We are presently extending our measurements to energies of the pump light greater than the band-gap energy. The author thanks Dr. G. Lampel for his constant interest and encouragement; also, it is a pleasure to thank Professor Solomon for very helpful discussions, and Dr. P. Lavallard and the other members of the Benoit à la Guillaume group for the loan of a sample and the use of their equipment.

[1]A. Kastler, J. Phys. Radium 11, 255 (1950).

[2]N. V. Karlov, J. Margerie, and M. D'Aubigne, J. Phys. Radium 24, 717 (1963).

[3]J. Brossel and J. Margerie, in Paramagnetic Resonance, edited by W. Low (Academic Press, Inc., New York, 1963), Vol. 2, p. 535.

[4]S. Geschwind, R. J. Collins, and A. L. Schawlow, Phys. Rev. Letters 3, 545 (1959); J. Brossel, S. Geschwind, and A. L. Schawlow, Phys. Rev. Letters 3, 548 (1959).

[5]G. Lampel, Phys. Rev. Letters 20, 491 (1968), and Proceedings of the International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (Nauka, Leningrad, U.S.S.R., 1968), p. 1139.

[6]For a description of the band structure of GaSb see: M. L. Cohen and T. K. Bergstresser, Phys. Rev. 141, 789 (1966); G. Dresselhaus, Phys. Rev. 100, 580 (1955); C. W. Higginbothman, F. H. Pollak, and M. Cardona, in Proceedings of the International Conference on the Physics of Semiconductors, Moscow, U.S.S.R., 1968 (Nauka, Leningrad, U.S.S.R., 1968), p. 57.

[7]E. J. Johnson, I. Filinski, and H. Y. Fan, in Proceedings of the International Conference on the Physics of Semiconductors, Exeter, England, 1962 (The Institute of Physics and The Physical Society, London, England, 1962), p. 375.

[8]P. Lavallard, thesis, presented at the Faculté des Sciences de l'Université de Paris, 1968 (to be published).

[9]G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, Properties of the Thirty-Two Point Groups (Massachusetts Institute of Technology Press, Cambridge, Mass., 1963).

[10]See the discussion of the so-called "Transverse Optical Pumping Experiments" on gases by C. Cohen-Tannoudji and A. Kastler, in Progress in Optics, edited by E. Wolf (North-Holland Publishing Co., Amsterdam, The Netherlands, 1966), Vol. 5, p. 33.

[11]E. Adachi, J. Phys. Chem. Solids 30, 776 (1969).

[12]M. A. Habegger and H. Y. Fan, Phys. Rev. Letters 72, 99 (1964).

CRYSTAL STRUCTURE OF GAMMA NITROGEN*

R. L. Mills and A. F. Schuch

Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico 87544

We have determined by x-ray diffreaction that high-pressure gamma nitrogen is tetragonal with two molecules per unit cell in special position f of space group $P4_2/mnm$. At an average pressure and temperature of 4015 ± 145 atm and 20.5 ± 1.7 K, respectively, the unit cell dimensions are $a = 3.957$ Å and $c = 5.109$ Å, giving a molar volume of 24.09 cm^3 which is in good agreement with the value 24.05 cm^3 taken from piston-displacement measurements.

Solid nitrogen is known to form three modifications; the α phase, which is cubic and exists below 35.6 K at vapor pressure; the β phase, which is hexagonal and extends from 35.6 K up to the melting curve; and the recently discovered γ phase,[1,2] which exists above 3500 atm at low temperature, and the boundary lines of which form a triple point with the other two phases at 44.5 K and 4650 atm.

The experimental difficulties in carrying out diffraction experiments on solidified gases at high pressure are considerable and no previous attempt has been made to determine the crystal structure of γ nitrogen. Such a determination is of interest in showing how N_2 molecules, which are already closely packed in the α and β phases, can be compacted further under high pressure. A knowledge of the structure is also basic to the interpretation of any future studies[3] of the properties of γ N_2.

We have determined by means of x-ray diffraction the crystal structure of γ N_2. A special technique was used to fill the sample holder in which a measured amount of hcp N_2 was first formed near vapor pressure and cooled to 50 K. The pressure was then increased to around 4500 atm with fluid He and the temperature was lowered to about 20 K. During this latter process, the He

solidified and its contraction on cooling caused a pressure drop of about 400 atm giving a final sample pressure in the neighborhood of 4000 atm. The diffraction pattern from the few crystals of He that appeared in the x-ray beam was easily distinguished from that of N_2.

Two different sample cells were used. The first was machined from heat-treated aluminum alloy No. 7178[4] in the form of a cylinder of 0.063-in. o.d. and 0.020-in. i.d. The absorption of this cell was very high and, even with molybdenum radiation, exposure times of up to 16 h were required. The N_2 diffraction patterns were characteristic of polycrystals, and at several angles the reflections were masked by the Al background.

During the course of the work, a high-strength beryllium cell of 0.125-in. o.d. and 0.025-in. i.d. became available and was used with filtered copper radiation in a second series of experiments. The N_2 solidified as a powder in this larger cell and several additional reflections could be observed because the cell was quite transparent to x rays and because there was little coincidence of Be and N_2 diffraction lines on the film.

Flexible copper braid allowed the cell to be cooled from a liquid-He pot.[5] Constant temperatures between about 20 and 50 K could be maintained by balancing the cooling against electrical heating. Oscillation x-ray photographs were taken using either a flat-plate camera 5 cm from the cell or a circular camera with a 7-cm radius.

Twenty photographs were taken of N_2 in the γ phase at an average sample pressure of 4015 $\pm$ 145 atm and an average temperature of 20.5 $\pm$ 1.7 K. A composite of ten different reflections was observed which could be indexed on the basis of a tetragonal lattice with $a = 3.957$ and $c = 5.109$ Å. Assuming two molecules per unit cell, one
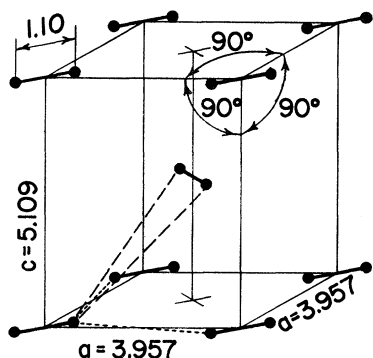
computes a molar volume of 24.09 cm^3, which is in good agreement with the value 24.05 cm^3 taken from the pVT data of Ref. 1.

Assuming that the surface of a molecule can be defined by its 0.002 contour level of electron density,[6] one computes[7] that N_2 molecules have the shape of a prolate spheroid with major and minor diameters of 4.34 and 3.39 Å, respectively. The size and shape of the N_2 molecule and the requirement of tetragonal symmetry place severe restrictions on possible locations and orientations of the two molecules in the unit cell. The structure which best fits all requirements is one in which the four atoms are at positions x, x, o; $\bar{x}, \bar{x}, o$; $\frac{1}{2}+x, \frac{1}{2}-x, \frac{1}{2}$; and $\frac{1}{2}-x, \frac{1}{2}+x, \frac{1}{2}$, where $2\sqrt{2}x$ is the interatomic distance in the molecule in units of the cell axis. For the interatomic distance, we used 1.100 Å. These locations are those of special position f of space group $P4_2/mnm$[8] and are shown in Fig. 1. Each atom has near neighbors in the order: one bound atom at 1.100 Å, two at 3.273 Å, eight at 3.447 Å, and four others at 3.957 Å, or one cell dimension away.

In Table I are presented the observed and cal-

Table I. Observed and calculated interplanar spacings and reflected intensities for tetragonal N_2.

hkl	d_{obs}[a] (Å)	d_{calc}[b] (Å)	I_{obs}	I_{calc}[c]
101	3.124	3.128	strong	661
110	2.778	2.798	medium	148
002	2.559	2.554	medium	122
111	2.451	2.454	weak	46
200	$\cdots$[d]	1.978	$\cdots$[d]	9
112	1.891	1.887	medium	58
120	1.763	1.770	weak	29
121	1.666	1.672	very weak	11
202	$\cdots$	1.564	$\cdots$	6
103	1.565	1.564	medium	35
122	1.450	1.455	weak	22
113	$\cdots$	1.455	$\cdots$	4
220	$\cdots$	1.399	$\cdots$	0.2
221	1.356	1.349	weak	21

[a]Average of 20 x-ray photos at $T = 20.5 \pm 1.7$ K and $p = 4015 \pm 145$ atm.

[b]Calculated from unit cell dimensions $a = 3.957$ Å and $c = 5.109$ Å obtained from least-squares fit of d_{obs}.

[c]Calculated assuming space group $P4_2/mnm$ for powder sample, Cu radiation, circular camera, interatomic distance 1.100 Å, and temperature parameter $B = 1.4$ Å^2.

[d]Possible N_2 reflection at this d value would be masked by a coincident diffraction line from either Be or Al cell.
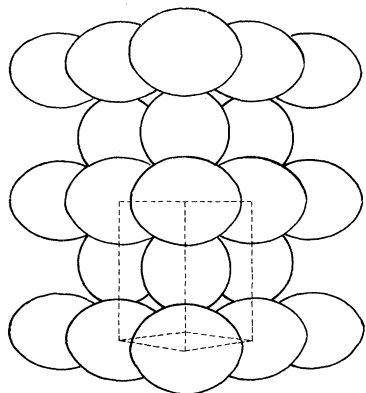

FIG. 1. Unit cell of γ N_2 (tetragonal) showing atom sites and cell dimensions in Å. Dotted lines connect nearest neighbors at 3.273 Å; dashed lines connect next-nearest neighbors at 3.447 Å.

FIG. 2. Perspective drawing of γ N_2 (tetragonal) viewed normal to (110) face showing close packing of prolate molecules.

culated interplanar spacings and reflected intensities for the proposed model of γ N_2. For hcp N_2 at low pressure, the constant B in the Debye-Waller temperature factor has been evaluated[9] as 1.53 Å^2. In keeping with the higher density and larger θ_D of tetragonal N_2, we have used the extimated value $B = 1.4$ Å^2 in computing the expected intensities of Table I.

The structure consists of two types of layers which are perpendicular to the unique axis of the unit cell as shown in Fig. 2. In one of these layers the molecules lie flat in a square array with their long axes parallel and directed along one of the square diagonals. Alternate layers are shift-ed with the molecules again lying flat and parallel, but with their long axes directed along the other square diagonal and at right angles to molecules in the adjoining layers. This arrangement would seem to minimize the electric-quadrupole-quadrupole energy of the crystal.

A complete treatment of the subject will be submitted to an appropriate journal and will include a discussion of the α and β phases at high pressure and all three phases in nitrogen 15.

[1]C. A. Swenson, J. Chem. Phys. <u>23</u>, 1963 (1955).
[2]J. W. Stewart, J. Phys. Chem. Solids <u>1</u>, 146 (1956).
[3]We are indebted to T. A. Scott and P. J. Haigh for pointing out to us the need for information about the structure of γ N_2.
[4]Metals Handbook, edited by T. Lyman (American Society for Metals, Metals Park, Ohio, 1961), 8th edition, Vol. I.
[5]R. L. Mills and A. F. Schuch, Phys. Rev. Letters <u>6</u>, 263 (1961).
[6]C. S. Barrett and Lothar Meyer, Phys. Rev. <u>160</u>, 694 (1967).
[7]R. F. W. Bader, W. H. Henneker, and P. K. Cade, J. Chem. Phys. <u>46</u>, 3341 (1967).
[8]International Tables for X-Ray Crystallography, The International Union of Crystallography, edited by N. F. M. Henry and K. Lonsdale (The Kynoch Press, Birmingham, England, 1952), Vol. I.
[9]W. E. Streib, T. H. Jordan, and W. N. Lipscomb, J. Chem. Phys. <u>37</u>, 2962 (1962).

OPTICAL DISPERSION AND THE STRUCTURE OF SOLIDS

S. H. Wemple and M. DiDomenico, Jr.
Bell Telephone Laboratories, Murray Hill, New Jersey 07974

A new energy parameter $\mathcal{E}_d$ is introduced to describe dispersion of the electronic dielectric constant. This dispersion energy is found to obey an extraordinarily simple empirical relation in the more than 50 ionic and covalent crystals for which reliable refractive-index dispersion data are available. Based on this result we derive a structure-dependent electronic dielectric response function consisting of constant optical-frequency conductivity with high- and low-frequency cutoffs.

A simple, physically appealing dielectric model of electronegativity and ionicity has been developed recently by Phillips and Van Vechten[1-3] using the concepts of homopolar and heteropolar energy gaps. These authors find that a so called "average energy gap" E_g can be computed for a large group of diatomic crystals using simple empirical expressions. This average gap may be decomposed into a homopolar gap E_h and a heteropolar gap C by the quadrature relation $E_g^2 = E_h^2 + C^2$ and is defined (apart from a factor of order unity) by the equation

$$E_g^2 = (\hbar\omega_p)^2/[\epsilon_1(0)-1], \tag{1}$$

where $\hbar\omega_p$ is the plasma energy of the valence electrons, and $\epsilon_1(0)$ is the static electronic dielectric constant ($\epsilon = \epsilon_1 + i\epsilon_2$).

In this Letter we introduce a new energy pa-