Piezoelectricity and crystal structure of α-nitrogen.* By J. R. Brookeman and T. A. Scott, *Department of Physics, University of Florida, Gainesville, Florida* 32601, *U.S.A.*

Detection of piezoelectric resonances from the low temperature α-phase of solid nitrogen confirms the crystal structure of this phase to be the noncentrosymmetric $P2_13$.

Nitrogen is known to exhibit three solid modifications depending on temperature and pressure, and whereas the structures of the β and γ forms are well established, there has been some doubt in the recent literature as to whether the low temperature α-phase belongs to space group $P2_13$ or $Pa3$. Since almost two dozen papers have been published on nitrogen during the past two years alone there is obviously much interest in the subject, and it is important to remove any uncertainty about the correct crystal structure. The most recent evidence for the $P2_13$ assignment comes from the careful single-crystal X-ray work of Jordan, Smith, Streib & Lipscomb (1964), who observed two faint reflections in violation of $Pa3$ symmetry. Recent X-ray work by Schuch & Mills (1970) was unable to confirm this. An electron diffraction study supports the $Pa3$ structure (Venables, 1970), and numerous infrared and Raman spectroscopy experiments (St. Louis & Schnepp, 1969; Brith, Ron & Schnepp, 1969; Cahill & Leroi, 1969; Anderson, Sun & Donkersloot, 1970), have found no evidence of the $P2_13$ structure, which because of its noncentrosymmetry would tend to produce coincidences between infrared and Raman frequencies. Theorists thus far have been unable to explain why the translational distortions of the $P2_13$ structure should occur for nitrogen as all the assumed crystalline potential models have led to a prediction of the equilibrium molecular locations in the $Pa3$ structure. All the recent calculations of lattice dynamics (Schnepp & Ron, 1969; Anderson, Sun & Donkersloot, 1970) have assumed a $Pa3$ structure and doubts have been raised that the true structure can be $P2_13$.

One simple way to distinguish between the two space groups is to test for piezoelectricity in α-nitrogen, because

the noncentrosymmetric $P2_13$ structure is piezoelectric whereas $Pa3$ is not. We have been engaged in an extensive study of nuclear quadrupole resonance (NQR) in solid nitrogen (Brookeman, McEnnan & Scott, 1971), and it is well known to users of this technique that a frequency modulated nuclear resonance spectrometer is also a sensitive detector of piezoelectric resonances (Frenkel, 1963). This fact is often a nuisance to NQR studies because the piezoelectric signals can interfere with the NQR signals which they resemble. Similar effects have also recently been reported for pulsed NQR in ferroelectric materials (Kessel, Safin & Goldman, 1971). As normally operated a NQR spectrometer contains the sample in the inductor coil of the LC resonant circuit, and detection of piezoelectric resonances occurs because of the electric fields across the coil. Greater sensitivity can be achieved by placing the sample between the capacitor plates instead, in the manner of Frenkel (1963) and Pepinsky, Baecklund, Diamant & Perdok (1954) based on the Giebe & Scheibe (1925) technique. We have observed piezoelectric resonances in α-nitrogen by both methods. Careful checks were made to ensure that the signals were indeed produced by the sample. There is no doubt therefore that the correct space group assignment is the noncentrosymmetric $P2_13$.

Piezoelectric signals from a 1·5 cm³ sample of nitrogen at a temperature of 4·2°K contained inside the inductor coil are shown in Fig. 1. These signals are the derivative recordings of the spectrometer absorption obtained using the conventional NQR technique of frequency modulation and lock-in amplifier detection to enhance the signal-to-noise ratio. Numerous resonances were observed reproducibly over a wide frequency range around 4 MHz. These signals were very weak and a Fabritek 1070 digital signal averager was employed to accumulate several scans through the frequency range selected. The signals were monitored as the sample was warmed from 4·2°K in a precision-temperature-controlled cryostat, and were found to persist throughout the temperature range of the α-phase. When the sample changed to the β-structure at the transition temperature of 35·6°K, the signals abruptly disappeared and only the background signal shown in Fig. 1 was observed.

Fig. 1. Spectrometer response *versus* frequency, 30 KHz scan at 3 MHz (*a*) α-Nitrogen at 4·2°K. (*b*) β-Nitrogen at 39°K.

References

Anderson, A., Sun, T. S. & Donkersloot, M. C. A. (1970). *Canad. J. Phys.* **48**, 2265.

Brith, M., Ron, A. & Schnepp, O. (1969). *J. Chem. Phys.* **51**, 1318.

Brookeman, J. R., McEnnan, M. M. & Scott, T. A. (1971). *Phys. Rev.* B **4**, 3661.
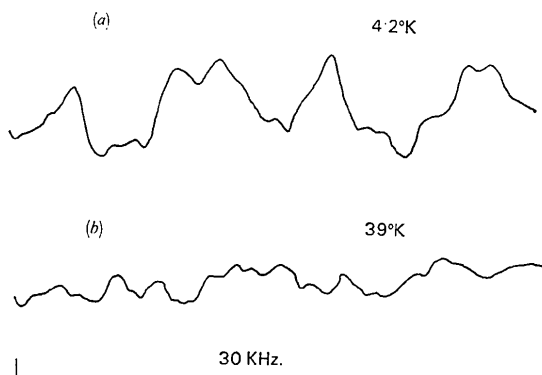
CAHILL, J. E. & LEROI, G. E. (1969). *J. Chem. Phys.* **51**, 1324.

FRENKEL, L. (1963). *J. Res. Natl. Bur. Std.* C67, 197.

GIEBE, E. & SCHEIBE, A. S. (1925). *Z. Phys.* **33**, 335, 760.

JORDAN, T. H., SMITH, H. W., STREIB, W. E. & LIPSCOMB, W. N. (1964). *J. Chem. Phys.* **41**, 756.

KESSEL, A. R., SAFIN, I. A. & GOLDMAN, A. M. (1971). *Sov. Phys. Solid State*, **12**, 2488.

PEPINSKY, R., BAECKLUND, J., DIAMANT, H. & PERDOK, W. G. (1954). *Rev. Sci. Instrum.* **25**, 1076.

SCHNEPP, O. & RON, A. (1969). *Discuss. Faraday Soc.* **48**, 26.

SCHUCH, A. F. & MILLS, R. L. (1970). *J. Chem. Phys.* **52**, 6000.

ST. LOUIS, R. V. & SCHNEPP, O. (1969). *J. Chem. Phys.* **50**, 5177.

VENABLES, J. A. (1970). *Phil. Mag.* **21**, 147.

Refinement of the crystal structure of α-N₂.*

By SAM J. LA PLACA and WALTER C. HAMILTON, *Chemistry Department, Brookhaven National Laboratory, Upton, New York 11973, U.S.A.*

An anisotropic refinement of previously collected X-ray diffraction data (Jordan, Smith, Streib & Lipscomb (1964). *J. Chem. Phys.* **41**, 746) confirms the displacement of the molecular center from the unit-cell origin ($X=0\cdot16\pm0\cdot02$ Å) and gives a librational amplitude of $17\pm5°$ and a mean atomic separation (uncorrected for thermal motion) of 1·05 (2) Å. Correction for the librational motion under the assumption of isotropic translational motion brings this value up to 1·15 (4) Å, in satisfactory agreement with the gas phase value of 1·10 Å.

Brookeman & Scott (1972) have shown that the structure of α-N₂ must be acentric, thus confirming the X-ray results of Jordan, Smith, Streib & Lipscomb (1964) from data collected at 20°K, that the correct space group for this structure is $P2_13$ and not $Pa3$. Jordan *et al.* reported the results of a least-squares refinement of the X-ray data which resulted in a value of $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ of 0·130, a bond length (uncorrected for thermal motion) of 1·10 Å and a displacement of the molecular center by 0·17 Å from the center of symmetry in $Pa3$. A single isotropic temperature factor was refined but not reported.

Because of current theoretical and experimental interest in this structure we have carried out a more detailed least-squares refinement of the original data than was possible for Jordan *et al.* The 49 observed data with estimated standard deviations given by Jordan *et al.* were used to refine the following parameters: $x(1)$ and $x(2)$ – the positional parameters of the two nitrogen atoms in the special position (x,x,x) – two thermal parameters U_{11} and U_{12} for each atom, a scale factor, and an isotropic extinction parameter (Zachariasen, 1967) (The minimum extinction ratio F^2_{obs}/F^2_{calc} was 0·41.) The refinement converged to an R index of 0·105 and a weighted R index of 0·105. The parameter values are given in Table 1. The bond length uncorrected for thermal motion is 1·054 (24) Å,† and the displacement of the center of molecule from the origin is 0·157 (19) Å. The U values for the two atoms do not differ significantly and correspond to average root-mean-square displacements of 0·045 (67) Å along the molecular axis and 0·166 (19) Å for each of two principal axes perpendicular to the molecular axis. The size of the errors on these thermal parameters do, however, indicate that the anisotropy is not well-determined by the experiment, although the difference between the perpendicular and parallel components

is quite significant. It is impossible to determine independently the amplitudes of librational motion around the two axes perpendicular to the molecular axes and the amplitude of the translation perpendicular to this axis. However, if we *assume* that the translational motion is isotropic, its magnitude is given by the parallel component, and subtraction of its mean square value $(U_{11}+2U_{12})=0\cdot0020$ (60) Å² from the perpendicular component $(U_{11}-2U_{12})=0\cdot0276$ (63) Å² results in a difference of 0·026 (8) Å²* to be associated with each of the two degrees of freedom for the librational motion. If one assumes simple librational motion around the center of mass, the root-mean-square angular amplitude of each of the two equal librations is 17° (5) and the correction to the bond length is $(2\times0\cdot026)/(1\cdot054\times\frac{1}{2})=0\cdot098$ Å. The corrected value of the bond length is $1\cdot054+0\cdot098=1\cdot15$ (4) Å in satisfactory agreement with the gas phase value of 1·0976. The librational amplitude is also in excellent agreement with the value of 16° at 24°K obtained by Cahill & Leroi (1969) from Raman measurements and the value of 14·8° at 20°K from nuclear quadrupole resonance results (Brookeman, McEnnan & Scott, 1971).

Table 1. *Final parameters* * *for the* α-N₂ *structure*

$a=5\cdot65$ Å (assumed from earlier X-ray work). Scale factor, $F_o=KF_c$: $K=8\cdot27$ (56); Extinction parameter: $g\times10^{-4}=5\cdot5$ (28)

	x	U_{11}	U_{12}
N(1)	0·0699 (21)	0·0210 (69)	−0·0092 (50)
N(2)	−0·0378 (24)	0·0171 (68)	−0·0078 (55)

* The Debye–Waller factor is defined as

$$\exp\{-(a^2/2\pi^2)[U_{11}(h^2+k^2+l^2)+U_{12}(2hk+2hl+2kl)]\}$$

---

† Estimated standard deviations in the last significant figure are given in parentheses.

* This difference is simply $3U_{12}$. A strong negative correlation between the U_{ij} for the two atoms results in the lower value of the standard deviation than would be naively expected from the individual σ's.