

References

- BARDOS, D. I. & BECK, P. A. (1966). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **236**, 64–69.
- BARDOS, D. I., MALIK, R. K., SPIEGEL, F. X. & BECK, P. A. (1966). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **236**, 40–48.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
- JOHNSON, C. K. (1976). *ORTEP-II*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
- KOMURA, Y., SLY, W. G. & SHOEMAKER, D. P. (1960). *Acta Cryst.* **13**, 575–585.
- KRIPYAKEVICH, P. I. & YARMOLYUK, Y. P. (1970). *Dopov. Akad. Nauk Ukr. RSR, Ser. A*, **32**, 948–951.
- KUZMA, YU. B. & HLADYSHEVSKII, E. I. (1964). *Zh. Neorg. Khim.* **9**, 674–681.
- KUZMA, YU. B., HLADYSHEVSKII, E. I. & CHERKASHIN, E. E. (1964). *Zh. Neorg. Khim.* **9**, 1898–1904.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERQ, J. P. & WOOLFSON, M. M. (1978). *MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univ. of York, England, and Louvain, Belgium.
- MANOR, P. C., SHOEMAKER, C. B. & SHOEMAKER, D. P. (1972). *Acta Cryst.* **B28**, 1211–1218.
- SAMSON, S. (1967). *Acta Cryst.* **23**, 586–600.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1963). *Acta Cryst.* **16**, 997–1009.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1967). *Trans. Am. Inst. Min. Metall. Pet. Eng.* **239**, 937–940.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1976). *Acta Cryst.* **B32**, 2306–2313.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1977). *Acta Cryst.* **B33**, 743–754.
- SHOEMAKER, C. B. & SHOEMAKER, D. P. (1978). *Acta Cryst.* **B34**, 701–705.
- YVON, K., JEITSCHKO, W. & PARTHÉ, E. (1969). *A Fortran IV Program for the Intensity Calculation of Powder Patterns*. Univ. of Pennsylvania.
- ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

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The Structure of N_2 at 49 kbar and 299 K*

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Abstract

A single crystal of N_2 at 49 kbar (4.9 GPa) and 299 K was produced in a Merrill–Bassett diamond-anvil high-pressure cell and examined by X-rays. Pressure was determined by the ruby-fluorescence method. The unit cell is cubic, $a_0 = 6.164$ (1) Å, space group $Pm\bar{3}n$, with eight molecules per unit cell. The structure is the same as that of β - F_2 and γ - O_2 at 50 K and atmospheric pressure. For seven refined parameters and 19 observations the final R_w is 0.0488.

Introduction

As a continuation of studies of N_2 at high pressure (Schuch & Mills, 1970; Mills, Liebenberg & Bronson, 1975; Schiferl, Cromer & Mills, 1978; Schwalbe, Schiferl, Mills, Jones, Ekberg, Cromer, LeSar & Shaner, 1980; LeSar, Ekberg, Jones, Mills, Schwalbe &

Schiferl, 1979), we made X-ray diffraction measurements on a single crystal of N_2 in a diamond cell at 49 kbar and 299 K. The structure is the same as that of β - F_2 (Jordan, Streib & Lipscomb, 1964) and γ - O_2 (Jordan, Streib, Smith & Lipscomb, 1964; Cox, Samuelsen & Beckurts, 1973).

Experimental

A Merrill–Bassett 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 by total immersion in liquid N_2 as described by Schiferl *et al.* (1978). Pressure was measured according to the ruby-fluorescence scale, assuming the R_1 line shift to be given by the linear relation, $d\lambda/dp = 0.365$ Å kbar⁻¹ (Forman, Piermarini, Barnett & Block, 1972; Barnett, Block & Piermarini, 1973).

Preparation of a single crystal for X-ray studies at 49 kbar was difficult because N_2 undergoes a phase

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transition from a h.c.p. structure at lower pressure (Schiferl *et al.*, 1978). By annealing the sample for two months at room temperature, a low-strain single crystal was obtained. This crystal was used for the present X-ray work and for Raman work reported elsewhere (Schwalbe *et al.*, 1980).

Preliminary X-ray photographs taken with a precession camera showed the N₂ sample to be a single crystal, but unfortunately not oriented so that a well-populated and identifiable reciprocal-lattice net could be recorded on film. The crystal was then placed on an automated Picker diffractometer and, eventually, the lattice was shown to be cubic. The lattice constant, $a_0 = 6.164(1) \text{ \AA}$, was determined by a least-squares refinement of six reflections, each measured by the eight-position Hamilton (1974) technique. This technique, which is particularly valuable when the crystal is not visible, permits the true values of 2θ , ω , and χ to be determined, even when the crystal is miscentered, and also permits any miscentering to be corrected.

Intensity data were collected and processed in the manner described by Cromer & Larson (1977). All reflections not shadowed by the pressure cell were

measured out to $2\theta = 41^\circ$ with graphite-monochromated Mo $K\alpha$ radiation. Systematic extinctions (hkl present only if $l = 2n$) indicated that the space group was $Pm\bar{3}n$. There were 294 non-space-group-extinct reflections which were reduced to 30 non-equivalent observations, 19 of which were observed according to the criterion $I \geq 3\sigma(I)$. Absorption corrections were judged to be unnecessary. A comparison of equivalent reflections gave $R_F = 0.036$ (Cromer & Larson, 1977).

Structure refinement

The unit-cell size and space group suggested that the structure might be the same as that of $\beta\text{-F}_2$ (Jordan, Streib, Smith & Lipscomb, 1964). Subsequent least-squares refinement confirmed this identity.

A drawing of the structure is shown in Fig. 1. The unit cell contains eight N₂ molecules giving a calculated molar volume of $17.63 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. In the unit cell there are two crystallographically different kinds of disordered N₂ molecules which we call type 1 and type 2. The two molecules centered at the $2(a)$ position, 000 and $\frac{111}{222}$, are type 1. These molecules are either freely rotating or, more probably, are statically disordered so they lie with equal probability along one of the four body diagonals. This static disorder, described by $\frac{1}{4}$ atom at xxx in the set $16(i)$ with $x = 0.045$, is shown in Fig. 1. The other six N₂ molecules are type 2 and are disordered about the $6(d)$ site. The best fit to the data has $\frac{1}{4}$ atom in the general position $48(l)$ with the statically disordered molecules assuming one of four positions near the $6(d)$ positions, as shown in Fig. 1. This model approximates hindered rotation.

Another possibility would be for the type-2 N₂ molecules to be freely rotating in a plane. Jordan, Streib & Lipscomb (1964) examined this model and concluded that a planar rotor did not fit their data. In view of their conclusions and the good fit already achieved, we did not think it worthwhile to test the planar rotor model.

Table 1 summarizes the models tested. Model 4 is better than model 3 at the 95% confidence level

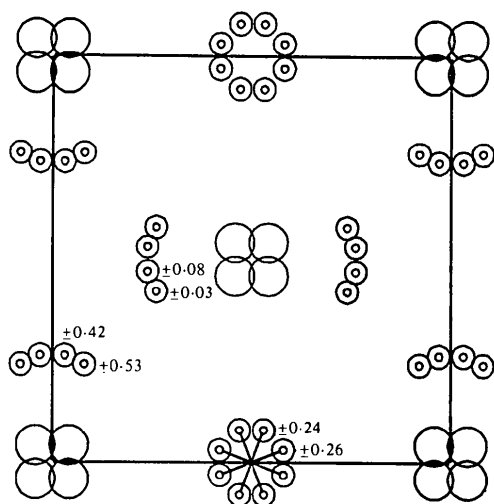


Fig. 1. Projection of the 49 kbar N₂ structure along the z axis. The origin is at the lower left. The x axis is horizontal and the y axis is vertical. The numbers indicate the z coordinates. There are mirrors at $x, y, z = 0$ and $\frac{1}{2}$.

Table 1. Summary of models tested for N₂ at 49 kbar and 299 K

Model	x	y	z	$B(\text{\AA}^2)$	Number of parameters	R	R_w	Goodness of fit
1. Spherical N ₂ at origin	0	0	0	3.3 (9)	5	0.0652	0.0902	6.0
$\frac{1}{4}$ N in set 24(k)	0	0.261 (4)	0.415 (2)	4.9 (6)				
2. $\frac{1}{4}$ N in set 16(i)	0.049 (4)	0.049 (4)	0.049 (4)	4.6 (19)	6	0.0561	0.0771	5.3
$\frac{1}{4}$ N in set 24(k)	0	0.260 (4)	0.415 (5)	5.1 (5)				
3. Spherical N ₂ at origin	0	0	0	3.4 (6)	6	0.0503	0.0584	4.0
$\frac{1}{4}$ N in set 48(l)	0.236 (3)	0.532 (4)	0.080 (2)	4.7 (4)				
4. $\frac{1}{4}$ in set 16(i)	0.042 (7)	0.042 (7)	0.042 (7)	7.3 (24)	7	0.0407	0.0488	3.5
$\frac{1}{4}$ N in set 48(l)	0.239 (3)	0.531 (4)	0.080 (2)	5.2 (4)				

Table 2. Comparison of observed structure factors for N₂ at 49 kbar and 299 K with those calculated for model 4

<i>h k l</i>	10 <i>F</i> _o	10 <i>F</i> _c	<i>h k l</i>	10 <i>F</i> _o	10 <i>F</i> _c
1 1 0	11	9	3 3 2	22	21
2 0 0	235	233	4 2 2	37	32
2 1 0	264	259	4 3 0	23	19
2 1 1	240	241	4 3 1	<12	9
2 2 0	30	36	5 1 0	<14	10
3 1 0	18	19	4 3 2	<11	3
2 2 2	93	85	5 2 0	<15	13
3 2 0	62	63	5 2 1	<12	0
3 2 1	64	66	4 4 0	<17	4
4 0 0	110	114	5 3 0	<16	11
4 1 0	52	54	4 3 3	<13	1
4 1 1	26	24	5 3 1	<13	7
3 3 0	30	30	6 0 0	28	35
4 2 0	48	47	4 4 2	<15	10
4 2 1	43	39	6 1 0	<14	11

Table 3. Scattering factor for a freely rotating N₂ molecule

Coefficients for the analytical fit for $\sin \theta/\lambda < 0.65 \text{ \AA}^{-1}$ are $a_1 = 110.400$, $b_1 = -0.03292$, $a_2 = 7.07882$, $b_2 = 16.0314$, $a_3 = 5.46793$, $b_3 = 5.27849$, $a_4 = 4.28718$, $b_4 = 35.5795$, $c = 113.24$ (*International Tables for X-ray Crystallography*, 1974).

$\sin \theta/\lambda$ (\AA^{-1})	<i>f</i>	$\sin \theta/\lambda$ (\AA^{-1})	<i>f</i>	$\sin \theta/\lambda$ (\AA^{-1})	<i>f</i>
0.00	14.00	0.16	8.45	0.38	0.96
0.01	13.96	0.17	7.94	0.40	0.65
0.02	13.87	0.18	7.45	0.42	0.38
0.03	13.73	0.19	6.96	0.44	0.15
0.04	13.53	0.20	6.49	0.45	0.05
0.05	13.28	0.22	5.59	0.46	-0.04
0.06	12.99	0.24	4.76	0.48	-0.21
0.07	12.65	0.25	4.38	0.50	-0.34
0.08	12.27	0.26	4.01	0.55	-0.54
0.09	11.86	0.28	3.33	0.60	-0.67
0.10	11.41	0.30	2.73	0.65	-0.71
0.11	10.95	0.32	2.20	0.70	-0.66
0.12	10.46	0.34	1.73	0.80	-0.40
0.13	9.97	0.35	1.51	0.90	-0.03
0.14	9.46	0.36	1.32	1.00	+0.19
0.15	8.95				

(Hamilton, 1965). Although R_w improves markedly for each of the four models, the improvement is significant only at the 95% level because the number of observations is only 19. Table 2 gives observed and calculated structure factors for model 4.

The scattering factor for a spherically disordered N₂ molecule, calculated for an N—N distance of 1.098 Å, is given in Table 3.

Discussion

The apparent N—N intramolecular distance is 0.89 Å for the type-1 molecules and 1.06 Å for the type-2 molecules. When corrected for the large thermal

motion, the distances become 0.99 and 1.13 Å, respectively. These distances approximate the zero-pressure value of 1.098 Å. Raman data (LeSar *et al.*, 1979) indicate that an increase in pressure from 0 to 49 kbar should cause a decrease in N—N length of only 0.2%. The number of data is too small to consider more sophisticated models that might yield more reliable N—N distances.

The empirical equation-of-state for fluid N₂ determined by Mills *et al.* (1975) yields a molar volume at 49 kbar and 299 K of $17.62 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$. This value differs by less than 0.1% from that found here for the solid. The good agreement indicates that the volume discontinuities at the phase boundaries are small, which is consistent with the observations by Schuch & Mills (1970) that the molar volumes of α -, β -, and γ -N₂ around the triple point differ from each other by less than 1%.

The splitting of the N₂ stretching-mode frequency, as observed with Raman spectroscopy (LeSar *et al.*, 1979), has a natural explanation in terms of our model 4 for the N₂ crystal structure at 49 kbar. The molecules occupy two sites of different symmetries and, therefore, are subject to somewhat different intermolecular potentials. Moreover, the 2.8 ratio observed in the intensities of the Raman peaks may be related to the fact that there are three times as many atoms in the 48(*l*) site as there are in the 16(*i*) site.

The molecules in the α , β , and γ phases of N₂ all have coordination 12, whereas the molecules in the β -F₂ structure are somewhat more densely packed. The nearly spherically disordered molecules at 000 and $\frac{111}{222}$ also have 12 coordination, but each of the remaining molecules has coordination 14. As Jordan, Streib, Smith & Lipscomb (1964) noted, the β -F₂ structure represents a kind of close packing of nonspherical molecules with limited disorder. The β -F₂ structure appears as a high-temperature phase in F₂ and O₂ and now in N₂, although for N₂ high pressure is also required. Thus this phase seems to occur when the temperature is sufficiently high that electric and magnetic forces can no longer orient the molecules and the requirement of efficient packing predominates. The β -F₂ structure may well be a common high-temperature high-pressure form for condensed diatomic gases.

We thank B. Olinger for lending us the diamond-anvil cell. We acknowledge useful discussions with R. LeSar, L. H. Jones and R. C. Hanson concerning the inferences about structure that could be drawn from the Raman data. Crystallographic calculations were performed on a CDC 7600 using the LASL system of crystallographic programs developed primarily by A. C. Larson.

Note: M. J. Clouter informed us that a group at Memorial University of Newfoundland, St. John's,

Newfoundland, Canada, measured Raman scattering in zero-pressure γ -O₂ and found a splitting, formerly overlooked, of about one wave number in the vibrational spectrum. The higher-frequency peak has one-third the intensity of the lower-frequency one. A paper describing the results was submitted by H. Kiefert, M. J. Clouter, N. H. Rich & S. F. Ahmand to *Chem. Phys. Lett.*

References

- BARNETT, J. D., BLOCK, S. & PIERMARINI, G. J. (1973). *Rev. Sci. Instrum.* **44**, 1–9.
- COX, D. E., SAMUELSEN, E. J. & BECKURTS, K. H. (1973). *Phys. Rev. B*, **7**, 3102–3111.
- CROMER, D. T. & LARSON, A. C. (1977). *Acta Cryst.* **B33**, 2620–2627.
- FORMAN, R. A., PIERMARINI, G. J., BARNETT, J. D. & BLOCK, S. (1972). *Science*, **176**, 284–285.
- HAMILTON, W. C. (1965). *Acta Cryst.* **28**, 502–510.
- HAMILTON, W. C. (1974). In *International Tables for X-ray Crystallography*, Vol. IV, pp. 282–284. Birmingham: Kynoch Press.
- International Tables for X-ray Crystallography* (1974). Vol. IV, p. 99. Birmingham: Kynoch Press.
- JORDAN, T. H., STREIB, W. E. & LIPSCOMB, W. N. (1964). *J. Chem. Phys.* **41**, 760–764.
- JORDAN, T. H., STREIB, W. E., SMITH, H. W. & LIPSCOMB, W. N. (1964). *Acta Cryst.* **17**, 777–778.
- KELLER, R. & HOLZAPFEL, W. B. (1977). *Rev. Sci. Instrum.* **48**, 517–523.
- LESAR, R., EKBERG, S. A., JONES, L. H., MILLS, R. L., SCHWALBE, L. A. & SCHIFERL, D. (1979). *Solid State Commun.* **32**, 131–134.
- MERRILL, L. & BASSETT, W. A. (1974). *Rev. Sci. Instrum.* **45**, 290–294.
- MILLS, R. L., LIEBENBERG, D. H. & BRONSON, J. C. (1975). *J. Chem. Phys.* **63**, 4026–4031.
- SCHIFERL, D. (1977). *High Temp.–High Pressures*, **9**, 71–75.
- SCHIFERL, D., CROMER, D. T. & MILLS, R. L. (1978). *High Temp.–High Pressures*, **10**, 493–496.
- SCHUCH, A. F. & MILLS, R. L. (1970). *J. Chem. Phys.* **52**, 6000–6008.
- SCHWALBE, L. A., SCHIFERL, D., MILLS, R. L., JONES, L. H., EKBERG, S., CROMER, D. T., LESAR, R. & SHANER, J. (1980). Proc. VII Int. AIRAPT Conf., LeCreusot, France. To be published.

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Structure de l'Antimoniate de Baryum BaSb₃O₅(OH)

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Abstract

The structure of BaSb₃O₅(OH) has been determined by single-crystal X-ray techniques. The crystals are monoclinic, space group $P2_1/c$, with $a = 8.974$ (5), $b = 5.714$ (2), $c = 14.195$ (6) Å, $\beta = 100.69$ (5)°, $Z = 4$, $d_m = 5.54$, $d_c = 5.56$ Mg m⁻³, $\mu(\text{Mo } K\alpha) = 16.86$ mm⁻¹. The structure has been determined by Fourier syntheses. After anisotropic least-squares calculations, the final R value was 0.042 for 2878 independent reflexions. The structure consists of chains of (Sb₃O₆)_n³ⁿ⁻ parallel to [100]. These chains are linked to form tunnels, into which the Sb^{III} lone pairs project.

Introduction

Dans le cadre des recherches effectuées sur l'étude de l'environnement des atomes présentant une paire

électronique non liée, nous avons été amenés à envisager avec intérêt les phases existant dans le système Sb₂O₃–H₂O–Ba(OH)₂. Nous exposons ici les résultats obtenus pour le composé BaSb₃O₅(OH) ainsi que nos conclusions concernant l'environnement de l'atome d'antimoine au degré d'oxydation III et plus spécialement l'influence stéréochimique de la paire non liée à cet atome.

Parmi les antimoniates(III et V) connus, seul l'antimoniate(V) de baryum BaSb₃O₆ a été préparé et étudié jusqu'alors (Coffeen, 1956; Felten, 1957).

La préparation des phases en milieu fondu est difficile par suite de l'agressivité du sesquioxyde d'antimoine vis à vis des métaux nobles, de sa volatilité et de son caractère réducteur.

Dans ce travail, la phase cristallisée BaSb₃O₅(OH) est en équilibre avec les solutions saturées dont le rapport molaire BaO/Sb₂O₃ est supérieur à 2.