Table 1. *Partial X-ray powder diffraction patterns*

	$U(PO_3)_4$		$Pu(PO_3)_4$		
hkl	d_c (Å)	d_o (Å)*	d_c (Å)	d_o (Å)*	I/I_1†
011	6·256	6·25	6·24	6·25	75
120	5·735	5·71	5·72	5·71	55
111	5·127	5·12	5·11	5·11	65
200	4·474	4·46	4·46	4·44	20
121	4·408	4·39	4·40	4·37	15
031	4·036	4·02	4·02	4·01	100
220	3·839	3·83	3·83	3·81	25
201	3·752	3·74	3·74	3·73	25
040	3·735		3·72		
131	3·680	3·64	3·67	3·64	65
211	3·640		3·63		
002	3·445	3·44	3·44	3·42	5
221	3·354	3·35	3·34	3·33	< 5
022	3·128	3·12	3·12	3·10	10
231	2·997	2·99	2·99	2·98	35
122	2·953	2·95	2·94	2·94	60
240	2·867	2·855	2·859	2·847	50
320	2·771	2·766	2·764	2·759	25
202	2·730	2·725	2·723	2·712	25
311	2·693	2·689	2·686	2·677	30
212	2·685		2·678		
151	2·621	2·609	2·613	2·603	30
321	2·571	2·562	2·564	2·560	5
222	2·564		2·557		
042	2·532	2·525	2·524	2·518	35
060	2·490	2·478	2·482	2·474	5
142	2·437	2·430	2·429	2·423	10
331	2·399	2·390	2·393	2·382	20
160	2·399		2·391		
232	2·394		2·387		
251	2·338	2·328	2·331	2·320	15
340	2·331		2·325		
013	2·270	2·268	2·263	2·260	15
400	2·238	2·232	2·233	2·223	10
312	2·230		2·224		
341	2·208	2·200	2·202	2·192	60
242	2·204		2·198		
113	2·200		2·194		
322	2·159	2·156	2·153	2·149	25

* Philips 114·6 mm. diameter powder camera, Straumanis film mounting; sample contained in 0·2 mm. diameter glass capillary with walls 0·01 mm. thick.

† Relative peak intensities above background from densitometer measurements of powder photograph of the uranium salt; values for the plutonium salt are not significantly different. Copper radiation with nickel filter; Eastman Kodak Type *A* film for which density was calibrated as a function of exposure time.

Table 2. *Absorption spectrum of* $U(PO_3)_4$

Band maxima in millimicrons, relative intensities (*VS*, *S*, *MS*, *M*, *MW*, *W*, *VW*) and relative band widths (*vw*, *w*, *m*, *n*) as viewed with Zeiss prism microspectrometer ocular

Parallel to *X*			Parallel to *Y*			Parallel to *Z*			In bulk	
680	*MW*	*n*	670	*S*	*n*	670–660	*VS*	*vw*	665	*VS*
669	*S*	*n*	662	*VS*	*m*	635–625	*M*	*vw*	656	*MS*
666	*S*	*n*	649	*S*	*m*	620–610	*M*	*vw*	648	*S*
660	*M*	*n*	638	*MW*	*w*	585	*MW*	*n*	637	*MW*
655	*S*	*m*	593	*MW*	*w*	544	*M*	*vw*	618	*W*
650	*M*	*n*	581	*M*	*n*	480	*MW*	*vw*	599	*VW*
639	*W*	*n*	537	*MS*	*vw*	442	*W*	*m*	587	*VW*
632	*MW*	*n*	493	*VW*	*vw*	439	*MS*	*vw*	542	*M*
598	*W*	*m*	475	*M*	*vw*				477	*MW*
589	*MW*	*m*								
544	*MS*	*w*								
537	*MS*	*w*								
484	*W*	*w*								
470	*MW*	*w*								

Table 3. *Absorption spectrum of* $Pu(PO_3)_4$

Band maxima in millimicrons and relative intensities (*VS*, *S*, *MS*, *M*, *MW*, *W*, *VW*) as viewed with Zeiss prism microspectrometer ocular

Parallel to *Z*			Parallel to *X* and *Y*	
665	*S*	wide	665	*S*
635	*VS*		635	*VS*
572	*MW*		572	*MW*
559	*W*			
552	*W*			
			522	*W*
518	*MW*		516	*MW*
509	*W*		509	*M*
497	*MS*			
			487	*M*
483	*M*			
			473	*VW*
454	*M*	wide	463	*W*
448	*MW*	wide	448	*MS*

References

Colani, A. (1907). *Ann. Chim. Phys.* [8], **12**, 103.

Douglass, R. M. & Staritzky, E. (1956). *Analyt. Chem.* **28**, 1211.

Johnsson, K. R. (1889). *Chem. Ber.* **22**, 976.

Zachariasen, W. H. (1954). Private communication cited in Seaborg, G. T. & Katz, J. J. (1954). *The Actinide Elements*, NNES IV–14A, p. 72. New York: McGraw-Hill.

Acta Cryst. (1962). **15**, 506

The disordered structure of $NaNO_2$ at 185 °C.*

By M. I. Kay, *National Aeronautics and Space Administration, Lewis Research Center, Cleveland, Ohio, U.S.A.*, B. C Frazer, *Brookhaven National Laboratory, Upton, L. I., New York, U.S.A.* and R. Ueda, *Waseda University, Tokyo, Japan*

(*Received* 20 *September* 1961 *and in revised form* 21 *December* 1961)

The discovery of ferroelectricity in sodium nitrite (Sawada *et al.*, 1958) has prompted renewed interest in the structural details of this compound. The structure has been examined at room temperature by several investigators (Ziegler, 1931; Truter, 1954; Carpenter, 1952, 1955; Kay & Frazer, 1961), and is accurately known. The transformation at about 160 °C., the ferroelectric Curie point, was found originally in an X-ray study by Strijk & MacGillavry (1943, 1946). They attempted a complete

---

* Work performed in part under the auspices of the U.S. Atomic Energy Commission.

structure analysis at 205 °C. and found a disordered centrosymmetric structure, but were unable to determine the nature of the disorder. The crystal gains a center of symmetry by adding a mirror plane perpendicular to **b**, and thus goes from the acentric low temperature space group *Im2m* to *Immm*. Shibuya (1961) has studied the temperature dependence of several Bragg reflections and critical scattering with X-rays from room temperature up through the Curie point. He reports evidence for incomplete long range order between 120 and 160 °C. and a fairly sharp order–disorder transition at 160 °C. Tanisaki (1961) has made some interesting X-ray measurements just above the Curie point which he interprets as indicating a structure built up of oppositely polarized 'microdomains' of about $4a$ lattice spacings in width. It is of interest that Hoshino & Shibuya (1961) have made precision measurements of the temperature dependence of the lattice constants, and find anomalies at 163 and 178 °C. As Hoshino & Shibuya suggest, between the Curie point and 178 °C. the crystal may be a special kind of imperfectly ordered antiferroelectric, perhaps an antiphase antiferroelectric, with true disorder setting in only above 178 °C.

In the present study we are concerned only with the disordered structure. Neutron diffraction data were collected at 185 °C. for 37 non-equivalent ($0kl$) reflections. In almost every case measurements were made at each equivalent position. The crystal used was grown from water solution at about 5 °C., and was cut to an **a** axis cylinder slightly less than 2 mm. in diameter and 5 mm. in length. Measurements in the heater indicated that the temperature over the length of the crystal varied no more than the range of control regulation (±1°).

Table 1. *Parameters at* 185 °C. *compared with Strijk & MacGillavry's results at* 205 °C.*

		Strijk & MacGillavry	Kay, Frazer & Ueda
Na	Y	0·547	0·5401 ± 0·0019
	β_{22}	—	0·021 ± 0·006
	β_{33}	—	0·028 ± 0·003
N	Y	0·090	0·0725 ± 0·0008
	β_{22}	—	0·021 ± 0·001
	β_{33}	—	0·026 ± 0·001
O	Y	−0·047	−0·0416 ± 0·0017
	Z	0·208	0·1920 ± 0·0007
	β_{22}	—	0·040 ± 0·006
	β_{33}	—	0·025 ± 0·001
	β_{23}	—	0·015 ± 0·004

* Positions in *Immm*: $\frac{1}{2}$ Na in $4g$, $\frac{1}{2}$ N in $4g$, and $\frac{1}{2}$ O in $8l$.

Preliminary calculations, based on the coordinates of Strijk & MacGillavry, were sufficient to rule out models involving full rotation and anomalously large thermal oscillations parallel to **b**. Refinements were accordingly made on hindered rotator and positional disorder models. In the final stages the data were corrected for extinction using Hamilton's (1960) IBM 704 program. Only one reflection, the (0,2,0), was significantly affected. The positionally disordered and hindered rotator models were refined on F using the least-squares IBM 704 programs of Hamilton (1958) and Busing & Levy (1959), respectively. The structure factor standard deviations used in computing weights ($W = (\sigma(F))^{-2}$) were assumed to be given by the counting statistics. Examination of the correlation matrices revealed no serious problems with parameter interactions. The largest coefficient, 0·71, occurred as expected for the y and β_{22} oxygen parameters. The final parameter results for the positionally disordered model are given in Table 1 with the results of Strijk & MacGillavry listed for comparison. Calculated and observed structure factors are compared in Table 2. The discrepancy factor $R = 0{\cdot}077$; the weighted R is 0·058.

Table 2. *Structure factor comparison*

$NaNO_2$ neutron data at 185 °C. Positional disorder model.
$R = 0{\cdot}077$

h k l	F_c	$\lvert F_o \rvert$	$\sigma(F_o)$
0 0 2	0·76	0·78	0·01
4	1·86	1·84	0·02
6	1·53	1·56	0·02
8	0·02	< 0·06	—
0 1 1	1·71	1·69	0·02
3	−0·72	0·73	0·01
5	1·65	1·60	0·02
7	−0·07	0·23	0·05
9	0·10	< 0·08	—
0 2 0	3·33	3·25	0·70*
2	0·27	0·26	0·02
4	1·26	1·28	0·02
6	0·97	0·89	0·01
8	−0·04	< 0·07	—
0 3 1	0·25	0·19	0·01
3	−0·84	0·86	0·02
5	0·59	0·72	0·01
7	−0·30	0·28	0·04
0 4 0	0·54	0·57	0·13
2	0·55	0·45	0·03
4	0·17	0·11	0·03
6	−0·01	0·16	0·07
8	−0·13	0·25	0·06
0 5 1	−0·81	0·74	0·01
3	−0·76	0·74	0·02
5	−0·28	0·34	0·02
7	−0·38	0·36	0·03
0 6 0	−0·79	0·80	0·02
2	−0·77	0·78	0·01
4	−0·39	0·47	0·02
6	−0·41	0·32	0·03
0 7 1	−0·66	0·72	0·02
3	−0·39	0·34	0·04
5	−0·35	0·28	0·04
0 8 0	−0·59	0·54	0·06
2	−0·42	0·34	0·07
0 9 1	−0·14	0·08	0·03

* Extinction correction large for this reflection.

In the hindered rotator calculations only the nitrite groups were treated as rotating. Sodium was considered as positionally disordered. The hindered rotator scattering factors were obtained by using the M function of King & Lipscomb (1950) and the tables of Chessin & Whitmore (1960). These were inserted into the Busing & Levy program as one would do in an X-ray refinement. The parameters a and b (calculated from the y coordinates and the heights of the barrier above the potential minimum) that determine the scattering factors could not be refined directly by the program, so that refinement was carried out only on y_{Na}, z_O, and the anisotropic temperature parameters. Fourier difference maps were computed after each set of least-squares refinements as guides for choosing new trial a and b values. The final results, obtained with $b=5$, gave an R of 0·085 and a weighted R of 0·075. It is probable that a higher hindering potential would have yielded a slightly better model, but even at $b=5$ the distinction between positional disorder ($b=\infty$) and hindered rotation is not very meaningful. The M function differs very little for values of b between 5 and ∞. Hence, it seems sensible to regard the structure at 185 °C. as positionally disordered, although we know from the field reversibility below the Curie point, and the disorder above it, that the orientation of the nitrite ion can change without too much difficulty.

Table 3. *Bond angles and interatomic distances at* 20 *and* 185 °C.*

		20 °C.	185 °C.
∢O–N–O		114·9±0·5°	116·5±0·9°
N–O		1·240±0·003 Å	1·223±0·007 Å
Na–O	(1)	2·471±0·004	2·523±0·006
	(2)	2·533±0·004	2·597±0·006
	(3)†	—	2·480±0·006
	(4)†	—	3·020±0·006
Na–N	(1)	2·589±0·009	2·662±0·012
	(2)†	—	2·205±0·012

* The 20 °C. results are from Kay & Frazer (1961). Those for 185 °C. were calculated using the cell dimensions of Ueda (1961): $a=3·681$, $b=5·692$, $c=5·395$ Å. Correlation effects were considered in calculating standard errors, but cell dimension errors were not.

† These distances can occur only in the disordered structure.

Table 4. *Root-mean-square displacements at* 20 *and* 185 °C. *from anisotropic temperature parameters**

		20 °C.	185 °C.
Na	U_M	0·128±0·015 Å	0·20±0·01 Å
	U_m	0·118±0·017 Å	0·19±0·03 Å
	δ	0°	90°
N	U_M	0·160±0·007 Å	0·20±0·02 Å
	U_m	0·112±0·007 Å	0·19±0·05 Å
	δ	90°	90°
O	U_M	0·160±0·007 Å	0·27±0·02 Å
	U_m	0·112±0·007 Å	0·18±0·02 Å
	δ	5·5±3°	19·5±9°

* The 20 °C. results are from Kay & Frazer (1961). The subscripts M and m refer to the major and minor vibration axes, respectively.

δ is the angle between the major axis and the **b** axis. In both oxygen cases, the inclinations are such as to make maximum angles with the N–O bond.

The interatomic distances, bond angles, and r.m.s. displacements calculated for the positionally disordered model are listed and compared with the room temperature structure in Tables 3 and 4. In view of the low melting point the large increases in the r.m.s. displacements are not surprising. Since there are appreciable differences in the cell dimensions at the two temperatures, one would also expect to find significant changes in the Na–O and Na–N distances, but the geometry of the NO_2 group should change very little. The differences observed are probably due to apparent shifts in the N and O positions because of thermal librations of the NO_2 group. Cruickshank (1961) has shown how the apparent position of an atom in a librating molecule can be shifted toward the center of rotation. While we have evidence for appreciable NO_2 libration in the bc plane, unfortunately we cannot calculate the corrections since we have no information on libration out of the plane. It is fairly obvious, however, that the corrections would increase the N–O distance and decrease the bond angle, as they should for better agreement with the 20 °C. structure.

Among the additional interatomic distances which become possible in the disordered structure, the short Na–N (2) distance appears to be most significant. Since the longer Na–N (1) distance, which is comparable with the 20 °C. value, should be preferred, this would seem to imply that there is a good deal of short range order in chains along the **b** direction. This probably breaks down at higher temperatures with the onset of hindered or free rotation. Canut & Amorós (1960) have observed some changes in X-ray diffuse scattering near 200 °C. which may be due to the development of NO_2 rotation. Cell dimension curves measured by Ueda (1961) with X-rays, and those of Hoshino & Shibuya, seem to show small changes in slope near 200 °C. which also might indicate some sort of structural change. If this is the case, the comparison made in Table 1 between the present 185 °C. results and those of Strijk & MacGillavry at 205 °C. must be considered accordingly.

References

Busing, W. R. & Levy, H. (1959). Oak Ridge National Laboratory Report 59-4-37.

Canut, M. L. & Amorós, J. L. (1960). Private communication.

Carpenter, G. B. (1952). *Acta Cryst.* **5**, 132.

Carpenter, G. B. (1955). *Acta Cryst.* **8**, 852.

Chessin, H. & Whitmore, R. W. (1960). U.S. Steel Research Report 875.

Cruickshank, D. W. J. (1961). *Acta Cryst.* **14**, 896.

Hamilton, W. C. (1958). Unpublished notes.

Hamilton, W. C. (1960). Unpublished notes.

Hoshino, S. & Shibuya, I. (1961). *J. Phys. Soc., Japan*, **16**, 1254.

Kay, M. I. & Frazer, B. C. (1961). *Acta Cryst.* **14**, 56.

King, M. V. & Lipscomb, W. N. (1950). *Acta Cryst.* **3**, 155.

Sawada, S., Nomura, S., Fujii, W. & Yoshida, I. (1958). *Phys. Rev. Letters*, **1**, 320.

Shibuya, I. (1961). *J. Phys. Soc., Japan*, **16**, 490.

Strijk, B. & MacGillavry, C. H. (1943). *Rec. Trav. Chim. Pays-Bas*, **62**, 705.

Strijk, B. & MacGillavry, C. H. (1946). *Rec. Trav. Chim. Pays-Bas*, **65**, 127.

Tanisaki, S. (1961). *J. Phys. Soc., Japan*, **16**, 579.

Truter, M. R. (1954). *Acta Cryst.* **7**, 73.

Ueda, R. (1961). To be published.

Ziegler, G. E. (1931). *Phys. Rev.* **38**, 1040.