

Experimental and theoretical study of Li_3N at high pressure

Allen C. Ho, Maurice K. Granger, and Arthur L. Ruoff

Department of Materials Science and Engineering, Cornell University, Ithaca, New York 14853

P. E. Van Camp and V. E. Van Doren

Department of Physics, University of Antwerpen (RUCA), Groenenborgerlaan 171, B-2020 Antwerpen, Belgium

(Received 16 December 1997; revised manuscript received 13 August 1998)

X rays from the Cornell High Energy Synchrotron Source were used to study the crystal structure of Li_3N over a pressure range of 0 to 35 GPa at ambient temperature. Before loading, both the hexagonal D_{6h}^4 ($P6_3/mmc$) and the hexagonal D_{6h}^1 ($P6/mmm$) phases were present. At modest pressure, the D_{6h}^1 structure transforms completely into the D_{6h}^4 structure. A two-parameter Birch equation was fitted to the data to determine the equation of state (EOS) of the D_{6h}^4 structure, which is compared with a theoretical equation of state produced by our total-energy calculations in the framework of the local-density approximation. The experimental EOS was then used to determine the change in Gibb's free energy as a function of pressure for Li_3N to 35 GPa at ambient temperature. The likelihood of a phase transition to a cubic structure at 35 GPa (as calculated by theory) based on observed optical changes is discussed. [S0163-1829(99)06609-6]

I. INTRODUCTION

The compound lithium nitride, Li_3N , has many interesting physical and chemical properties.¹ Lithium nitride is a superionic conductor.² A more fundamental aspect of Li_3N is that it may be a compound known to have N^{3-} ions in an anomalous state.^{3,4} Multiply charged anions such as O^{2-} and N^{3-} , though unstable as free ions, are stabilized by the electrostatic potential in a crystal. It is well known that the large intraionic polarizability of the O^{2-} ion plays a vital role in the lattice dynamical properties of alkaline earth oxides such as MgO .⁵ It is expected that the N^{3-} ions will also play a significant role in the lattice dynamics of Li_3N .

The crystal structure of Li_3N was shown to be a hexagonal D_{6h}^1 ($P6/mmm$) structure at room temperature.⁶ The existence of a high-pressure phase was first revealed in a nuclear magnetic resonance (NMR) experiment.⁷ Subsequently, this high-pressure phase was confirmed by powder x-ray diffraction to have a hexagonal D_{6h}^4 ($P6_3/mmc$) structure when the compound was annealed under 1 GPa of N_2 pressure.⁸ The lattice dynamic of Li_3N has been investigated by a number of groups using inelastic neutron scattering,⁹ infrared and Raman spectroscopy,¹⁰ and *ab initio* calculations.¹¹ However, these studies all involved the D_{6h}^1 structure at ambient pressure.

Interestingly, lithium nitride has been used by reacting it with gallium chloride, GaCl_3 , in a solution of benzene to produce nanosized crystals of GaN .¹² This method used by Xie *et al.* is similar to a hydrothermal process where positive pressure was generated by heating benzene in an autoclave. Since the kinetics at the crystal-fluid interface is profoundly affected by the nature of the fluid and the temperature, there is a potential for using other organic as well as inorganic solvents at higher temperatures to grow large crystals of GaN . However, at higher temperatures, higher pressures are required to insure the stability of the GaN .¹³ Therefore, to more fully understand the thermodynamics of GaN growth

using Li_3N , the EOS for Li_3N was measured up to 35 GPa and compared with an *ab initio* calculation. The EOS was then used to calculate the change in Gibb's free energy as a function of pressure or normalized volume.

II. THEORETICAL MODEL

In the present work the total energies at different pressures of Li_3N in the D_{6h}^1 , D_{6h}^4 , and T_d^1 structures were calculated. The last structure (which has four molecules per cell) was included because it is the structure of the related compound Li_3Bi . The calculations were performed in the framework of the local-density approximation using ultrasoft pseudopotentials¹⁴ and a large plane-wave basis (kinetic energy cutoff of 100 Ry). For the exchange-correlation part we used the Ceperley-Alder expression¹⁵ as parametrized by Perdew and Zunger.¹⁶ The optimization of the lattice parameters and of the internal parameters was performed with the Broyden-Fletcher-Goldfarb-Shanno algorithm.¹⁷ The calculated total energies were then fitted to the two-parameter Birch equation of state¹⁸ from which the bulk modulus and its pressure derivative were determined.

III. EXPERIMENT

Lithium nitride powder of 99.5% purity was purchased from Strem Chemical Inc. The powder had a dark red color and was opaque. A preliminary powder x-ray-diffraction pattern indicated that both the hexagonal D_{6h}^4 ($P6_3/mmc$) and the hexagonal D_{6h}^1 ($P6/mmm$) structures were present at ambient pressure.

Static pressure was generated by the use of a diamond-anvil cell. Two separate experiments were carried out. A pair of 1/3-carat brilliant-cut diamond anvils with 300- μm flat culets was employed for this experiment. Sample handling was done in an argon environment since lithium nitride is hygroscopic. The powder was loaded, without pressure medium, into a 100- μm hole drilled in the center of a prein-

TABLE I. The calculated lattice constants, bulk moduli, and their pressure derivatives for several structures.

Crystal structure	a (Å)	c (Å)	V_0 (Å ³ /atom)	u (Å)	u' (Å)	c/a	B_0 (GPa)	B'_0
D_{6h}^1	3.508	3.745	9.978			1.0674	61.02	3.70
D_{6h}^4	3.418	6.100	7.715	0.5776		1.7846	78.166	3.77
T_d^1	4.824		7.016	0.250	0.750		82.75	3.84

dentified T301 stainless-steel gasket. Pressures were determined *in situ* from the calibrated shift of the ruby R_1 fluorescence line.¹⁹

Energy-dispersive x-ray diffraction (EDXD) measurements were performed at room temperature at the Cornell High Energy Synchrotron Source (CHESS). A $25 \times 25 \mu\text{m}^2$ aperture was used to collimate the polychromatic white beam. A Bragg diffraction angle of 6° was maintained throughout this experiment. Because of the low scattering efficiency of this low- Z material, long exposure times (~ 10 h) were required for pressures above 30 GPa.

IV. RESULTS AND DISCUSSION

A. Theoretical results

The calculated lattice constants, bulk moduli, and their pressure derivatives for Li_3N are given in Table I. The calculated ground state at zero pressure is the D_{6h}^4 structure. The calculated transition between the D_{6h}^1 and D_{6h}^4 is at a negative pressure (-1.1 GPa) with a volume increase of 23% and an energy difference at the transition of only 16 meV/atom. The transition from D_{6h}^4 to T_d^1 is computed to be at

37.9 GPa, with a volume decrease of 8% and an energy difference at the transition of 109 meV/atom.

B. Experimental results

Upon loading, the D_{6h}^1 ($P6/mmm$) structure was completely transformed to the D_{6h}^4 ($P6_3/mmc$) structure. The D_{6h}^1 structure was not observed at or above the lowest pressure of 3 GPa. This is in good agreement with the theory and the NMR experiment.⁷ Some representative EDXD spectra of Li_3N are shown in Fig. 1 at several pressures. Five diffraction peaks from this phase were indexed and followed as a function of pressure to 35 GPa. The indexed peaks are listed in Table II. The other peaks are mainly due to Li_2O and the T301 steel gasket (hcp-Fe). The contribution from the gasket was likely due to leakage around the slits used to collimate the incident beam. This has been eliminated for future studies.

The d spacings vs volume are shown in Fig. 2, and the c/a ratio as a function of the unit-cell volume is shown in Fig. 3. Furthermore, within the error of this experiment the c/a ratio is in good agreement with the calculation (see Table I).

In Fig. 4, the experimental data are shown in comparison with our *ab initio* calculation. The experimental pressure-volume data were fitted to the two-parameter Birch equation of state (EOS) of the form¹⁸

$$P = \frac{3}{2} B_0 \left[\left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right] \times \left\{ 1 + \frac{3}{4} (B'_0 - 4) \left[\left(\frac{V}{V_0} \right)^{-2/3} - 1 \right] \right\},$$

where B_0 is the bulk modulus at ambient pressure, and B'_0 is the derivative of the bulk modulus. The parameters of the fit are $B_0 = 74 \pm 6$ GPa and $B'_0 = 3.7 \pm 0.7$, with $V_0 = 8.763 \text{ \AA}^3$

TABLE II. Observed d spacings for x-ray-diffraction peaks of Li_3N at 8.6 GPa are compared to calculated d spacings for the D_{6h}^4 ($P6_3/mmc$) structure at $E_d = 58.612 \pm 0.026$ keV Å.

hkl	d_{obs} (Å)	d_{calc} (Å)
002	3.082	3.083
100	2.997	3.001
101	2.700	2.699
110	1.734	1.733
103	1.699	1.696

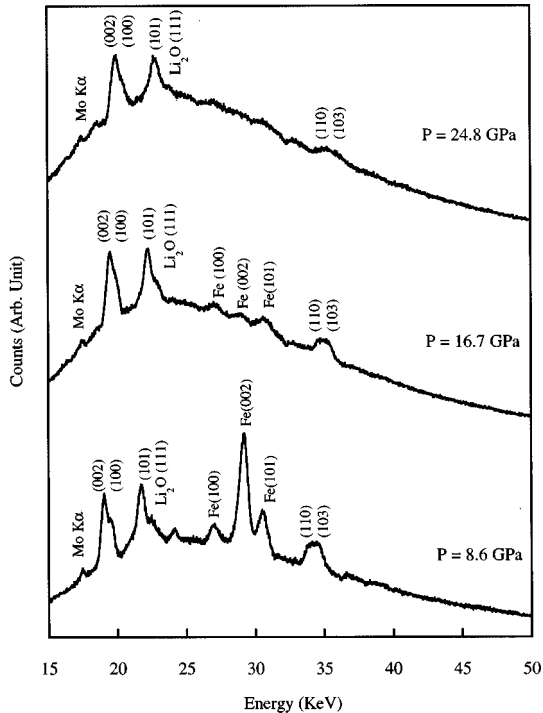


FIG. 1. The EDXD spectra of Li_3N at high pressures. The indexed peaks are followed as a function of pressure to 35 GPa.

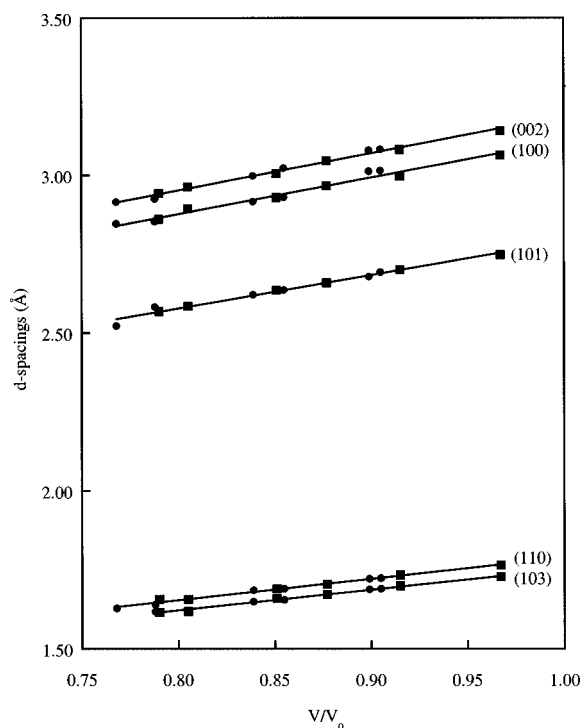


FIG. 2. Volume dependence of the d spacings of Li_3N . The solid lines are simple linear fit to the data. Solid squares and solid circles represent run 1 and run 2, respectively.

per atom. These values are in good agreement with the parameters produced by the *ab initio* calculation (see Table I).

The change in the Gibb's free energy of lithium nitride was calculated by integrating VdP . Figure 5 shows the

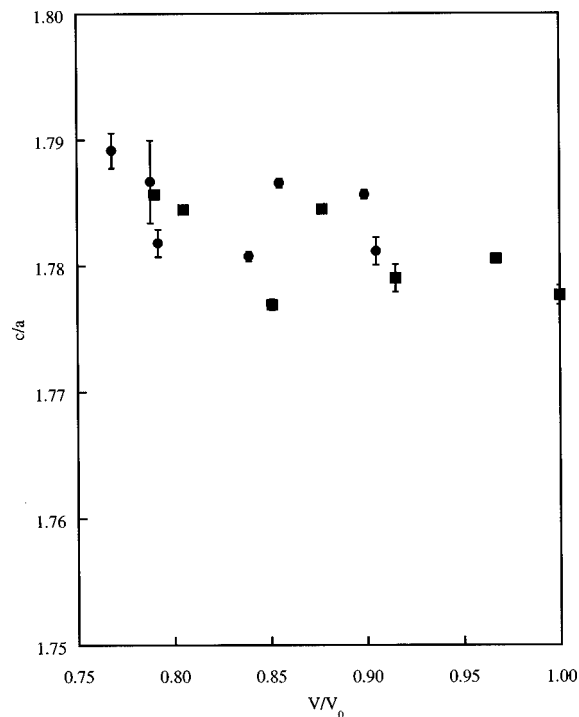


FIG. 3. Volume dependence of the c/a ratio of Li_3N . Solid squares and solid circles represent run 1 and run 2, respectively. The average c/a ratio is 1.783 ± 0.004 . The calculated c/a ratio is 1.7846.

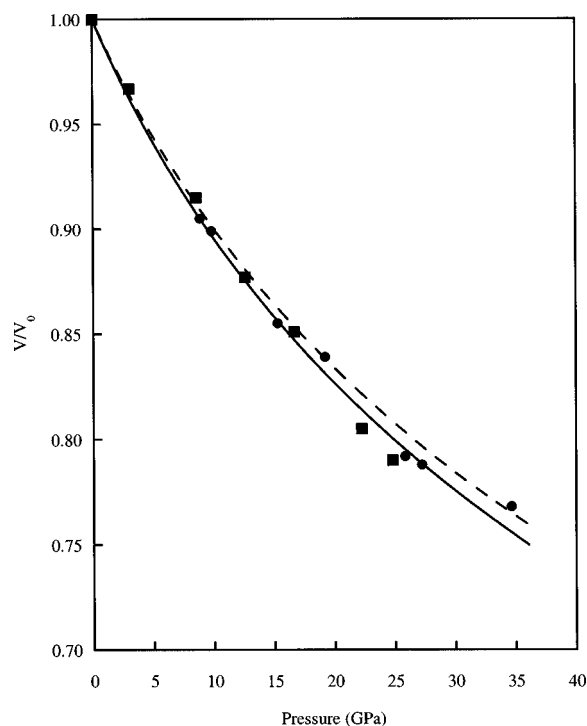


FIG. 4. The equation of state of Li_3N . Solid squares and solid circles represent run 1 and run 2, respectively. The solid curve is the fit of the two-parameter Birch equation of state to the experimental data. The dashed curve is the calculated equation of state.

Gibb's free energy as a function of volume or pressure.

The spectra degraded significantly as the pressure was increased to above 26 GPa. Analysis of the spectra became extremely difficult due to the weakness of the peaks. Upon close examination, it was discovered that a small fraction of the sample began to transmit light in orange-red at about 28 GPa. At pressures above 35 GPa, nearly the entire sample became translucent. Moreover, the sample appeared to have a granular texture. The sample became increasingly opaque on unloading and was totally opaque when the pressure was

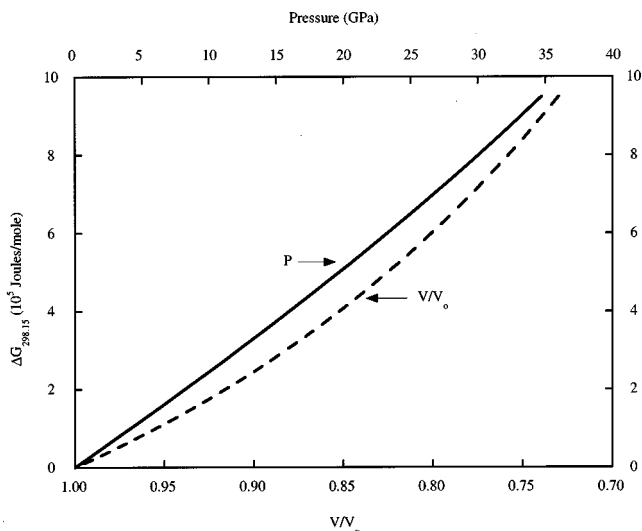


FIG. 5. The Gibb's free energy of Li_3N as a function of pressure (solid curve) and normalized volume (dashed curve) calculated from the equation of state.

below 5 GPa. This procedure was repeated several times and the results have been consistent.

The fact that the sample becomes transparent at the pressure at which the x-ray pattern changes suggests two possibilities. First, the new phase is indeed cubic as suggested by theoretical calculation. Optically, there is negligible internal scattering from a polycrystalline aggregate because cubic crystals are not birefringent. Another possibility is that the sample is gradually becoming amorphous, causing the diffraction pattern to weaken as the pressure increases. However, this question cannot be answered without further Raman study.

V. CONCLUSION

Lithium nitride, Li_3N , exists in both the hexagonal D_{6h}^4 ($P6_3/mmc$) and the hexagonal D_{6h}^1 ($P6/mmm$) structures at ambient pressure. The hexagonal D_{6h}^1 ($P6/mmm$) structure transforms into the hexagonal D_{6h}^4 ($P6_3/mmc$) at modest pressure. Theoretical calculations show the latter phase to be the stable phase at ambient conditions. The equation of

state (EOS) of the D_{6h}^4 phase has been measured up to 35 GPa and it is shown to be in good agreement with our *ab initio* calculation. The Gibb's free energy of Li_3N as a function of pressure has been calculated using this equation of state. Theoretical calculations suggest a transition to a cubic phase at 38 GPa. The thinness of the low-Z sample and the line broadening due to plastic deformation of this phase precluded x-ray determination of this phase with the present technique. Much thicker samples and the use of a hydrostatic pressure medium are required. Experimentally we observed that the opaque sample begins to change to a translucent sample at approximately 28 GPa. This optical change is a possible indicator of a transition to a cubic phase.

ACKNOWLEDGMENTS

The authors would like to thank the staff of Cornell High Energy Synchrotron Source (CHESS) for their assistance. We appreciate the support of the Office of Naval Research (ONR) under Grant No. N00014-96-1-1105.

-
- ¹A. Rabenau, in *Advances in Solid State Physics*, edited by J. Treusch (Vieweg, Braunschweig, 1978), Vol. 18, p. 77–108; *Solid State Ionics* **6**, 277 (1982).
- ²B. A. Boukamp and R. A. Huggins, *Mater. Res. Bull.* **13**, 23 (1978).
- ³G. Bhattacharya, H. Bilz, H. Brendecke, H. R. Chandrasekhar, R. Migoni, G. Müller, A. Rabenau, B. Reiser, E. Schönherr, H. Schulz, U. Von Alpen, and E. Wagner, in *Proceedings of the International Conference on Lattice Dynamics* (Flammarion, Paris, 1978), p. 133–135.
- ⁴H. Schulz and K. Schwarz, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.* **43**, 999 (1978).
- ⁵R. Haberkorn, M. Buchanan, and H. Bilz, *Solid State Commun.* **12**, 681 (1973).
- ⁶A. Rabenau and H. Schulz, *J. Less-Common Met.* **50**, 155 (1976).
- ⁷M. Mali, J. Roos, and D. Brinkmann, *Phys. Rev. B* **36**, 3888 (1987).
- ⁸S. Mitrokhina, K. Burdina, and K. Semenko, *Moscow Univ. Chem. Bull.* **45**, 89 (1990).
- ⁹W. Kress, H. Grimm, W. Press, and J. Lefebvre, *Phys. Rev. B* **22**, 4620 (1980).
- ¹⁰H. R. Chandrasekhar, G. Bhattacharya, R. Migoni, and H. Bilz, *Solid State Commun.* **22**, 681 (1977); *Phys. Rev. B* **17**, 884 (1978).
- ¹¹J. Sarnthein, K. Schwarz, and P. E. Blöchl, *Phys. Rev. B* **53**, 9084 (1996).
- ¹²Y. Xie, Y. Qian, W. Wang, S. Zhang, and Y. Zhang, *Science* **272**, 1926 (1996).
- ¹³J. Karpinski, J. Jun, and S. Porowski, *J. Cryst. Growth* **66**, 1 (1984).
- ¹⁴N. Troullier and J. L. Martins, *Solid State Commun.* **74**, 613 (1990); *Phys. Rev. B* **43**, 1993 (1991).
- ¹⁵D. Ceperley and B. Alder, *Phys. Rev. Lett.* **45**, 566 (1980).
- ¹⁶J. P. Perdew and A. Zunger, *Phys. Rev. B* **23**, 5048 (1981).
- ¹⁷J. Olsen and P. Jorgensen, *J. Chem. Phys.* **77**, 6109 (1982).
- ¹⁸F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- ¹⁹H. K. Mao, P. M. Bell, J. W. Shaner, and D. J. Steinberg, *J. Appl. Phys.* **49**, 3276 (1978).