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Structure of N_2 at 2·94 GPa and 300 K

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Abstract. A single crystal of β-N_2 was grown in a Merrill–Bassett diamond-anvil cell and examined by X-ray diffraction at 2·94 (6) GPa and 300 (2) K. As observed in an earlier high-pressure study, the structure is hexagonal, space group $P6_3/mmc$, with two molecules per unit cell. The lattice constants are $a = 3{\cdot}595$ (1) and $c = 5{\cdot}845$ (1) Å, giving a molar volume of 19·71 (1) cm^3. The value of R_w, refined from 9 observed reflections, is 0·041, for a model with statistically disordered molecules tilted 54° from the c axis, and 0·040 for a spherically disordered model. Calculations using a Gordon–Kim electron-gas model show that the $P6_3/mmc$ structure has a minimum energy when the N_2 molecules are tilted at an angle of 51°.

Introduction. The phase boundaries of a few solidified gases have now been measured over a wide range of pressures and temperatures by X-ray diffraction and optical scattering in diamond-anvil cells. In general, the two competing effects of pressure and temperature combine to force molecules into new and interesting structures. An important goal of solid-state theorists is to be able to predict from *a priori* considerations the structures and phase diagrams of these simple molecular crystals.

In an attempt to learn the way subtle differences in molecular interactions affect structures, Cromer, Schiferl, LeSar & Mills (1983) recently studied CO which is a molecule having almost identical charge and mass as N_2. They found that hexagonal β-CO (space group $P6_3/mmc$) at 2·7 GPa and room temperature is composed of molecules tilted 49° from the c axis, statistically disordered, and randomly polarized. This form of disorder appears to be somewhat different from that reported for β-N_2 by Schiferl, Cromer & Mills (1978), whose X-ray data indicated that N_2 molecules in the solid at 2·5 GPa and 296 K are arranged as in the zero-pressure solid (Streib, Jordan & Lipscomb, 1962), where the N_2 molecules are either precessing around the c axis at an angle of 54·5 (25)°, or statistically disordered at this angle.

A later refinement of β-N_2 by Jordan, Smith, Streib & Lipscomb (1964) favored the precession model, but with the N_2 molecules tipped at 56·0 (25)°. Press & Hüller (1978), however, pointed out the difficulty in choosing between a model with spherically disordered molecules and one with molecules statistically disordered at an angle ψ from the c axis near 54·7°, where the $(3\cos^2\psi - 1)$ terms in the spherical Bessel functions that describe the structure factors go to zero.

Unfortunately, the available X-ray intensity data for β-N_2 at high pressure (Schiferl *et al.*, 1978) are not as accurate as those for β-CO (Cromer *et al.*, 1983). To see whether the disorder in these two closely related solids is, indeed, different, we carried out an improved study of N_2. Reported here are X-ray diffraction measurements on a single crystal of β-N_2 in a diamond cell at 2·94 GPa and 300 K. The structure is hexagonal ($P6_3/mmc$), with molecules most likely statistically distributed about the c axis and tilted 54°, compared to 49° for β-CO (Cromer *et al.*, 1983). This finding is consistent with the earlier results of Schiferl *et al.* (1978), although there remains a possibility that the molecules in β-N_2 are spherically disordered.

Experimental. A diamond-anvil cell (Merrill & Bassett, 1974), modified to utilize stronger beryllium pieces (Schiferl, 1977) and to provide uniform X-ray absorption and better optical access (Keller & Holzapfel, 1977), was loaded with N_2 by the immersion technique (Schiferl *et al.*, 1978). Pressures were measured with the ruby-fluorescence method, assuming the R_1 lineshift to be given by the linear relation $d\lambda/dP = 0{\cdot}365$ nm GPa^{-1} (Forman, Piermarini, Barnett & Block, 1972; Barnett, Block & Piermarini, 1973).

We pressurized the sample at room temperature to 3 GPa where two N_2 crystals of approximately equal size were formed. One of the crystals was favorably oriented in the cell so at least one reflection for each of the non-equivalent (hkl) types could be observed. We made X-ray measurements on this crystal at an average pressure of 2·94 (6) GPa and temperature of 300 (2) K.

Our measurements were made on an Enraf–Nonius CAD-4 X-ray diffractometer, using graphite-monochromatized Mo $K\alpha$ radiation. Since this diffractometer is not compatible with the eight-position Hamilton (1974) technique for most reflections, we substituted the King & Finger (1979) four-position modified technique to center the reflections in determining lattice constants. The four-position method,

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however, does not allow an independent determination of all diffractometer alignment errors, so we adjusted the diffractometer in a separate experiment with a ruby test crystal under ambient conditions.

The lattice constants of the hexagonal unit cell (see *Abstract*) were determined from a least-squares refinement of four reflections, each with $13° < 2\theta < 15°$. We were limited in the number of reflections we could use and in their 2θ values because of a large ($B > 6$ Å^2) Debye–Waller factor. The wavelength of Mo $K\alpha_1$ radiation was taken as $\lambda = 0{\cdot}7093$ Å.

Intensity data were collected with ω scans and processed by the method of Cromer & Larson (1977). We made multiple scans of the weakest reflections to improve statistics. All reflections not shadowed by the high-pressure cell were measured out to $2\theta = 31°$. Assuming our N_2 crystal had space group $P6_3/mmc$, we found 40 non-space-group extinguished reflections, which were reduced to 11 non-equivalent reflections. Of these, 9 were observed according to the criterion $I \geq 3\sigma(I)$. We judged absorption corrections to be unnecessary. A comparison of equivalent reflections gave $R_F = 0{\cdot}050$ (Cromer & Larson, 1977).

With the assignment of two molecules per unit cell, we calculate a molar volume V of 19·71 (1) cm^3 for β-N_2 at 2·94 GPa and 300 K. Equation-of-state (EOS) measurements by Mills, Liebenberg & Bronson (1975) show that at 300 K nitrogen freezes at 2·44 GPa into a solid with $V = 20{\cdot}39$ cm^3. Taking the compressibility of solid N_2 to be about 0·9 times that of the fluid, we extrapolated the EOS data to 2·94 GPa and 300 K and obtained $V = 19{\cdot}61$ cm^3, in excellent agreement with the present results.

Structure refinements were performed on β-N_2 using all of the realistic models suggested by Streib *et al.* (1962). We tested the following models, which assume space group $P6_3/mmc$:

1. Statistically disordered molecules with their intramolecular axes tilted from the crystalline c axis. The molecules are centered at the 2(d) positions $\frac{1}{3},\frac{2}{3},\frac{3}{4}$; $\frac{2}{3},\frac{1}{3},\frac{1}{4}$. They are probably not rotating, but exhibit a static disorder that can be described by placing $\frac{1}{6}$ nitrogen atom at the site 24(l). Refinements were performed for tilt angles of 45, 50, 53, 54, 55, 56, 57, and 60°.
2. Spherically disordered molecules centered on sites 2(d). The scattering factor for a spherically disordered N_2 molecule is taken from Cromer, Mills, Schiferl & Schwalbe (1981).*
3. Intramolecular axis parallel to the c axis. This model is generated by placing nitrogen atoms at the 4(f) site.

In all cases the intramolecular distance was fixed at the gas-phase value of 1·10 Å (Sutton, 1958). The values of x, y, and z in model 1 were chosen to produce equally spaced points about the $\bar{6}$ axis. The small number of reflections, coupled with uncertainties due to the large thermal motion (Busing & Levy, 1964), preclude an independent determination of the N—N bond length. Only two parameters were refined for each model, the scale factor and an isotropic temperature factor B.

Table 1. *Observed and calculated structure factors* ×10 *for* N_2 *at* 2·94 GPa *and* 300 K, *in order of increasing Bragg angle*

hkl	F_o	F_c^{a*}	F_c^b	F_c^c
100	719	711	711	803
002	1253	1277	1303	567
101	1054	1028	1025	998
102	327	349	347	175
110	459	401	408	633
103	266	247	252	88
200	<121	105	−110	212
112	189	217	−202	152
201	150	157	159	273
004	127	94	156	246
202	154	59	52	52
Tilt angle (°)		54	—	0
x		0·2096	—	$\frac{1}{3}$
y		0·5429	—	$\frac{2}{3}$
z		0·8053	—	0·8441
B(Å^2)		6·5 (9)	6·5 (8)	10·1 (7)
R_w		0·040	0·040	0·370
R		0·049	0·050	0·379
Goodness of fit		3·07	2·64	24·70

* (a), (b), (c) Models 1, 2 and 3, respectively, are described in the text.

The observed structure factors are compared in Table 1 with values calculated from each of the models described above. For model 1 only the results for a tilt angle yielding the minimum value of R_w are given. Values for R_w as a function of tilt angle (ψ) are: 0·119 (45°), 0·068 (50°), 0·043 (53°), 0·041 (54°) (best), 0·042 (55°), 0·046 (56°), 0·052 (57°), and 0·077 (60°).

Discussion. The results in Table 1 show that model 2 with a spherical charge density, fits the data slightly better than model 1 with a tilt angle of 54°. Nevertheless, considering the paucity of data, we do not feel we can choose between the two models on this basis alone. As Press & Hüller (1978) pointed out, the intensities of low-angle reflections related to H_{00} and H_{20} do not distinguish between a spherical distribution of the electron density and a 54·7° precession model. In principle, one might determine which of the two models is correct by fitting higher surface harmonics. Press & Hüller (1978) show, however, that even for a single-crystal neutron-diffraction experiment, which would be more favorable than the present X-ray one, deducing the higher surface harmonics would be very difficult.

Solid β-CO (Cromer *et al.*, 1983) under similar crystal conditions (2·7 GPa and 299 K) has a close-packed hexagonal structure with exactly the same c/a ratio (1·626) and almost the same molar volume

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* In Table 3 of Cromer *et al.* (1981) the coefficient c for calculating the scattering factor of a freely rotating N_2 molecule should read: $c = -113{\cdot}24$. The numbers in Table 3 are correct.

(20·05 cm^3) as the present N_2 sample. From X-ray measurements on CO, the 'tilted-molecule' model with a tilt angle of 49° is clearly preferable to a model with spherically disordered molecules.

Calculations were performed on N_2 in the $P6_3/mmc$ structure using a recently reported theory that allows computation of the structure-dependent energy of molecular crystals at 0 K (LeSar & Gordon, 1982,1983). Based on the Gordon–Kim electron-gas model for calculating short-range interactions between molecules (Gordon & Kim, 1972), the theory requires no empirical or adjustable parameters. To find the optimum orientations of the molecules in the $P6_3/mmc$ structure, the unit-cell parameters and molecular centers of mass were fixed at the experimental high-pressure room-temperature values (Schiferl *et al.*, 1978) and the free energy was then minimized by varying the molecular orientations. Although many initial orientations were tried, only a few energy-equivalent minima were found. In the optimum configurations, the molecules point toward square faces in the cage of h.c.p. lattice points that surround the molecules (Streib *et al.*, 1962). For each energy minimum, the projections of the orientation vectors (with positive *c* components) of the two molecules in the unit cell onto the *ab* plane are collinear, but with opposite direction.

A final minimum energy was found for molecules tilted relative to the *c* axis at an angle of 51°. The nitrogen molecules definitely prefer to align along specific directions in the unit cell, with positions consistent with the 'tilted-molecule' model. Similar calculations on CO (Cromer *et al.*, 1983) gave tilt angles of 48 and 50° for polarized and unpolarized molecules, respectively. For both N_2 and CO, we find that the optimum angle is determined by the short-range intermolecular forces. The two molecular systems have slightly different electronic structures and, therefore, shapes. Considering the similarities in the calculated properties of these systems, the most likely structure for β-N_2 is best described by statically disordered molecules tilted relative to the *c* axis.

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Synthèse et Structure d'un Niobate de Césium non Stoechiométrique, $Cs_3Nb_{5,96}O_{16,4}$

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Abstract. $M_r = 1214{\cdot}86$, orthorhombic, *Amam*, $a = 18{\cdot}315\,(3)$, $b = 24{\cdot}506\,(4)$, $c = 7{\cdot}296\,(2)$ Å, $V = 3274{\cdot}6$ Å^3, $Z = 8$, $D_x = 4{\cdot}93$ Mg m^{-3}, $\lambda = 0{\cdot}7107$ Å, μ(Mo $K\alpha$) = 10·9 mm^{-1}, $F(000) = 4324{\cdot}48$, room temperature, $R = 0{\cdot}040$ for 3034 reflections. The crystal composition is very close to $Cs_2O.2Nb_2O_5$ but the

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