## DISCUSSION

W. C. HAMILTON: What are the O-H and O···O distances in this crystal?

H. DACHS: The distance O···O is 2.58Å and the distance O-H about 1Å.

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# X-ray and Neutron Study on the Phase Transformation of $NaNO_2$*

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The crystal structure of sodium nitrite was studied by neutron diffraction. The lattice parameters and temperature factors at room temperature were already reported by Kay and Frazer. The agreement between observed and calculated intensities was quite good.

The high temperature phase of the compound was studied at 185°C by X-ray and neutron diffraction. Refinements were carried out using models of $NO_2$ group as a free rotator, hindered rotator and as a disordered structure. The final results obtained as an hindered rotator gave an $R$ of 0.085. The distinction between positional disorder and hindered rotation is not very meaningful at 185°C. It seems sensible to regard the structure at 185°C as positionally disordered.

### Introduction

Interest in the details of the phase transformation in sodium nitrite has been renewed since the discovery of ferroelectricity (Sawada, *et al.*[1], Frazer[2]) in the compound. As was more or less to be expected from the great increase in coercive field with descreasing temperature, the room temperature structure showed no unusual properties (Kay and Frazer[3]). Shibuya's work[4] seems to indicate a range of partial ordering between 120°C and 160°C. Lattice parameter measurements as a function of temperature indicate the discontinuities at 158°C and at 200°C, the latter being probably assigned to the onset of rotation.

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The crystal attains a center of symmetry and a mirror plane above the transition temperature (158°C). The space group goes from $Im2m$ to $Immm$. The extra mirror plane perpendicular to $b$ implies some sort of disorder. Sets of neutoron diffraction data was taken with the crystal at room temperature and at 158°C in a heater.

### Refinement of the low temperature phase

There are two formula units per cell. Cell dimensions are $a$=3.569Å, $b$=5.563Å, and c=5.384Å. The atomic positions are (0, 0, 0; 1/2, 1/2, 1/2)+2Na in 2(a): (0, $y$, 0) 2N in 2(a): (0, $y$, 0) and 4O in 4(d): (0, $y$, $z$; 0, $y$, $z$). The $y$ coordinate for oxygen was set equal to zero to define the origin. The scattering lengths used were: $b_{Na}$=0.35. $b_N$=0.94, and $b_O$=0.58 (in

units of $10^{-12}$cm).

A set of ($0kl$) single crystal data was collected. Carpenter's results[5] were taken as starting parameters in a general least squares refinement using the I.B.M. 704 program of Busing and Levy[6]. 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. The agreement between the observed and the calculated structure factors is quite good. The discrepancy factor $R=0.027$.

The positional coordinates and their standard deviations, are compared with those of Truter and Carpenter. The agreement is also quite good. The distances and bond angles found are as follows: Na−O= 2.471±0.004Å, Na−N=2.589±0.009Å, N−O= 1.240±0.003Å, O−N−O=114.9±0.5Å. The accuracy for the bond angle is substantially better than that of Truter[7] and Carpenter[5].

**Structure determination and refinement of the high temperature phase**

Refinements were carried out, considering the $NO_2$ group as a free rotator, hindered rotator and as a disordered structure. The ($0k0$) reflections immediately eliminated the free rotator and the hindered rotator with a low potential barrier.

Refinement of the disordered model was carried out starting with Strijk and MacGillavry's[8] parameters using least square 704 program and difference maps.

The scattering factor for the hindered rotator is given for the ($0kl$) projection of $NaNO_2$, as (following the results of King and Lipscomb[9]).

$$M_2^0(a, b),$$

where the subscript (0) is the rotation angle corresponding to a potential minimum. The subscript 2 is the number of potential minima.

$a$—for the projection under discussion is $2\pi ky$, where $y$ is the radius of rotation in terms of a fraction of a cell edge. $b-V_0/2kt$, where $V_0$ is the height of the potential barrier above the minimum, $k$ is the Boltzman constant and $T$ the absolute temperature. The values of the above function which have been calculated by Chessin and Whitmore[10] were inserted into the Busing and Levy least square program as scattering factors. Refinement was carried out on $y_{Na}$, $z_O$, and anisotropic temperature factors. Since the $M$ function depends only on $y$, reciprocal $c$ was set equal to zero.

Then, let

$$2\pi ky=(1/2)kb^* \quad \text{or} \quad 4\pi y=b^* .$$

In other words, the argument of $M(b)$ was set equal to the argument of $f(\sin\theta/\lambda)$.

Refinement was started with $b=5$. The distance along $b$ found in the low temperature form were retained. The best position for the center of symmetry was found to be the same as that for the disordered model. $R$ for the disordered model is 0.077; for the hindered rotator ($b=5$), 0.085 and for the hindered rotator ($b=4$); 0.095. The weighted $R$ factor, $R'=\sum W(F_o-F_c)/\sum WF_o=0.058$ and 0.075 for the disordered nitrite group and the hindered rotator, respectively. It is then probable that the disordered model is most correct ($b=\infty$), although a very high hindering potential is possible. Since it is known from the fact of the phase transformation that the molecule must be able to go from one position to another, the meaning of the difference between the rotator and disorder is rather meaningless.

**Conclusion**

The refinement shows that the potential barrier between the two possible positions of $NaNO_2$ in the cell is quite high, i.e., at 185°, $V_0/2kT \gg 5$ if a cosine potential can be used. The short Na—N distance of 2.20Å is significantly smaller than the 2.59Å found in the low temperature phase. This would seem to imply that a good deal of short range order should occur in the $b$-direction. The mean square displacements show significant rocking motion of the $NO_2$ group in the $b, c$ plane. The amplitudes of vibration are about 1.6 times those found at room temperature. It may also be noticed that the bond distance in the nitrite group are shorter than in the low temperature form.

The X-ray measurements on the lattice constants showed anomalies at 178°C (Hoshino and Shibuya)[11] and also 200°C (Ueda)[12] above the Curie temperature. It might be a future problem whether micro-domains found by Tanisaki[13] in this temperature range would correspond to these anomalies or not. The detailed X-ray work is now being in progress.

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# Vacancy Distribution in $\gamma$-$Fe_2O_3$

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The vacancy distribution in $\gamma$-$Fe_2O_3$ is determined by the X-ray and neutron diffraction. The vacancies do not distribute uniformly through cation sites, but occupy the particular positions of the lattice on the average. We can observe a number of extra lines in the diffraction patterns of both the X-ray and neutron, which do not appear in the magnetite structure.

The intensity calculations were performed by estimating various kinds of vacancy contributions to the diffraction intensities. The existence of the extra lines ruled out the Verwey model in which vacancies distribute in disorder. Among the several models in which vacancies occupy the special positions statistically in cation sites, we could select the most probable one. The agreement between calculated and observed intensities was quite good.

## 1) Introduction

The ferrimagnetic $\gamma$-$Fe_2O_3$ is formed by the oxydation of the magnetite or dehydration of the lepidocrocite $\gamma$-$Fe_2O_3 \cdot H_2O$. The structure of this crystal was first studied by Hägg[1] and Verwey[2] by means of X-ray powder method. They pointed out that it had the same inversed spinel structure as the magnetite and vacancies in the crystal distribute uniformly in the cation sites.

Haul and Schoon[3] and Chaudron[4] found a number of extra lines in X-ray patterns which cannot be assigned to the lines due to magnetite lattice. Braun[5] and Shinha and Shinha[6] suggested that light atoms like hydrogen were trapped in the vacancies of the cation sites. On the other hand, Néel[7] pointed out from the calculation of the saturation magnetization for $\gamma$-$Fe_2O_3$ that the vacancies distribute in the 16 (d) cation site of the spinel structure, which was confirmed by magnetic measurements.

Quite recently, Ferguson and Haas[8] studied this vacancy distribution of $\gamma$-$Fe_2O_3$ by neutron diffaction and supported the Verwey model; i.e. the uniform distribution of the vacancies. In our present studies, the powder data of X-ray and neutron diffraction were taken in detail. From these data, some vacancy distribution in special sites was concluded.

## 2) Specimen

The extensive studies have been performed to make a stoichiometric $\gamma$-$Fe_2O_3$. However,

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