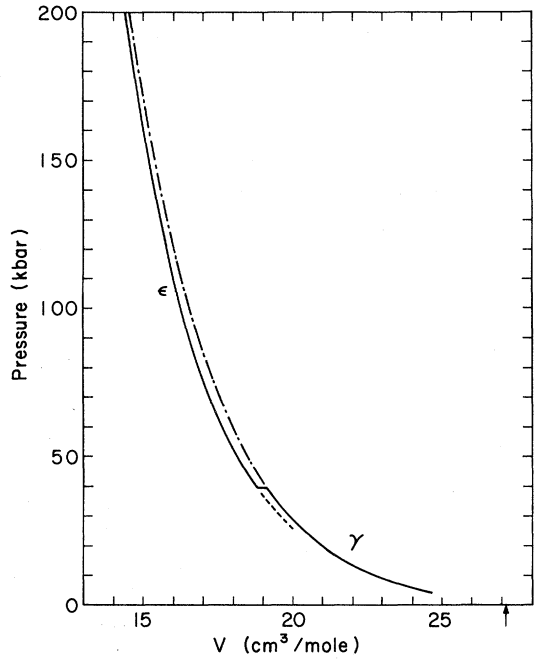

FIG. 4. Calculated P-V relation for γ- and ϵ-N_2. The arrow has the same meaning as in Fig. 3. The dash-dotted and dashed curves are the continuations for γ and ϵ phases, respectively.

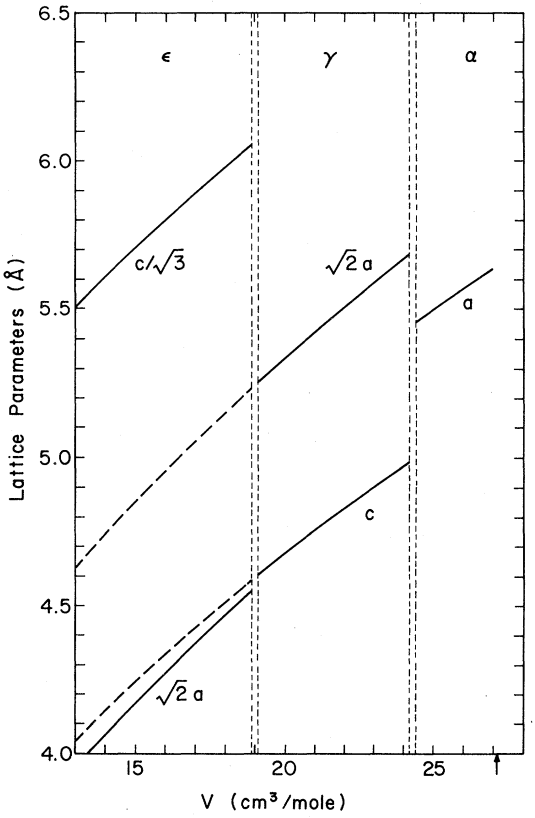

FIG. 5. Calculated lattice parameters for α-, γ-, and ϵ-N_2. The dashed curves are the parameters for γ-N_2. The arrow has the same meaning as in Fig. 3.

have been obtained for β-N_2 using computer simulations.[15]

The atom-atom representation of the *ab initio* potential of Berns and van der Avoird[9,10] does not correctly resolve the stability of γ-N_2 over α-N_2 at $V \gtrsim 24$ cm^3/mole and $P \geqslant 3.6$ kbar,[16] as is the case for all atom-atom-type N_2 potentials. Because of this widely recognized flaw in the potential form,[17] the ϵ phase is predicted to become stable with respect to α-N_2 at $V \simeq 14.4$ cm^3/mole and $P \simeq 200$ kbar. This transition, of course, is not physical but it does point out the ultimate stability of ϵ-N_2 at high pressures.

It is to be emphasized that, while the calculations show very clearly that a transition into ϵ-N_2 is expected, the quantitative reliability of the results depends both on the quality of the potential and on the calculational model. Except for the neglect of zero-point energy, which is of negligible importance compared to the static lattice energy at high pressures, the calculational model is nearly exact. The *ab initio* data[10] and the atom-atom fit[9] to that data are of high quality, but uncertainty still exists in the pair potential which makes numerical predictions of the phase transition reliable to only about a factor of 2 in pressure. Experiments are in progress at our institution and at the Los Alamos Scientific Laboratory that should test the predictions made in this work.

Note added in proof. D. Schiferal and R. L. Mills of Los Alamos Scientific Laboratories have just found evidence from Raman scattering of a new phase in solid N_2 at low temperature above $\sim$ 20 kbars. The spectrum is similar to that observed in the $Pm3n$ structure. If this structure is confirmed, we predict that a transition into β-O_2 phase will occur at higher pressures.

ACKNOWLEDGMENTS

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