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Refinement of the crystal structure of α-N_2.*

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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 ($X=0{\cdot}16\pm0{\cdot}02$ Å) and gives a librational amplitude of 17 ± 5° 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-N_2 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 $F^2_{\rm obs}/F^2_{\rm calc}$ 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 $(U_{11}+2U_{12})=0{\cdot}0020$ (60) Å^2 from the perpendicular component $(U_{11}-2U_{12})=0{\cdot}0276$ (63) Å^2 results in a difference of 0·026 (8) Å^{2*} 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 $(2\times0{\cdot}026)/(1{\cdot}054\times\frac{1}{2})=0{\cdot}098$ Å. The corrected value of the bond length is $1{\cdot}054+0{\cdot}098=1{\cdot}15$ (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-N_2 *structure*

$a=5{\cdot}65$ Å (assumed from earlier X-ray work). Scale factor, $F_o=KF_c$: $K=8{\cdot}27$ (56); Extinction parameter: $g\times10^{-4}=5{\cdot}5$ (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

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

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† 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.

Although this new refinement confirms and extends the refinement of Jordan *et al.* and gives results in agreement with more recent experiments, a set of more precise diffraction data is very much needed.

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Mise en evidence d'une transformation ordre–désordre dans un cristal de type pyrochlore.

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By X-ray diffraction from a single crystal three forms of a complex oxide $(U,Na)_{2-x}Nb_2O_{7-y}$ of the pyrochloride type have been distinguished which differ according to the order between the atoms of uranium and the atoms of sodium: (1) A fully disordered form (positions 16(*d*) of *Fd*3*m* are randomly occupied by uranium and sodium). (2) A partly ordered form in which single crystals are made up of domains containing approximately 4 to 5 unit cells in each of the three directions. (3) A long-range-ordered form, obtained by reheating the second form. In the forms 2 and 3, positions 16(*d*) are not equivalent and the space group becomes $P4_332$ with uranium and sodium atoms in positions 4(*b*) and 12(*d*).

Des monocristaux de type pyrochlore (cubique *Fd*3*m*, avec $a = 10{,}40$ Å), de formule $(U, Na)_{2-x}Nb_2O_{7-y}$, ont été obtenus par synthèse à 1400 °C. Les clichés de rayons X de ces cristaux révèlent, en plus des taches de diffraction normales, des réflexions diffuses évoquant un ordre à courte distance. Nous avons essayé de les interpréter sur un cristal pour lequel une analyse quantitative à la sonde de Castaing conduit à la formule $Na^{+}_{0,82}U^{6+}_{0,45}Nb^{5+}_{2}O_{6,76}$, en supposant que l'uranium est à l'état d'oxydation 6+.

Dans un premier temps, en ne prenant en considération que les taches de diffraction normales, nous avons bien retrouvé la structure pyrochlore connue en supposant une répartition statistique des atomes d'uranium et de sodium en 16(*d*). L'affinement par moindres carrés des mesures recueillies sur un diffractomètre converge jusqu'à une valeur de *R* égale à 0,10, et conduit aux valeurs consignées dans le Tableau 1.

Etude des taches de diffusion

Des diagrammes de précession faits avec un monochromateur de graphite les mettent bien en évidence: leur largeur permet de constater que le cristal est constitué de domaines, dont l'extension est de l'ordre de 50 Å. Elles se placent aux noeuds du réseau *P* de paramètre 10,40 Å, avec des extinctions qui correspondent au groupe non centré $P4_332$, sous-groupe de *Fd*3*m*.

Les positions équivalentes 16(*d*) du groupe *Fd*3*m* s'y répartissent en deux groupements de la façon suivante:

$$4(b)\ \tfrac{5}{8}\ \tfrac{5}{8}\ \tfrac{5}{8}$$
$$12(d)\ \tfrac{1}{8}\ x\ \tfrac{1}{4}-x,\ \text{avec } x=\tfrac{3}{8},$$

et leur partage entre ces deux sites est tel que les facteurs de structure y sont en phase pour les noeuds *hkl* de même parité (noeuds fondamentaux) et en opposition de phase pour les noeuds *hkl* de parité mixte (taches de diffusion) – on a donc:

$$F_{hkl}\ (\text{même parité}) \propto f_1+3f_2=4f(\text{U, Na})=\text{constante}$$
$$F_{hkl}\ (\text{parité mixte}) \propto f_1-f_2,$$

f_1 et f_2 étant les facteurs de diffusion des atomes dans les positions 4(*b*) et 12(*d*) du groupe $P4_332$

Le programme d'affinement par moindres carrés, par le jeu des multiplicateurs variables affectés à chaque sorte d'atome ne permet d'affiner que la quantité $K|f_1-f_2|$, K étant le facteur d'échelle qui doit être fixé à une valeur telle que les F_{obs} soient à l'échelle absolue. $|f_1-f_2|$ est déterminé par rapport à la table de diffusion f(U, Na) à sin sin $\theta/\lambda=0$. Nous avons donc raccordé la mesure densitométrique des taches de diffusion à l'échelle des fondamentales par l'intermédiaire de trois taches faibles du réseau *F*: 620, 660 et 10,2,0, réflexions dues seulement aux oxygènes en 48(*f*).

Tableau 1. *Paramètres atomiques et facteurs d'agitation thermique de la phase désordonnée*

Les facteurs d'agitation thermique anisotropes sont ceux qui interviennent dans l'expression

$$\exp\left[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{23}kl+2\beta_{13}hl)\right].$$

		x	*y*	*z*	$\beta_{11}=\beta_{22}=\beta_{33}$	$\beta_{12}=\beta_{13}=\beta_{23}$	*B*
(U, Na)* × $\frac{1,27}{2}$	16(*d*)	$\frac{5}{8}$	$\frac{5}{8}$	$\frac{5}{8}$	14×10^{-4}	4×10^{-4}	
Nb	16(*c*)	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	10×10^{-4}	1×10^{-4}	
$O_1\times0{,}76$	8(*b*)	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$			4,5 Å²
O_2	48(*f*)	0,187	0	0			0,92 Å²

*(U, Na) = (0,45U + 0,82 Na)/1,27