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A neutron diffraction refinement of the low temperature phase of $NaNO_2$.[*]

By M. I. Kay[†] and B. C. Frazer, *Brookhaven National Laboratory, Upton, New York, U.S.A.*

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$NaNO_2$ is ferroelectric below its transition point of 158 °C. (Sawada *et al.*, 1958; Frazer, 1958). The structural nature of spontaneous polarization and the transition mechanism appear to be quite simple, and hence this crystal would seem to be especially well suited for theoretical treatment. An accurate knowledge of the crystal structure of both phases, including the thermal vibration parameters, will facilitate such work. The solution of the first part of the structural problem is reported in the following short communication.

The structure of the low temperature phase of $NaNO_2$ was determined in an X-ray analysis by Ziegler (1931) and subsequently refined by Truter (1954) and Carpenter (1952, 1955). Individual anisotropic temperature parameters were not determined in any of the refinements, however. Since in the high temperature phase (Strijk & MacGillavry, 1943) the problem is mainly one of distinguishing between a disordered model and two models involving pronounced thermal anisotropy, the thermal vibration parameters in the low temperature phase are of some importance. In an X-ray study the accuracy obtainable in determining temperature parameters depends upon the validity of the scattering factor curves used in refinement. Due to uncertainty in the electronic distribution of the NO_2^- group, there is some question as to the proper X-ray scattering factors for nitrogen and oxygen. This is not serious for oxygen in this particular problem, but there are appreciable differences in the N and N^{+3} curves out as far as 0·4 in $\sin\theta/\lambda$. Moreover, since nitrogen is the lightest atom,[‡] its coordinates and temperature parameters are more subject to error than sodium and oxygen even if the proper scattering factor is used.

It therefore seemed worthwhile to examine this structure with neutrons. Neutron scattering lengths are independent of angle, which provides considerable advantage in the determination of the thermal vibration parameters. Also, in the neutron case, nitrogen is the 'heaviest' atom in the structure.

The space group is *Im2m*. There are two formula units per cell. Cell dimensions are

$$a = 3{\cdot}560 \pm 0{\cdot}010, \quad b = 5{\cdot}563 \pm 0{\cdot}005, \quad c = 5{\cdot}384 \pm 0{\cdot}005\ \text{Å}$$

(from X-ray powder photographs).

The atomic positions are

$$(0, 0, 0;\ \tfrac{1}{2}, \tfrac{1}{2}, \tfrac{1}{2}) + 2\ \mathrm{Na}\ \text{in}\ 2(a){:}\ (0, y, 0),$$
$$2\ \mathrm{N}\ \text{in}\ 2(a){:}\ (0, y, 0),$$
$$4\ \mathrm{O}\ \text{in}\ 4(d){:}\ (0, y, z;\ 0, y, \bar{z}).$$

The y coordinate for oxygen was set equal to zero to define the origin. The scattering lengths (Shull & Wollan, 1956) used were: $b_{\mathrm{Na}} = 0{\cdot}35$, $b_{\mathrm{N}} = 0{\cdot}94$, and $b_{\mathrm{O}} = 0{\cdot}58$ (in units of 10^{-12} cm.).

A set of (0*kl*) single crystal data was collected at room temperature. Carpenter's (1955) results were taken as starting parameters in a general least-squares refinement using the I.B.M. 704 program of Busing & Levy (1959). The refinement was carried out on F^2 with the weight factors set equal to $(1/\sigma(F^2))^2$. The standard deviation in F^2 was determined from the counting statistics. This was only an approximation since extinction effects were present. At an intermediate stage of refinement the data were corrected for extinction by means of an I.B.M. 704 program written by W. C. Hamilton. Only five structure factors were affected by more than 3% by these corrections, and of these, only one was affected by more than 5%. The final set of calculated structure factors are compared with the observed values in Table 1. The discrepancy factor $R = 0{\cdot}027$.

The positional coordinates and their standard deviations obtained in the present study are compared with

Table 1. *Structure factor comparison*

$NaNO_2$-low temperature modification. Final neutron data. $R = 0{\cdot}0269$

h k l	$\|F_o\|$	$\|F_c\|$	$\|\Delta F\|$	*h k l*	$\|F_o\|$	$\|F_c\|$	$\|\Delta F\|$
0 0 2	0·82	0·76	0·06	0 3 7	1·52	1·51	0·01
4	2·47	2·52	0·05	0 4 0	0·75	0·72	0·03
6	2·55	2·64	0·09	2	3·40	3·25	0·15
8	< 0·2	0·06	—	4	1·59	1·55	0·04
0 1 1	1·73	1·78	0·05	6	0·82	0·78	0·04
3	1·48	1·42	0·06	0 5 1	1·22	1·17	0·05
5	2·48	2·48	0·00	3	2·18	2·17	0·01
7	0·75	0·72	0·03	5	1·09	1·08	0·01
0 2 0	3·47	3·55	0·08	0 6 0	1·51	1·51	0·00
2	2·48	2·57	0·09	2	2·12	2·16	0·04
4	2·19	2·19	0·00	4	1·22	1·18	0·04
6	1·98	1·95	0·03	6	1·08	1·05	0·03
8	1·57	1·58	0·01	0 7 1	1·56	1·59	0·03
0 3 1	0·82	0·79	0·03	3	0·66	0·71	0·05
3	2·59	2·68	0·09	0 8 0	1·83	1·84	0·01
5	1·00	0·93	0·07	2	0·56	0·67	0·11

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[†] Visiting scientist on leave from the Crystal Research Laboratory, Pennsylvania State University. Present address: Institutt for Atomenergi, Kjeller, Norway.

[‡] Comparing average $N^{+1{\cdot}5}$ and O^{-1} curves in the forward direction: $f_{\mathrm{N}} = 5{\cdot}5$ and $f_{\mathrm{O}} = 9{\cdot}0$.

those of Truter* & Carpenter in Table 2. The agreement between the three sets is quite good. As might be expected, the principal differences occur for nitrogen. The standard deviations for the neutron analysis are considerably lower than the X-ray values. The improved accuracy is perhaps overstated, however, since scattering length errors were not considered.

Table 2. *Comparison of atomic coordinates*

	Truter	Carpenter	Kay & Frazer
y_{Na}	0·5852	0·5862	0·5853
$\sigma(y_{\text{Na}})$	0·002	0·002	0·001
y_{N}	0·1217	0·1188	0·1200
$\sigma(y_{\text{N}})$	0·005	0·004	0·0007
z_{O}	0·1946	0·1944	0·1941
$\sigma(z_{\text{O}})$	0·003	0·002	0·0006

The distances and bond angles found are as follows:

$$\text{Na–O} = 2{\cdot}471 \pm 0{\cdot}004,\ \text{Na–N} = 2{\cdot}589 \pm 0{\cdot}009,$$
$$\text{N–O} = 1{\cdot}240 \pm 0{\cdot}003\,\text{Å};$$
$$\sphericalangle\ \text{O–N–O} = 114{\cdot}9 \pm 0{\cdot}5^\circ.$$

The errors were calculated assuming no error in cell dimensions, so that they are too small by perhaps as much as a factor of two. Even so, the accuracy for the bond angle is substantially better than that of Truter (1954) and Carpenter (1955). Their standard deviations were 4° and 1·73°, respectively.

Table 3. *Root mean square displacements in Ångströms from anisotropic temperature factors**

Atom	u_M	$\sigma(u_M)$	u_m	$\sigma(u_m)$	d†
Na	0·128	0·015	0·118	0·017	0°
N	0·125	0·007	0·114	0·005	90°
O	0·160	0·007	0·112	0·007	5·5 ± 3°

* Subscripts M and m refer to the major and minor vibration axes, respectively.

† Angle between the major axis, and the crystallographic b axis. In the case of oxygen, the inclination is away from N, so as to approach being transverse to the N–O bond.

The thermal vibration results are given in Table 3 as root mean square displacements. Oxygen is the only atom that shows a definitely measurable degree of anisotropy. Since the phase transition is marked by the gain of a mirror plane perpendicular to b, implying a rotating or disordered structure above θc, thermal anisotropy along $\bar{b}$ may become significant for nitrogen and sodium at higher temperatures. Investigation of the effects of temperature on the structure are now under way in collaboration with Dr R. Ueda of Waseda University, Tokyo, Japan.

The spontaneous polarization calculated on the basis of simple Na^+, N^{+3}, and O^{-2} ions is 74 μ coulombs/cm^2, which is off by an order of magnitude from the observed value of 7 μ coulombs/cm.^{2} (Sawada *et al.*, 1958). This poor agreement is of course a result of the highly covalent nature of the nitrite group. It is of interest to see what effective ionic charges n_{N} and n_{O} would have to be placed at the N and O positions in order to obtain agreement with the observed polarization. These can be determined from the two equations

$$P_s = 1{\cdot}6 \times 10^{-19} \times V^{-1} \Sigma n_j Y_j = 7\ \mu\ \text{coulombs/cm.}^2,$$

and

$$n_{\text{N}} + 2n_{\text{O}} = -1\ ,$$

where V is the cell volume in cm.^{3}, the Y_j are the atomic coordinates in cm., and Σ extends over all atoms in the cell. For sodium $n = +1$. The calculation yields $n_{\text{N}} = -0{\cdot}36$ and $n_{\text{O}} = -0{\cdot}32$. While this result is only a rough approximation, it is of qualitative significance. The fact that n_{N} comes out to be as strongly negative as n_{O} suggests that the Na^+ ion exerts a strong counter polarizing influence on the NO_2^- group. The net electric moment for NO_2^- is still in the same direction as one would expect, however.

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* Truter's coordinates have been taken from Carpenter (1955), where they appeared as a privately communicated improved set.

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The structure of Hf_5Sn_3.*

By D. M. Bailey and J. F. Smith, *Institute for Atomic Research and Department of Chemistry, Iowa State University, Ames, Iowa, U.S.A.*

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Compounds with the formula M_5N_3 often occur between transition elements, M, and Group IV B elements, N. An appreciable number of these compounds crystallize in the $D8_8$ structure if interstitial impurities, particularly carbon, are present (Nowotny, Lux & Kudielka, 1956). In the case of silicides and germanides, reduction in content or absence of interstitial impurities results in

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