membered ring containing the nickel atom. Each single bond appears to be 0·04–0·12 Å shorter than a normal single bond, and the double bond appears to be 0·15 Å longer than the normal isolated double bond. The double bond between C_3 and C_8, which is involved in the six-membered chelate ring and the benzene ring, is the shortest (1·36 Å) of the bonds in the benzene ring. Since the true values for the Ni–O and Ni–N bonds are not precisely known, it cannot be stated definitely that these bonds are shortened. If there really is some resonance in this chelate ring, then some 4*d* orbitals must be involved.

The short O–O hydrogen bond distance was unexpected. The two oxygen atoms in this complex are bonded differently and are not exactly similar, as they are in nickel dimethylglyoxime in which Rundle & Parasol (1952) believe there is a symmetrical hydrogen bond. It is probable that the bond is not symmetrical in this complex although it is very short.

There are no unusually close approaches between atoms of different molecules and thus the crystal must be held together primarily by van der Waals forces. There is no indication in this complex of nickel-nickel bonding as there is in the nickel dimethylglyoxime crystals (Godycki & Rundle, 1953).

Before any conclusions can be drawn about the distortion of the salicylaldoxime molecule upon formation of the nickel complex the structure of salicylaldoxime must be determined. We hope to work upon this structure in the near future.

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High-Temperature Structure Transitions in Sodium Niobate*

BY M. H. FRANCOMBE

Research Laboratories of The General Electric Company Limited, Wembley, England

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A detailed X-ray 'powder' study of sodium niobate at high temperatures has confirmed the conclusion, reached from optical investigations on single crystals, that the crystal structure does not become strictly cubic until the temperature reaches 650° C.

At temperatures between 420° C. and 480° C. the X-ray evidence is consistent with a slightly distorted multiple unit cell with a tetragonal axial ratio very near to 2. At temperatures above 480° C. tetragonal-type diffraction line splitting reappears and the axial ratio increases to 2·0038 at 560° C. This effect is accompanied by a reduction in the intensity of superlattice reflexions. At 640° C. both these reflexions and the line splitting disappear, indicating a completely isotropic perovskite-type structure.

An explanation of the X-ray effects is suggested in terms of atomic displacements.

1. Introduction

Single-crystal X-ray studies of sodium niobate ($NaNbO_3$) by Wood (1951) and Vousden (1951) have shown that the room-temperature structure is orthorhombic. The structure may also be referred to a pseudo-cubic perovskite-type unit cell with monoclinic axes. The presence of extra X-ray reflexions indicates that this cell is multiple, containing 16 molecules and possessing doubled a_0 and c_0 dimen-

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* Communication from the Staff of the Research Laboratories of The General Electric Company Limited, Wembley, England.

sions and a quadrupled b_0 dimension. Wood's values for these parameters are:

$$a_0 = c_0 = 2\times 3{\cdot}921,\ b_0 = 4\times 3{\cdot}885\ \text{Å},\ \beta = 90^\circ\,40'.$$

The structure modifications at high temperatures have been studied in some detail both by X-ray and optical means. Thus, combined X-ray and optical studies by Wood (1951), and more recently by Shirane, Newnham & Pepinsky (1954), have indicated an abrupt structural transition from orthorhombic to tetragonal crystal symmetry at about 360° C. Detailed optical observations, however, by Cross & Nicholson (1955) indicate that the symmetry above 360° C. is only 'pseudo-tetragonal' (truly orthorhombic) and that there is still a small 'birefringence' between the orthorhombic *a* and *b* directions. Reference to their published graph shows that this effect is only about 5 or 6% of the 'birefringence' between the *a* and *c* directions.

At 470–480° C. optical studies all seem to agree that there is a slight drop in birefringence and the graph given by Cross & Nicholson indicates that this drop is about the same for all directions in the crystal. The graph further shows a clear structure transition from 'pseudo-tetragonal' to fully tetragonal at 520° C., the birefringence between the *a* and *b* directions reducing to zero. A final sharp transition to the completely isotropic condition is detected optically at about 640° C.

In contrast, Shirane, Newnham & Pepinsky's X-ray work has shown a *gradual* decrease in the pseudo-tetragonal-type powder-diffraction-line splitting as the temperature rises above 360° C. until at just above 430° C. the structure is reported as being effectively cubic. No further structural modifications have so far been noticed in X-ray studies up to 640° C., the temperature at which optically the isotropic condition is achieved.

Wood (1951) originally suggested that the differences between the effects observed in the X-ray and optical studies might be explained by assuming that the X-ray method is sensitive to changes in the array of niobium atoms, whilst the optical effects are produced by movements in the oxygen–sodium array. The conclusion drawn by Shirane *et al.* (1954) was that the X-ray technique was probably less sensitive than the optical method to small structural changes.

Since high-angle diffraction lines of the orders used in this work should be particularly sensitive indicators of minute deformations in crystal structure, it is difficult to accept the second suggestion without further examination. A careful X-ray study over the temperature range in question has therefore been made and the results are described in the present report.

2. High-temperature X-ray measurements

A powder specimen of $NaNbO_3$ was prepared by firing Na_2CO_3 and Nb_2O_5 together in a platinum boat at 1280° C. The product was ground and refired at the same temperature until clear, well-resolved diffraction patterns were obtained. Measurements made at 20° C. with a 19 cm. powder camera from diffraction line groups with Σh^2 values of 22 and 24 gave for the unit-cell dimensions

$$a_0 = c_0 = 2\times 3{\cdot}914,\ b_0 = 4\times 3{\cdot}881\ \text{Å},\ \beta = 90^\circ\,39'\,.$$

Using a 19 cm. high-temperature camera, a number of X-ray photographs were taken at temperatures between 20° C. and 640° C. The usual abrupt structural change was observed at about 350° C. A superficial examination of line-splitting effects above this temperature (leaving aside for the moment the fact that 'superlattice' effects continued to persist) indicated a tetragonal crystal structure.

Careful comparison, however, of certain diffraction lines with those obtained on photographs above 640° C., where the structure is known to be completely isotropic, indicated that the symmetry was not in fact fully tetragonal. Thus, residual broadening effects were observed in some X-ray reflexions, and in particular for the diffraction line corresponding to $\Sigma h^2 = 12$ (which should be unsplit in a tetragonal structure) the $K\alpha$ doublet was not properly resolved. The observed effects were in keeping with a structure possessing a symmetry very slightly lower than tetragonal. At 420° C. the splitting of the diffraction line groups had substantially disappeared but slight relative broadening, for example of lines 21 and 22, persisted above this temperature.

It should also be noted that 'extra' reflexions were still present on powder photographs taken up to 420° C., showing that the 'pseudo-tetragonal' cell continues to be a multiple one in which the c_0 dimension is approximately twice the a_0 dimension.

At 505° C. signs of line splitting typical of a tetragonal structural deformation reappeared on the diffraction pattern. At 560° C. further separation of the line components was evident and the axial ratio of the tetragonal (multiple) structure cell had increased to

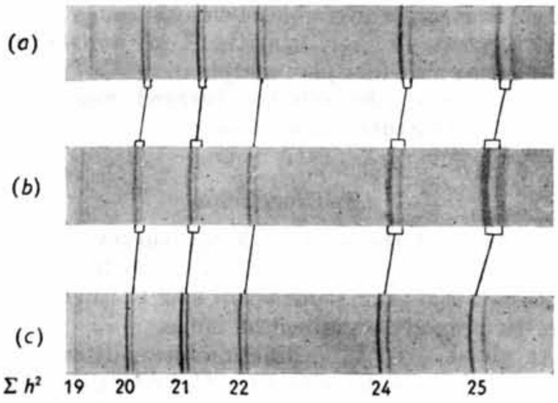

Fig. 1. Reappearance of tetragonal-type diffraction-line splitting in sodium niobate (Cu $K\alpha$ radiation). (*a*) 470° C., (*b*) 560° C., (*c*) 640° C.

Table 1. *X-ray structural data for* $NaNbO_3$ *at different temperatures*

Temperature (°C.)	Crystal symmetry	Lattice parameters: Present values	Lattice parameters: Values obtained by Shirane *et al.**
20	Monoclinic	$a_0 = c_0 = 2 \times 3{\cdot}914$ Å $b_0 = 4 \times 3{\cdot}881$ Å $\beta = 90° 39'$	$a_0 = c_0 = 2 \times 3{\cdot}915$ Å $b_0 = 4 \times 3{\cdot}881$ Å $\beta = 90° 40'$
390	Pseudo-tetragonal	$a_0 = 2 \times 3{\cdot}920$ Å $c_0 = 4 \times 3{\cdot}926$ Å $c_0/a_0 = 2{\cdot}0032$	$a_0 = 2 \times 3{\cdot}919$ Å $c_0 = 4 \times 3{\cdot}927$ Å $c_0/a_0 = 2{\cdot}0040$
420	Pseudo-tetragonal	$a_0 = 2 \times 3{\cdot}924$ Å $c_0 = 4 \times 3{\cdot}924$ Å $c_0/a_0 \sim 2{\cdot}0000$	$a_0 = 2 \times 3{\cdot}921$ Å $c_0 = 4 \times 3{\cdot}927$ Å $c_0/a_0 = 2{\cdot}0028$
560	Tetragonal (changing to simple perovskite-type cell)	$a_0 = 2 \times 3{\cdot}933$ Å $c_0 = 4 \times 3{\cdot}940$ Å $c_0/a_0 = 2{\cdot}0038$	— — —
640	Cubic	$a_0 = c_0 = 3{\cdot}942$ Å	—

* The axial ratios in this column have been modified to correspond to the true multiple unit cell.

2·0038. It seems clear that the structure in this temperature range may be accurately termed tetragonal since the X-ray diffraction line with $\Sigma h^2 = 12$ was now clearly resolved. A photograph at 600° C. showed a slight decrease in the axial ratio to 2·0034, and at 640° C. the diffraction lines were sharp and typical of a strictly cubic structure. Fig. 1 shows the X-ray effects observed at 470, 560 and 640° C. respectively. The variations of unit-cell dimensions with temperature are indicated in Table 1.

Besides changes in the line-splitting effects, diffraction photographs taken at 560° C. and above, compared with photographs taken at lower temperatures, showed another change. There was a sharp reduction in the intensity of those 'extra' reflexions that originate with the multiple unit cell. Thus in the high-temperature range a further modification is taking place such that the structure can be truly described by the simple perovskite cell.

The possibility that these phenomena might have arisen from an irreversible chemical change of some kind was tested by repeating the X-ray exposures and then taking a further photograph at 20° C. The results confirmed that the effects observed were in fact reversible structural alterations.

3. Discussion

The results of the present X-ray survey of sodium niobate in the temperature range above 350° C. have confirmed that at no point below 640° C. can the structure be properly described as cubic.

At about 420° C. diffraction-line-splitting effects point to a near-cubic structure. Consideration of both superlattice effects and residual line broadening, however, indicate a structure which is more truly represented by a multiple 'pseudo-tetragonal' structure cell with the c_0 lattice parameter approximately twice that of the a_0 dimension. Above 480° C. a truly tetragonal structure begins to develop which is probably based on a deformed simple perovskite unit cell. This new tetragonal structure deformation reaches a maximum at about 560° C. and shows only a small decrease up to 600° C. Further increase in temperature from 600° C. to 640° C. is accompanied by a fairly abrupt transition to truly cubic symmetry.

The degree of tetragonal structure deformation must be gauged by two criteria (*a*) the prominence of the X-ray superlattice effects which indicate the presence of a tetragonal unit cell with an axial ratio of approximately 2, and (*b*) splitting in the high-angle X-ray reflexions.

In the temperature range above 520° C. both the optical results of Cross & Nicholson (1955) and the splitting of the X-ray reflexions here observed indicate a purely tetragonal structure. Between 420° C. and 520° C. the picture is confused because, whilst there are marked birefringence effects, there is only a feeble suggestion of splitting in the X-ray diffraction lines. It now seems clear that in this temperature range it is the 'pseudo-tetragonality' based on superlattice effects which must be correlated with birefringence measurements.

The measurements of Shirane *et al.* (1954) show that as the temperature is raised between the 'Curie' point and 480° C. the a_0 dimension of the 'pseudo-tetragonal' unit cell increases uniformly, but the c_0 dimension maintains approximately the same value. A likely explanation is that expansion in the c_0 direction is inhibited by those forces which maintain some of the ions in their displaced, non-special sites. Such a situation would involve a degree of lattice strain. It may be that this strain is manifested in the small and fairly constant birefringence which Cross & Nicholson observe between the orthorhombic a and b directions at temperatures up to 520° C. In effect this means that the 'pseudo-tetragonal' unit cell retains a small but constant shear about its b_0 axis, producing a slight departure of the monoclinic β angle from 90°.

Above 520° C. increased thermal motion permits movement of the displaced ions into sites more typical of the simple lattice possessing an unmodified unit cell. It is probable that the observed dilatation of the crystal lattice in the c_0 direction and the removal of the residual shear distortion mentioned above accompanies or perhaps precedes this process.

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Scattering of X-rays by Defect Structures

By W. Cochran

Crystallographic Laboratory, Cavendish Laboratory, Cambridge, England

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The intensity of X-ray scattering from a crystal containing defects is shown to depend in a simple way on the Fourier transforms of the defects considered separately. An example of the application of the theory is worked out.

1. Introduction

General theories of the coherent scattering of X-rays by a crystal which is disordered or contains imperfections have been given by Zachariasen (1945), and by Matsubara (1952). The effects of imperfections of a particular kind have often been calculated, for example for 'impurity' atoms (Huang, 1947) and for screw dislocations (Wilson, 1952). The general theory given here has the same starting-point as that of Matsubara, but is developed in a different way. The results are equivalent to those of Zachariasen, but are more easily applied to particular problems, as is shown by some examples.

2. General theory

We consider a spherical crystal of radius $\mathscr{R}$, containing N units cells. If we denote the crystal by C, and its Fourier transform by T_C, then

$$T_C(\mathbf{S}) = T_L(\mathbf{S})F(\mathbf{H})\,. \qquad (2\cdot1)$$

$\mathbf{S}$ is a vector in reciprocal space, $\mathbf{H}$ a vector to a point of the reciprocal lattice. $T_L(\mathbf{S})$ is the transform of a lattice bounded by a sphere, and, as is well known, it has an appreciable value only within about $\mathscr{R}^{-1}$ of $\mathbf{S} = \mathbf{H}$. The transform of the contents of one unit cell, $F(\mathbf{S})$, which varies comparatively slowly with $\mathbf{S}$, has therefore been replaced in (2·1) by the structure factor $F(\mathbf{H})$.

We now imagine a defect Δ to be introduced into the crystal to produce an imperfect crystal $C+\Delta$. This defect will in general be an assemblage of both positive and negative atoms—negative at points from which atoms have been displaced, positive at points to which they have been displaced. We thus have

$$T_{C+\Delta}(\mathbf{S}) = T_C(\mathbf{S})+T_\Delta(\mathbf{S})\,. \qquad (2\cdot2)$$

The transform of the defect, $T_\Delta(\mathbf{S})$, will be given by

$$T_\Delta(\mathbf{S}) = \sum_L \sum_m \left(f'_{m,L}\exp\left[2\pi i(\mathbf{R}'_L+\mathbf{r}'_{m,L})\cdot\mathbf{S}\right] - f_m\exp\left[2\pi i(\mathbf{R}_L+\mathbf{r}_m)\cdot\mathbf{S}\right]\right). \qquad (2\cdot3)$$

In this expression, the outer sum is over all unit cells and the inner over all atoms in one unit cell. $\mathbf{R}_L$ locates a particular unit cell in the crystal, and $\mathbf{r}_{m,L}$ a particular atom in that unit cell. The defect is taken to consist of the replacement of atoms of scattering factor f at $\mathbf{R}+\mathbf{r}$ by others of scattering factor f' at $\mathbf{R}'+\mathbf{r}'$.

We next introduce $F_M(\mathbf{H})$, the structure factor of the average unit cell of $C+\Delta$. Thus

$$F_M(\mathbf{H}) = \frac{1}{N}\sum_L \sum_m f'_{m,L}\exp\left[2\pi i(\mathbf{r}'_{m,L})\cdot\mathbf{S}\right]. \qquad (2\cdot4)$$

From (2·3) and (2·4) it follows that

$$T_\Delta(\mathbf{H}) = N(F_M(\mathbf{H})-F(\mathbf{H}))\,. \qquad (2\cdot5)$$

Next we define

$$T_M(\mathbf{S}) = T_L(\mathbf{S})F_M(\mathbf{H})\,; \qquad (2\cdot6)$$

T_M is thus the transform of a crystal of radius $\mathscr{R}$,