

High *P-T* transformations of nitrogen to 170 GPa

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X-ray diffraction and optical spectroscopy techniques are used to characterize stable and metastable transformations of nitrogen compressed up to 170 GPa and heated above 2500 K. X-ray diffraction data show that ϵ -N₂ undergoes two successive structural changes to complex molecular phases ζ at 62 GPa and a newly discovered κ at 110 GPa. The latter becomes an amorphous narrow gap semiconductor on further compression and if subjected to very high temperatures (\sim 2000 K) crystallizes to the crystalline cubic-gauche-N structure (*cg*-N) above 150 GPa. The diffraction data show that the transition to *cg*-N is accompanied by 15% volume reduction. © 2007 American Institute of Physics. [DOI: 10.1063/1.2723069]

I. INTRODUCTION

The molecular-to-atomic transition is a fundamental transformation in condensed matter. At high densities, more itinerant electronic configurations become energetically preferable, which drive the transition from an ensemble of covalently bonded molecules to a monatomic state. Elucidating the nature of these transformations is important in simple diatomics such as H₂ and N₂ because of their possible use as energetic materials and their relevance to the deep interiors of planets.¹ Nitrogen was predicted to polymerize at relatively low compressions. N₂ has the second highest covalent binding energy owing to its triple bond; thus, this polymeric single-bonded nitrogen is expected to have high stored energy. At very high temperatures, shock-wave experiments revealed an anomaly in Hugoniot at 40 GPa ($T=4000$ K) that was interpreted as molecular dissociation.² Static experiments showed that much higher pressures are required to reach the monatomic state compared to the theoretically predicted equilibrium transition pressure and that inferred in shock-wave experiments.^{3,4} At low temperatures (≤ 300 K), the transition was predicted to be inhibited by a large potential barrier (~ 1.8 eV) between the molecular and monatomic configurations.⁵

Recent detailed experimental and theoretical investigations have substantially improved our knowledge of the high pressure behavior of nitrogen.⁶⁻¹⁴ A large hysteresis associated with molecular dissociation has been shown at low temperatures;^{7,8} the nonmolecular material produced on cold compression is strongly disordered or amorphous as inferred from optical studies;⁷ new molecular phases have been discovered;⁹ and finally a cubic-gauche (*cg*-N) single-

bonded monatomic nitrogen has been reported as being directly synthesized from a diatomic molecular phase.¹² Theoretical calculations predict that the polymeric phases with fully satisfied bonding (e.g., *cg*-N) have a large band gap. However, experimentally the nonmolecular phase reached on “cold” compression is opaque. The previous experimental results have been inferred from optical spectroscopy data (mainly Raman), so there is a need for study by different techniques. Accurate x-ray diffraction data are necessary to examine the newly observed phases; such high quality x-ray diffraction techniques have become feasible with the development of new synchrotron sources.

In this article, we report a sequence of phase transformations in solid nitrogen that ultimately results in the formation of a monatomic phase. We combined external and laser heating for annealing the sample and for facilitating the phase transformations. We determined the unit cell structure of the high pressure molecular phases, so the structural and optical data can reconcile and extend the equation of state of molecular nitrogen by a factor of 3 in pressure. The amorphous nature of the semiconducting nonmolecular material produced on cold compression inferred previously from optical measurements is confirmed.⁷ Finally, we show that the latter transforms to the crystalline *cg*-N phase¹² on heating above 2000 K, indicating a sequence of transitions associated with the molecular-to-atomic transition of solid nitrogen.

II. EXPERIMENTAL METHODS

Nitrogen was loaded in diamond anvil cells as compressed gas at room temperature in a sample chamber in rhenium gaskets ranging in diameter from 35 to 100 μm . No

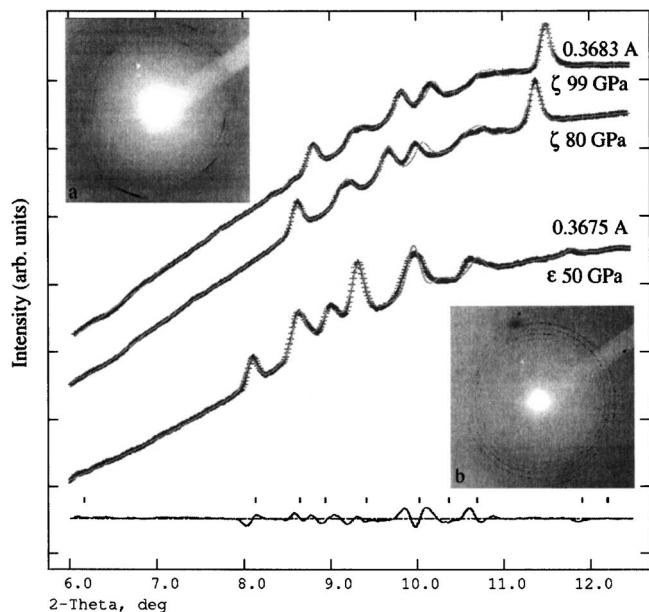


FIG. 1. Rietveld refinement of ϵ -N₂ at 50 GPa, LeBail fits of the integrated 2D x-ray pattern of ζ -N₂ at 80 (and 99) GPa with $a=6.507(2)$ Å, $b=2.578(2)$ Å, and $c=6.846(2)$ Å and the corresponding CCD image [inset (a)]. Notice an increased amount of texture in this pattern compared with the excellent powder pattern of ϵ phase at 30 GPa [inset (b)]. Lower curve: difference between data and fit for the Rietveld refinement of ϵ -N₂.

couplers have been used for the laser heating to avoid possible chemical reactions. Pressures were increased at room temperature and measured using ruby fluorescence before and after heating and usually did not change substantially. The diffraction data were collected at the 16-ID beamline of HPCAT at the APS. A focused, monochromatic beam of different wavelength was used, while the data were recorded on a MAR charge coupled device (CCD) (calibrated with a CeO₂ standard). Raman spectra were excited by 514.5 and 488.0 nm lines of an Ar⁺ laser. In order to reduce the broadening of the diffraction and Raman lines, we annealed the sample using resistive heating (see also Refs. 15–17). The annealing process was monitored by *in situ* Raman spectroscopy and lasted from 10 to 90 min, sometimes reaching temperatures above 1000 K. The changes in the sample were easily noticeable in Raman and x-ray patterns; e.g., the width of the most intense Raman vibron typically decreased by factor of 3 and x-ray diffraction peaks that appeared as asymmetric band with shoulders split. Above ~60 GPa, the annealing did not change the texture of the material.

III. RESULTS

A. ϵ - ζ transition

X-ray diffraction patterns measured in the stability field of ϵ -N₂ agree with previous studies^{15,18} (see Figs. 1 and 2). The ϵ -N₂ structure was confirmed to be rhombohedral (space group $R\bar{3}c$) with 24 molecules per cell²¹ (see also Table I). At 64 GPa, x-ray diffraction data start to show an asymmetry and broadening of peaks corresponding to the (113) and (122) reflections of the ϵ phase, indicating peak splitting (see Figs. 2 and 3 where clear peak splitting at 80 GPa is shown). We infer that these changes correspond to the ϵ - ζ phase

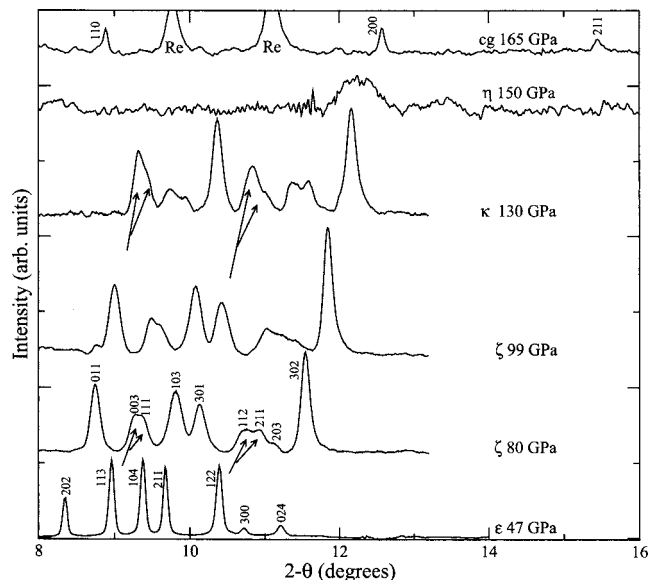


FIG. 2. X-ray diffraction patterns of ϵ , ζ , κ , amorphous, and cubic-gauche phases measured at different pressures (background subtracted). The arrows point at the two split peaks in the ζ and κ phases.

transition,¹⁴ the transition pressure is in good agreement with the previous Raman data.^{19,20} X-ray patterns can be indexed by a primitive orthorhombic cell with $a=6.533(0.013)$, $b=2.574(0.005)$, and $c=6.844(0.013)$ Å at 90 GPa (for the d spacings see Table I).

Assuming continuity of molecular volume through the ϵ - ζ phase transition,¹⁴ ζ -N₂ contains eight molecules per cell. The highest symmetry space group consistent with the observed systematic extinctions is $Pmma$. It is impossible to keep a 3/1 ratio of different molecules characteristic of ϵ -N₂ (Ref. 21) in the orthorhombic setting unless one uses an unrealistically large cell. Sixteen atoms per cell are possible on three sites of symmetry, $8l$, $4i$, and $4j$. The atoms on the $36f$ site in the ϵ phase therefore split into two sites in the ζ phase, (e.g., Ref. 22). Hence, the ratio of the molecules on the different symmetry sites becomes 2/1/1. ζ -N₂ results from a slight distortion of the rhombohedral structure. Raman and IR data are in excellent agreement with the structural model proposed. At the ϵ - ζ transition, the strongest Raman peak splits and gives rise to a higher frequency component, and no frequency discontinuity is observed. Group theory predicts an increase in the number of Raman-active modes in the ζ phase ($3A_{1g}+B_{1g}+B_{3g}$ Raman-active vibrons compared to $2A_g+E_g$ in the ϵ phase), which reflects the increase in the number of sites with distinct molecular site symmetries.

B. ζ - κ transition

Above 115 GPa (Figs. 2 and 3), the x-ray patterns show two new peak splittings, indicating further lowering of cell symmetry, consistent with Raman vibron branching^{3,19,21,23} and appearance of additional IR vibron bands,⁶ both reported at above 100 GPa. Since ζ -N₂ has an orthorhombic structure and changes are slight, we fitted a monoclinic structure for this new phase (named κ here). To estimate the unit cell volume, we again assumed that the number of molecules per cell is such that the volume discontinuity is small. At

TABLE I. Observed and fitted d -spacings of ϵ (47 GPa), ζ (90 GPa), and κ (130 GPa) nitrogen and their corresponding Miller indices.

ϵ -N ₂			ζ -N ₂			κ -N ₂		
hkl	Observed (Å)	Fitted (Å)	hkl	Observed (Å)	Fitted (Å)	hkl	Observed (Å)	Fitted (Å)
110	3.448	3.447	011	2.409	2.410	220/300	2.300	2.308/2.305
202	2.556	2.556	003	2.283	2.281	001	2.281	2.288
113	2.383	2.383	111	2.257	2.261	-101	2.196	2.192
104	2.285	2.285	103	2.152	2.154	101	2.151	2.152
211	2.201	2.300	301	2.081	2.075	030/-111	2.069	2.067
122	2.053	2.053	112	1.967	1.962	130	1.981	1.981
300	2.000	1.990	211	1.939	1.939	-201	1.935	1.936
024	1.903	1.905	203	1.892	1.870	201	1.884	1.881
220	1.726	1.724	302	1.832	1.837	320/-211	1.852	1.850/1.848
312	1.570	1.570				121	1.765	1.768
						131	1.484	1.491

130 GPa, fitted cell parameters with the highest figure of merit are $a=6.918(\pm 0.014)$ Å, $b=6.202(\pm 0.014)$ Å, $c=2.289(\pm 0.003)$ Å, and $\beta=91.774(\pm 0.2)^\circ$ (for the list of the d spacings see Table I). We find that the volume discontinuity at the ζ to κ transition is about 2%. The pressure-volume relations were fitted by the Vinet equation of state ($K_{T,0}=20.1$ GPa, $K'_{T,0}=4$ GPa; Fig. 5) and show a smaller compressibility than for δ -N₂ and ϵ -N₂ phases.¹⁸

C. Higher pressure transitions

Starting from a pressure of 110 GPa, the sample was heated several times to 800–900 K to initiate the transformation to the nonmolecular phase as detected by Raman and visible light absorption measurements. At 130 GPa, after the heating, the sample (which was opaque with no detectable Raman vibron) showed the x-ray pattern of the κ -N₂ presented in Fig. 2 with no changes of intensities or positions of the diffraction peaks. We estimate that at this pressure after

the heat treatment, the quantity of the η phase was at least 50% by volume. Further increase in pressure and subsequent heating below 1000 K led to a gradual disappearance of the diffraction lines leaving only one broad diffuse peak at $2\theta \sim 12.5^\circ$ which can be traced to the 302 peak of ζ -N₂ (Fig. 3). The observed width of the peak is too big to be explained by the pressure induced broadening and other mechanisms need to be employed. We attribute the broadening to pressure induced amorphization which confirms the conclusion about the disordered nature of η nitrogen previously inferred from optical data.^{6,7} Due to the low signal to noise ratio and the lack of the proper background data available at these pressures (>130 GPa), it is not possible to gain more reliable structural information on the disordered material at the moment.

The latter sample was kept under pressure at room temperature for about one year and periodically diffraction data were collected but no changes were detected. At 165 GPa,

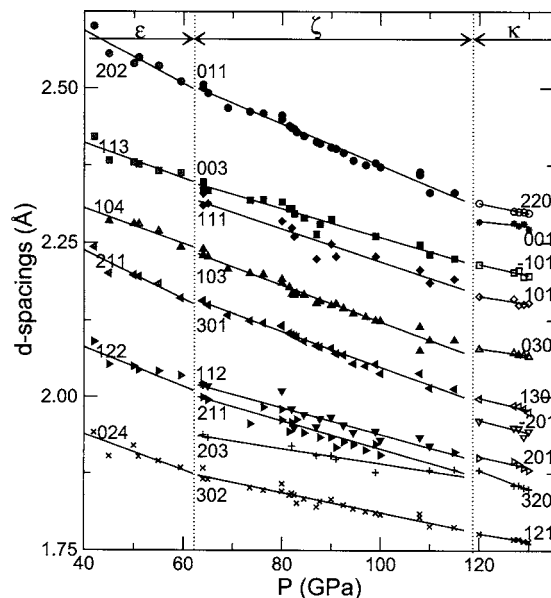


FIG. 3. d spacings of the ϵ , ζ , and κ phases as a function of pressure. For ϵ -N₂, data are from Ref. 18 up to 43.9 GPa. Solid lines are guides to the eyes.

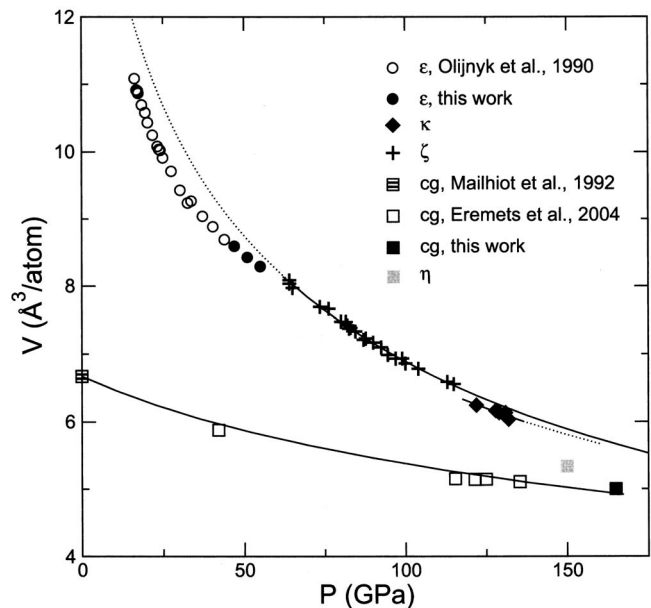


FIG. 4. Pressure-volume relation for ϵ -N₂, ζ -N₂, κ -N₂, and cg -N. The line through ζ -N₂ points corresponds to the fitted equation of state (see text). For ϵ , data are from Ref. 18 up to 43.9 GPa.

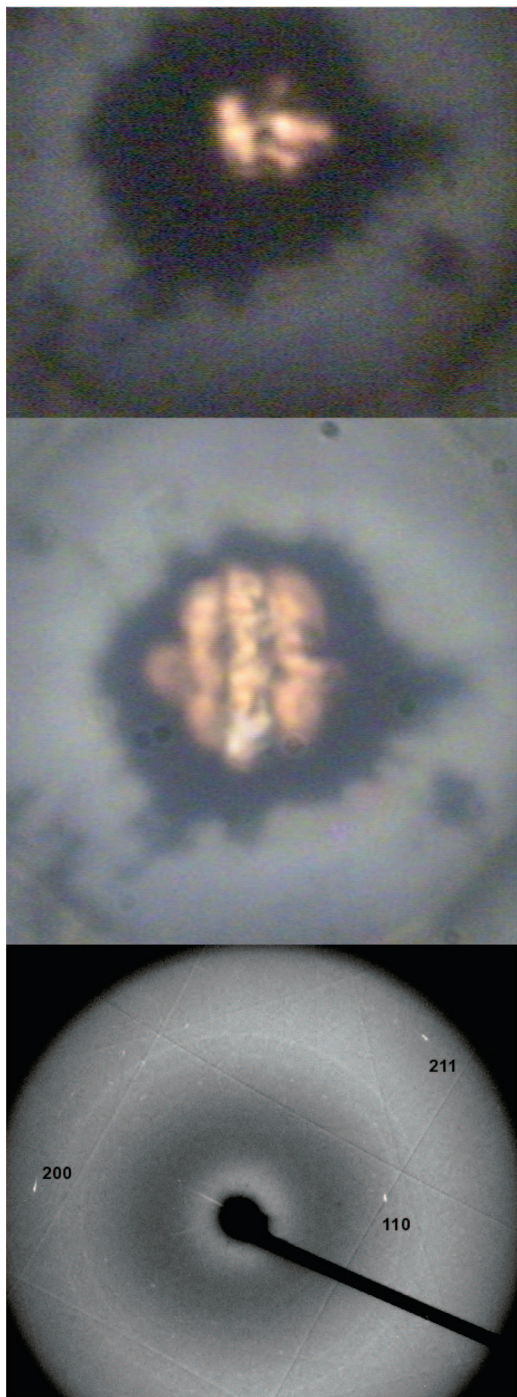


FIG. 5. (Color) Upper and middle panels: Transformations of nonmolecular semiconducting amorphous η nitrogen to crystalline insulating cg -N after laser heating. The photo was made with transmitting and reflecting white light. The dark areas are nonreacted η nitrogen and the white areas are the ones transformed to cg -N. Four traces of the IR laser beam used in the heating experiment are clearly visible in the middle panel. Lower panel: Diffraction image of the cg -N at 170 GPa showing the well defined spots indicative of the several single crystals formed during the heating.

the sample was finally laser heated to temperatures in excess of 2000 K (see Fig. 2 to see the P - T conditions described here). The sample strongly absorbed the near IR laser radiation.^{6,7} This resulted in the transformation to a translucent crystalline phase (see Fig. 5, upper panels). Further, x-ray diffraction showed that the sample has become highly textured and single crystal-like (Fig. 5, lower panel) with a

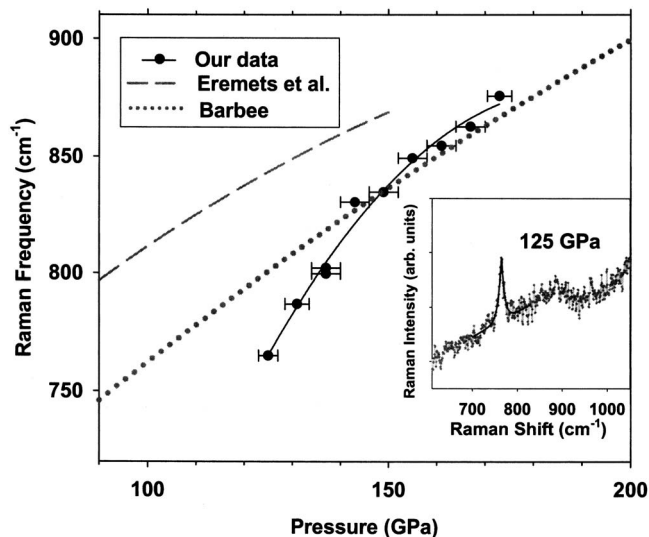


FIG. 6. Pressure dependence of the A symmetry Raman mode. Solid symbols, this work; gray dotted line, Ref. 24; and gray dashed line, Ref. 12. Inset: Raman spectra at 125 GPa.

diffraction pattern consistent with the cg structure having $a = 3.42(1)$ Å at 165 GPa, in broad agreement with previous experiment¹² and theory.⁵ Raman spectroscopy also showed good agreement with theoretical calculation of the vibrational frequencies²⁴ (see Fig. 6). Four Raman bands are predicted for the cubic-gauche phase, $A+E+2T$. Our Raman spectra of the cg phase show a weak peak, corresponding to the mode of A symmetry (Fig. 7). The weak intensity is probably due to the only partial transformation of the sample into cg -N. Higher frequency modes of E and T symmetries are expected to be even weaker by 1%–3% of the mode A intensity as obtained from density functional theory (DFT) calculations,²⁵ so they could not be observed. The pressure dependence of the A mode differs from that reported by Eremets *et al.*, but it is close to that calculated theoretically in Ref. 24.

IV. DISCUSSION

The study of the sequence of transformations of nitrogen to megabar pressures with and without heating reconciles

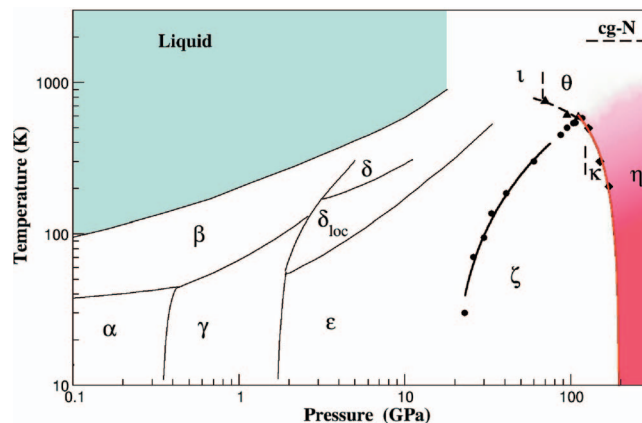


FIG. 7. (Color) Schematic representation of transformation observed in nitrogen. Shaded areas are the noncrystalline and liquid states. The transformation lines between molecular and nonmolecular phases and between ι - and θ -nitrogen are kinetic boundaries. The positions of ι - and θ -N₂ are from Ref. 9. The melting curve is from Ref. 28.

previously reported structural and optical observations. Figure 7 summarizes the higher P - T phases of nitrogen, including both stable and metastable phases. High pressure molecular phases have structures derived from the ϵ phase by lowering the unit cell symmetry. Molecular site symmetries also change at these transitions, and the distribution of molecules at different sites changes. The different pressure dependence of the Raman spectrum compared to previous experiments and difference in the appearance of the x-ray pattern powderlike¹² versus single crystal-like indicate a need for further experimental study. For both the ϵ - ζ and ζ - κ transitions, Raman spectroscopy shows that the phases have closely related structures,^{3,19,22} in agreement with the structural data presented here: both structures derive from ϵ by lowering of the symmetry. There is no measurable volume discontinuity at the ϵ - ζ transformation but, instead, slight change of the slope at the transition pressure. This fact suggests a continuous second-order phase transition which is supported by the smooth change of the Raman frequencies through the transition²⁰ and indicative of the higher compressibility of the ζ - N_2 . In contrast, the ζ - κ transformation has a small ($\sim 2\%$) volume discontinuity (see Fig. 4). The κ - N_2 is the densest molecular phase observed before transformation to the nonmolecular state. Nonmolecular amorphous semiconducting nitrogen formed without heating likely has a distribution of different coordination environments. It is possible that η is close to cg -N but has defects (e.g., not all nitrogens three coordinated); these then anneal out on heating to produce well crystallized wide band gap material.

We comment on the apparent discrepancies between experiment and theory (e.g., for the transformation pressure to the non-molecular phase) and between different theoretical calculations [from 50 GPa (Ref. 5) to 94 GPa (Ref. 26)]. On the other hand, the calculations assumed simplified ideal molecular structures because more complex “real” structures were not known and are more difficult to treat theoretically.^{5,26,27} The newly characterized ζ and κ phases are denser than the ϵ - N_2 , which has been used as a prototype molecular phase in theoretical calculations.^{5,26,27} In order to obtain the volume of the molecular phase at the molecular-to-atomic transition, we extrapolated the equation of state of ζ - N_2 up to 150 GPa. The volume obtained is $11.87 \text{ \AA}^3/\text{molecule}$ ($5.935 \text{ \AA}^3/\text{at.}$). The molecular volume of κ is about 2% smaller than the volume predicted by the

equation of state of ζ at the same pressure. Since at the transition pressure the volume of the nonmolecular phase is predicted to be close to $5 \text{ \AA}^3/\text{at.}$,^{5,26,27} the volume change would be 15%, much smaller than theoretical estimations of 25%–35%.^{26,27} We suggest that the use of the true molecular structure in the DFT calculation would shift the molecular-to-atomic transition line to a higher pressure (>100 GPa), making it closer to that experimentally observed.

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- ¹R. J. Hemley, *Annu. Rev. Phys. Chem.* **51**, 763 (2000).
- ²H. B. Radousky *et al.*, *Phys. Rev. Lett.* **57**, 2419 (1986).
- ³R. Reichlin *et al.*, *Phys. Rev. Lett.* **55**, 1464 (1985).
- ⁴P. M. Bell, H. K. Mao, and R. J. Hemley, *Physica B & C* **139–140**, 16 (1985).
- ⁵C. Mailhot, L. H. Yang, and A. K. McMahan, *Phys. Rev. B* **46**, 14419 (1992).
- ⁶A. F. Goncharov *et al.*, *Phys. Rev. Lett.* **85**, 1262 (2000).
- ⁷E. Gregoryanz, A. F. Goncharov, R. J. Hemley, and H. K. Mao, *Phys. Rev. B* **64**, 052103 (2001).
- ⁸M. Eremets, R. J. Hemley, H. K. Mao, and E. Gregoryanz, *Nature (London)* **411**, 170 (2001).
- ⁹E. Gregoryanz *et al.*, *Phys. Rev. B* **66**, 224108 (2002).
- ¹⁰W. Mattson, D. Sanchez-Portal, S. Chiesa, and R. Martin, *Phys. Rev. Lett.* **93**, 125501 (2004).
- ¹¹H. L. Yu *et al.*, *Phys. Rev. B* **73**, 012101 (2006).
- ¹²M. Eremets *et al.*, *Nat. Mater.* **3**, 558 (2004).
- ¹³M. Eremets *et al.*, *J. Chem. Phys.* **121**, 11296 (2004).
- ¹⁴E. Gregoryanz *et al.*, *J. Chem. Phys.* **124**, 16102 (2006).
- ¹⁵M. Hanfland *et al.*, *Rev. High Pressure Sci. Technol.* **7**, 787 (1998).
- ¹⁶E. Gregoryanz *et al.*, *Phys. Rev. Lett.* **90**, 175701 (2003).
- ¹⁷E. Gregoryanz *et al.*, *Phys. Rev. Lett.* **94**, 185502 (2005).
- ¹⁸H. Olijnyk, *J. Chem. Phys.* **93**, 8968 (1990).
- ¹⁹H. Olijnyk and A. P. Jephcoat, *Phys. Rev. Lett.* **83**, 332 (1999).
- ²⁰A. F. Goncharov, E. Gregoryanz, H. K. Mao, and R. J. Hemley, *Low Temp. Phys.* **27**, 866 (2001).
- ²¹R. L. Mills, B. Olinger, and D. Cromer, *J. Chem. Phys.* **84**, 2837 (1986).
- ²²R. Bini, L. Ulivi, J. Kreutz, and H. Jodl, *J. Chem. Phys.* **112**, 8522 (2000).
- ²³A. Goncharov and E. Gregoryanz, in *Chemistry under Extreme Conditions*, edited by R. Manaa (Elsevier Science, New York 2005), pp. 241–267.
- ²⁴T. Barbee, *Phys. Rev. B* **48**, 9327 (1993).
- ²⁵M. Lazzeri (private communications).
- ²⁶A. K. McMahan and R. LeSar, *Phys. Rev. Lett.* **54**, 1929 (1985).
- ²⁷R. M. Martin and R. J. Needs, *Phys. Rev. B* **34**, 5082 (1986).
- ²⁸D. Young *et al.*, *Phys. Rev. B* **35**, 5353 (1987).