Acta Cryst. (1959). **12**, 247

A re-examination of the crystal structures of α and β Nitrogen.*

By L. H. Bolz, M. E. Boyd, F. A. Mauer and H. S. Peiser, *National Bureau of Standards, Washington 25, D.C., U.S.A.*

(*Received* 23 *August* 1958)

Vegard (1929) published a structure for α nitrogen in the space group $P2_13$. If correct, this structure would be the simplest example of a very rare occurrence: crystallization of a centrosymmetric molecule in a non-centrosymmetric space group. Herbstein & Schoening (1957) in a recent discussion of the few known instances do not mention α-N_2. In essence Vegard's choice of space group is based on his reported photographic observation of 110 and 310 X-ray powder lines, forbidden in the corresponding centrosymmetric arrangement $Pa3$. These lines, however, appear to be absent from recent data we obtained using polycrystalline specimens in an X-ray diffractometer with a liquid-helium cold cell (Black, et. al. 1958).

Ruhemann (1932) questioned Vegard's choice of space group $P2_13$ for α-N_2 and suggested that the centrosymmetric cubic structure in $Pa3$ might be correct. His arguments, however, appear to have been discounted in some later literature summaries (e.g. Wyckoff, 1951), perhaps because Ruhemann was doubtful about whether Vorländer & Keesom's (1926) observation of birefringence implied lower-than-cubic (namely, tetragonal) symmetry. Pseudo-uniaxial optical properties, however, might easily arise when cubic solids are deposited from the vapour. Our X-ray data taken before annealing (Fig. 1) show considerable intensity anomalies, such as could be caused by structural faults that would also give rise to pseudo-uniaxial character.

As X-ray evidence of lower-than-cubic symmetry has not been found there is no support for questioning a cubic structure. It is, however, necessary to decide between $P2_13$ and $Pa3$ structures. Our X-ray intensities for 23 observed reflections fit the $Pa3$ structure better. The agreement is as yet not fully convincing; there are small intensity anomalies apparently due to orientation and faults. It is desirable, therefore, to scrutinize the evidence for Vegard's 110 and 310 reflections. He said he did not separate the $K\alpha$ 110 from the $K\beta$ 111 line, but only claimed an appreciable enhancement of the $K\beta$ 111 diffraction by the weaker $K\alpha$ 110 reflection. At least in our diffractometer plot there can be no such overlap; with the Cu K radiation used the separation is 2·4° (2θ)! We would place an upper experimental limit for F^2_{110} of $F^2_{111}/10{,}000$, much smaller than the value of $F^2_{111}/50$ calculated for the $P2_13$ structure. Vegard observed a reflection with a total intensity, including that due to $K\alpha$ 110 and $K\beta$ 111, of $F^2_{111}/7$. Apparently he did not use a β filter, so it is not clear why he judged the intensity too high for the $K\beta$ 111. In any event his estimated intensities hardly appear to be trustworthy to $\pm F^2_{111}/50$ in $F^2_{111}/7$, so that his data on this point give no evidence in support of the $P2_13$ structure.

Vegard claimed only a very weak 310 reflection. If it is compared with the neighbouring 311 line his estimate amounts to $F^2_{311}/20$, but his own structure gives a calculated value of only $F^2_{311}/30$, which is at our estimated lower limit of detection (Fig. 1).

It is concluded from the experimental data at present available that α-N_2 is cubic $Pa3$ with $a_0 = 5{\cdot}644 \pm 0{\cdot}005$ Å at 4·2 °K. The average coefficient of linear expansion in the range 4·2 °K. to 20 °K. we determine to be 2×10^{-4} per degree. There is evidence that the coefficient actually increases appreciably with temperature within that range. There are four molecules per cell, with eight atoms in Wyckoff positions '*c*' (provisionally $x = 0{\cdot}054$). An accurate value for the parameter x requires further experimental work with well-annealed α-N_2 specimens. Most line broadening is eliminated irreversibly on annealing to 13 °K., but residual intensity anomalies (not explicable by orientation or thermal vibrations) point to higher annealing temperatures being required. Nitrogen deposited at 20 °K. shows more disorder than that deposited at 4·2 °K. and subsequently annealed at 13 °K. This effect may be due to local overheating during exothermic ordering processes, when the temperatures may momentarily rise above those indicated by the thermocouples (Black et al., 1958).

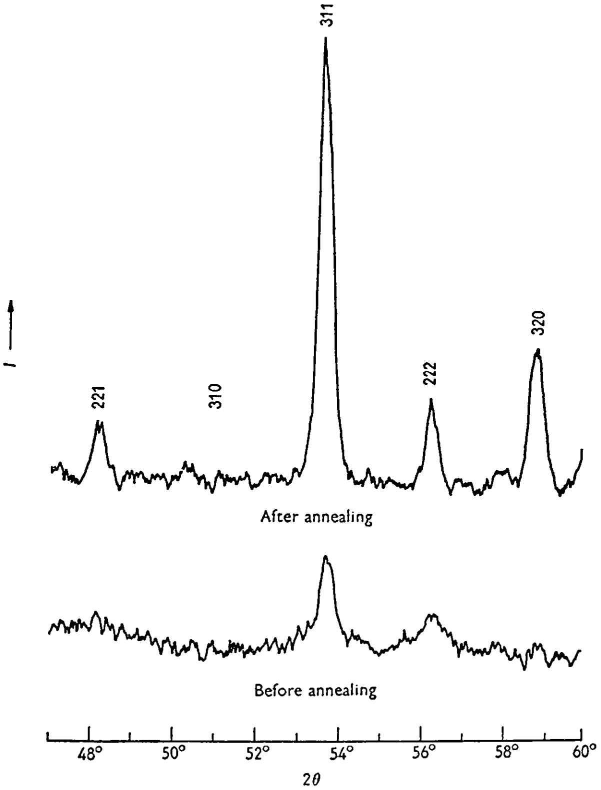

Fig. 1. Effect of annealing on a portion of the α-N_2 diffraction pattern.

---

* This research was performed under the National Bureau of Standards Free Radicals Program, supported by the Department of the Army.

The β-N_2 structure Vegard (1932, 1934) assigned to the centrosymmetric space group $P\bar{3}m1$ with N atoms in Wyckoff positions '*d*' with the molecular centers not coinciding with the space-group symmetry centers. Ruhemann (1932) implied preference for space-group $P6_3/mmc$ with N atoms in Wyckoff positions '*f*' and molecular centers on symmetry centers. This solution appears to fit our, and indeed Vegard's own, data equally well. It has found wider acceptance in the literature (e.g. Wyckoff, 1951).

The $\alpha \rightarrow \beta$ transformation on warming is preceded by an anomaly in the specific-heat curve (Giauque & Clayton, 1933) indicating the onset of restricted rotation. The molecular-volume data (Table 1) suggest that the molecules do not, however, attain free spherical rotation below the melting point. Models for the restricted rotation must conform to the observed axial ratio.

Table 1. *Molecular volume data* ($\times 10^{24}$ cm.$^{-3}$)

		β Solid			
	α Solid	Molecular volume	c/a	Liquid	Freely rotating sphere
Present authors	44·5	48·1	1·627	57·5*	64·7†
Vegard	45·3	47·1	1·651	—	—
Ruhemann	45·6	46·4	1·633	—	—

* Calculated from density = 0·8084 g.cm.$^{-3}$ (*Int. Crit. Tables*, Vol. III, p. 20. New York: McGraw–Hill 1928).

† Calculated from distance of approach of closest atoms in α-N_2 at 4·2° = 3·44 Å. This must be considered an upper limit.

Helpful discussion with Dr Lipscomb and many colleagues is gratefully acknowledged.

References

Black, I., Bolz, L., Brooks, F., Mauer, F., Peiser, H. S. (1958). *J. Research Nat. Bur. Standards.* **61**, 367.

Giauque, W. F. & Clayton, J. O. (1933). *J. Amer. Chem. Soc.* **55**, 4875.

Herbstein, F. H. & Schoening, F. R. L. (1957). *Acta Cryst.* **10**, 657.

Ruhemann, M. (1932). *Z. Phys.* **76**, 368.

Vegard, L. (1929). *Z. Phys.* **58**, 497.

Vegard, L. (1932). *Z. Phys.* **79**, 471.

Vegard, L. (1934). *Z. Phys.* **88**, 235.

Vorländer, D. & Keesom, W. H. (1926). *Comm. Phys. Lab. Leiden*, no. 182c.

Wyckoff, R. W. G. (1951). *Crystal Structures*, vol. 1, p. 14. New York: Interscience Publishers.

Acta Cryst. (1959). **12**, 248

On the space group of 2-4-dinitroaniline.

By A. K. M. Siddiq, Joykumar Saraogi and Shamsher Ali, *X-ray Crystallographic Laboratory, Dacca University, Dacca, East Pakistan*

(*Received* 11 *November* 1958)

The crystals of 2-4-dinitroaniline, which are light yellowish, crystallize in well developed prismatic plates with forms {011}, {110}, {101}, and {010} dominating. Fig. 1 shows a typical crystal in a clinographic drawing.

The crystals, when examined under the polarizing microscope, show oblique extinction on the *b*-face. The crystals therefore belong to the monoclinic system.

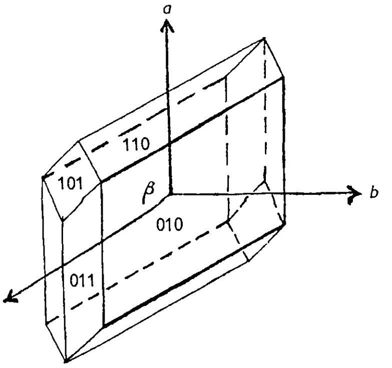

Fig. 1. Clinographic drawing of a crystal of 2-4-dinitroaniline.

Oscillation and Weissenberg photographs taken with unfiltered Co $K\alpha$ radiation from crystal specimens oscillated about all the three principal axes gave (for λ = 1·78 Å) the following real and reciprocal cell dimensions.

a = 8·46 Å a^* = 0·214
b = 12·50 b^* = 0·142
c = 7·40 c^* = 0·245
β = 101° 54′ β^* = 78° 6′

The density as measured by the method of flotation is 1·615 g.cm.$^{-3}$. Thus there are four (calculated 4·007) molecules per unit cell.

Among the X-ray reflections, systematic absences occurred for reflections of the type ($0k0$) for $k = 2n+1$. The space group is therefore $P2_1/m$.

The authors are grateful to Dr A. M. Chaudhury for his helpful suggestions during the progress of the work.