It follows from our experimental data that the measurements of the time modulation of a neutron beam gives a real possibility of determining the dynamical effects together with a very small velocity of motion of crystallographic lattice planes of the specimen under investigation. This method can be also applied for the measurements of amplitudes of vibrations of single crystals, excited piezoelectrically or by magnetostriction. The velocities of motion of crystallographic lattice planes are of the order of several tens of cm.sec<sup>-1</sup>, and the corresponding amplitudes in the range of  $10^{-4}$  cm.

The authors wish to thank Doc. Ing. J. Zelenka and Doc. Dr J. Tichý for supplying us with quartz single crystals and Mr J. Vávra for his valuable help throughout the measurements.

#### References

ALEFELD, B., BIRR, M. & HEIDEMANN, A. (1968). Proceedings of the Symposium on Neutron Inelastic Scattering, International Atomic Energy Agency, Vienna.

- BROCKHOUSE, B. N. (1961). Proceedings of the Symposium on Inelastic Scattering of Neutrons, International Atomic Energy Agency, Vienna.
- CADY, W. G. (1964). *Piezoelectricity*. New York: Dover.
- CHALUPA, B., MICHALEC, R., PETRŽÍLKA, V., TICHÝ, J. & ZELENKA, J. (1968). *Phys. stat. sol.* 29, K51.
- JAHNKE, E., EMDE, F. & LÖSCH, F. (1960). Tafeln höherer Funktionen. Leipzig: B. G. Teubner Verlagsgesellschaft.
- JEFFREYS, H. & JEFFREYS, B. S. (1946). Methods of Mathematical Physics. Cambridge Univ. Press.
- MICHALEC, R., CHALUPA, B., PETRŽÍLKA, V., GALOCIOVÁ, D., ZELENKA, J. & TICHÝ, J. (1969). *Phys. stat. sol.* 31, K95.
- MICHALEC, R., VAVŘÍN, J., CHALUPA, B. & VÁVRA, J. (1967). Report ÚJV 1562, Nuclear Research Institute, Prague-Řež.
- PETRŽÍLKA, V. (1968). Nature, Lond., 218, 80.
- PETRŽÍLKA, V. (1968). Czech. J. Phys. B18, 1111.
- SHULL, C. G. & GINGRICH, N. S. (1964). J. Appl. Phys. 35, 678.
- SHULL, C. G., MORASH, K. R. & ROGERS, J. G. (1968). Acta Cryst. A24, 160.

Acta Cryst. (1971). A27, 414

# X-ray Diffuse Scattering from NaNbO3 as a Function of Temperature

# BY F. DENOYER, R. COMÈS AND M. LAMBERT

Laboratoire de Physique des Solides,\* Faculté des Sciences, 91 Orsay, France

### (Received 1 December 1970)

A qualitative description of the X-ray diffuse scattering from NaNbO<sub>3</sub> single crystals as a function of temperature up to 800 °C is given. Two types of distinct diffuse scattering where observed in {100} reciprocal planes and on  $\langle 100 \rangle$  reciprocal axes. While the diffuse scattering in reciprocal planes shows no critical behaviour at the different phase transitions and can be attributed to a 'linear disorder' similar to that suggested earlier for KNbO<sub>3</sub>, the diffuse scattering on reciprocal axes is critical in the vicinity of the 641 °C phase transition. The atomic displacements involved with the linear disorder that persists up to 800 °C are attributed to the niobium atoms; the critical planar disorder in the cubic phase is attributed to rotations of oxygen octahedra similar to those suggested for SrTiO<sub>3</sub> and KMnF<sub>3</sub>. Both types of disorder exist in the cubic paraelectric phase.

#### Introduction

Many recent papers describe experiments in X-ray or neutron scattering from perovskite related compounds [SrTiO<sub>3</sub> (Shirane & Yamada, 1969), KMnF<sub>3</sub> (Minkiewicz & Shirane, 1969; Minkiewicz, Fujii & Yamada, 1970), LaAlO<sub>3</sub> (Plakhty & Cochran, 1968; Axe & Shirane, 1969), KTaO<sub>3</sub> (Shirane, Nathans & Minkiewicz, 1967), PbTiO<sub>3</sub> (Shirane, Axe, Harada & Remeika, 1970), BaTiO<sub>3</sub> (Harada & Honjo, 1967; Comès, Lambert & Guinier, 1968), KNbO<sub>3</sub> (Comès, Lambert & Guinier, 1970*a*)]. Nevertheless, the distribution in the reciprocal space of the scattered intensity which provides direct information on atomic displacements that are responsible for the scattering is only known with some precision in the cases of KNbO<sub>3</sub> (Comès, Lambert & Guinier, 1970a) and BaTiO<sub>3</sub> (Shirane, Axe & Harada, 1970; Comès *et al.* 1970a). These two crystals, which are isomorphous in all their phases, have structures that always result from a slight distortion of the ideal perovskite unit cell; but they never show multiplecell structures as can be found for example in SrTiO<sub>3</sub> (Müller, 1958; Alefeld, 1969), WO<sub>3</sub> (Ueda & Kobayashi, 1963; Andersson, 1963), NaNbO<sub>3</sub> (Vousden, 1951; Bouillaud, 1968), or KMnF<sub>3</sub> (Minkiewicz *et al.* 1970; Beckman & Knox, 1961). Thus, it seemed of interest to study the distribution of the diffuse X-ray scattering as a function of temperature in such a mul-

<sup>\*</sup> Laboratoire associé au C.N.R.S.

tiple-cell perovskite compound with the same photographic technique used for  $KNbO_3$  (Comès, *et al.*, 1970*a*). This was undertaken with NaNbO<sub>3</sub> and the present paper describes the first experimental results.

NaNbO<sub>3</sub> shows a great variety of phases among which the low-temperature rhombohedral phase is ferrielectric, the high-temperature cubic phase is paraelectric (T > 640 °C), and most of the intermediate phases are probably antiferroelectric. Besides the cubic phase only a few structures are known with some precision (Sakowski-Cowley, Lukaszewicz & Megaw, 1969). Even the symmetry of the higher-temperature phases is not well known (Solov'ev, Venevtsev & Zhdanov, 1961; Lefkowitz, Lukaszewicz & Megaw, 1966). But the unit cell is always a multiple of a slightly distorted, ideal perovskite unit cell.

The NaNbO<sub>3</sub> single crystals were grown by C. Flicoteau in the Laboratory of Professor H. Brusset\* and have the form of platelets (about  $2 \times 2 \times 0.1$  mm). The different transition temperatures (above room temperature) of these crystals, and as determined from  $\mu$  DTA analysis, are shown in Fig. 1. Besides small shifts in temperature these transitions are in good agreement with those reported by Lefkowitz *et al.* (1966). In particular the  $\mu$  DTA analysis confirms the existence of a stable phase in the narrow temperature range of 523 °C to 528 °C, which has not always been detected (Bouillaud, 1968). In this paper we distinguish the different phases by the alphabetic symbols introduced by Lefkowitz *et al.* (1966), which are shown in Fig. 1.

The diffuse scattering experiments showed the existence of two completely different types of scattering: in relplanes (reciprocal planes) and on relrods (reciprocal axes).

\* Ecole Centrale des Arts et Manufactures, 92-Chatenay Malabry, France.

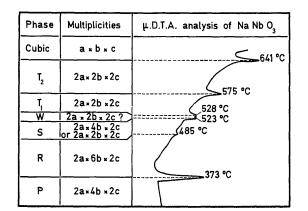


Fig. 1. Microdifferential thermal analysis of NaNbO<sub>3</sub> crystals between room temperature and 700°C. The transition temperatures determine seven phases for which the unit-cell multiplicities and the alphabetic symbols introduced by Lefkowitz *et al.* (1966) are mentioned.

1. Diffuse scattering restricted to reciprocal planes

The diffuse scattering restricted to relplanes is generally similar to that found with  $KNbO_3$  (Comès *et al.*, 1970*a*). At room temperature, and referred to the pseudo-cubic axes of the single unit cell, the scattering is found to be particularly intense in the (010) set of planes, *i.e.* the same set as found with  $KNbO_3$  in the orthorhombic phase.

Nevertheless, two differences exist in the case of KNbO<sub>3</sub>:

(a) A weaker and broader scattering can be seen in the (001) relplanes [Fig. 2(a)]. Taking into account the observed superlattice Bragg reflexions it does not seem that this scattering can be explained by a small amount of twinning.

(b) The new feature of scattering in the planes is the existence of a weak but detectable superlattice scattering in the (010) relplanes passing through the  $0, k + \frac{3}{4}, 0$  and  $0, k + \frac{3}{4}, 0$  relpoints (reciprocal points). This scattering is related to the 4b periodicity along the [010] axes of the room temperature phase P.

# Variation of scattering with temperature in fundamental relplanes

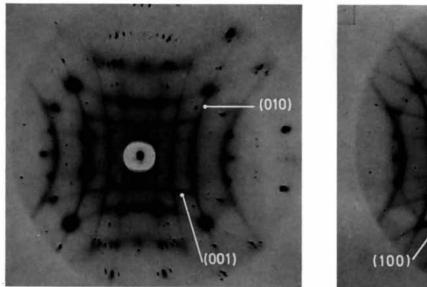
Considering the variation of scattering with temperature in the fundamental  $\{010\}$  relplanes (passing through the relpoints 0k0 with k integers) three temperature regions have to be distinguished:

(a) From room temperature to about  $373 \,^{\circ}$ C (firstphase transition) in which the intensity of the scattering in the fundamental (010) relplanes grows linearly with temperature. Such a growth is also observed with the (001) relplanes; but while the ratio I(010)/I(001) is of the order of 2 at room temperature it has dropped to 1·12 at 300  $^{\circ}$ C so that the intensity in the two sets of planes is nearly the same [Fig. 3(a)]. In following the width of the diffuse lines corresponding to these two sets of planes, identical values are found in the vicinity of the 373  $^{\circ}$ C phase transition [Fig. 3(b)].

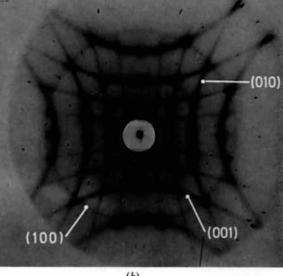
The third set of (100) relplanes becomes detectable in the higher part of this temperature region; the (100) relplanes are perpendicular to the incident X-ray beam and appear as rings in Fig. 2. For experimental reasons, the scattering in these planes always appears weaker, on the photographs [Fig. 2(a)], than in the (001) and (010) sets. Consequently, it is difficult to compare the respective intensities. From the symmetry point of view the intensity of the scattering in the (100) and (001) relplanes should be the same in phase P as well as in phase R.

(b) From 373 to 641 °C which includes all the phase transitions. At 390 °C [Fig. 2(b)], if the very weak superlattice scattering and small differences in intensity are excepted, the X-ray patterns with respect to the diffuse scattering look very similar to those of the cubic phase of KNbO<sub>3</sub> (Comès *et al.* 1970), *i.e.* with scattering in the three sets of  $\{100\}$  relplanes. At the present time it is impossible to give any quantitative data about the

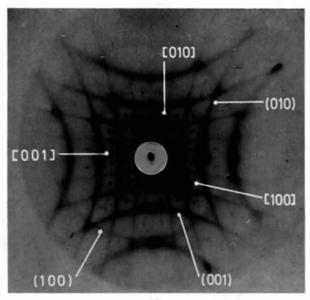
1



(a)



(b)



(c)

Fig. 2. Diffuse X-ray scattering patterns from NaNbO<sub>3</sub> performed with Mo  $K\alpha$  radiation, and with a fixed crystal ([100] parallel to incident beam). (a) Phase P (room temperature). The curved vertical diffuse lines correspond to scattering restricted to (010) relplanes; also, the existence of very weak super lattice scattering in the (010) relplanes passing through the 0,  $k+\frac{1}{4}$ , 0 and  $0, k + \frac{3}{4}, 0$  reciprocal points is noted. The curved horizontal diffuse lines which are broader correspond to (001) relplanes. (b) Phase  $R(390^{\circ}C)$ . The curved diffuse lines and circles correspond to the three sets of  $\{100\}$  relplanes; the superlattice scattering is now found to be restricted to the relplanes passing through the 0,  $k + \frac{1}{2}$ , 0 and 0, 0,  $l + \frac{1}{2}$  relpoints. (c) Cubic phase (680 °C). The diffuse scattering in the three sets of  $\{100\}$  relplanes coexists with a critical scattering along reciprocal  $\langle 100 \rangle$  axes, which appears as short straight streaks halfway between the diffuse relplanes, and as dots for the axes parallel to the incident X-ray beam.

intensity variation of the diffuse scattering in this region. Several small discontinuities in scattering intensity in the relplanes appear at the different phase transitions. Definite conclusions will need more precise quantitative data.

(c) Above  $641 \,^{\circ}$ C (in the paraelectric phase) in which the scattering intensity in the relplanes is found to be constant from  $641 \,$  to  $800 \,^{\circ}$ C.

# Variation of superlattice scattering in relplanes with temperature

Two modifications of the superlattice scattering can be observed at the 373 °C phase transition when the multiplicity along the [010] axis changes from 4 in phase P to 6 in phase R:

(a) The superlattice scattering becomes detectable in the (001) as well as in the (010) relplanes. In the new set of superlattice relplanes, *i.e.* (001), the scattering is restricted to those relplanes passing through the  $0,0,l+\frac{1}{2}$  relpoints.

(b) The multiplicity of the scattering in the (010) relplanes is altered. In phase P, the scattering is restricted to the relplanes passing through the  $0, k + \frac{1}{4}, 0$  and  $0, k + \frac{3}{4}, 0$  relpoints. In phase R, it is restricted to the relplanes passing through the  $0, k + \frac{1}{2}, 0$  relpoints. Despite the difference of multiplicity along the [001] and [010] divide the superlattice scattering in the (001) and (010) relplanes is identical [Fig. 2(b)].

For reasons already mentioned, it is impossible to obtain any information about the superlattice scattering in the third set of planes (100). From the symmetry point of view it should be identical with that found for the (001) relplanes.

At higher temperatures the distribution of the superlattice scattering in relplanes remains unchanged; but its intensity decreases progressively and becomes undetectable at about 600 °C.

# Critical scattering along reciprocal axes

In addition to the scattering in reciprocal planes, a new type of scattering along  $\langle 100 \rangle$  reciprocal axes, passing through the superlattice nodes of the  $T_2$  phase (node types:  $h + \frac{1}{2}, k + \frac{1}{2}, l + \frac{1}{2}$ ), appear in the vicinity of the 641 °C phase transition, *i.e.* as the structure changes to the ideal perovskite cubic structure. This scattering appears in Fig. 2(c) as short straight streaks halfway between the scattering in two successive relplanes and as dots for the axes parallel to the incident beam. This scattering is critical. It grows rapidly in the  $T_2$  phase as the transition temperature is approached and it decreases at a slower rate above 641 °C in the cubic phase. It is still apparent at 800 °C (Fig. 4).

## Discussion

The interpretation of experiments in the X-ray and neutron diffuse scattering from perovskite-related com-

pounds aroused controversial discussions about the dynamical or static character of the disorder responsible for it, and about its relation with the soft-phonon theory of phase transitions (Müller, 1969; Comès,

120 110 100 90 INTENSITY (arbitrary units) + (010) relplane 80 o(001) relplane 70 60 50 40 30 20 10 0Ì 100 200 300 400 500 600 700 800 TEMPERATURE (°C) (a) (010) AND (001) RELPLANES (010) relplane (001) relplane arbitrary units) COMPARED WIDTH OF o 100 200 300 400 500 600 700 800 TEMPERATURE (°C) **(b)** 

Fig. 3. Variation of scattering with temperature in fundamental relplanes. (a) Variation of the intensity of the scattering restricted to the (010) and (001) relplanes as a function of temperature (measured at the relpoints h=0.05, k=1, l=0.35 and h=0.35, k=0.05, l=1). (b) Variation of the width of the diffuse lines corresponding to the (010) and the (001) relplanes as a function of temperature.

Lambert & Guinier, 1970b). As X-rays cannot distinguish a dynamical disorder from a static one, we will limit our interpretation of the diffuse scattering in NaNbO<sub>3</sub> to a description of the atomic displacements that could be responsible for it.

For this reason we must look somewhat deeper into the different structures of NaNbO<sub>3</sub>. These structures seem to involve two different types of distortions of the ideal cubic perovskite unit cell (Lefkowitz et al., 1966; Megaw, 1968): an off-centred displacement of the niobium atom, and different types of tilts or rotations of the oxygen octahedra. The off-centred displacement of the niobium atoms has been found by Megaw (1968) to decrease with rising temperature, becoming zero or small for temperatures higher than 470°C. The distortions of the higher-temperature phases, i.e. phases S, W,  $T_1$  and  $T_2$  (Fig. 1) which are between 485 and 641 °C, seem to involve mainly tilting of the oxygen octahedra which has been found for the multiple-cell structures of SrTiO<sub>3</sub> and KMnF<sub>3</sub>, for example. These considerations are a help in finding the atomic displacements involved with the diffuse scattering.

### The linear disorder in NaNbO<sub>3</sub>

Diffuse scattering restricted to reciprocal planes, produced by a crystal in which no substitutional disorder can be involved, must be attributed to the existence of a displacement disorder. The atomic displacements are correlated along axes of the structure perpendicular to the reciprocal planes in which the diffuse scattering is found, *i.e.* a linear disorder exists in the crystal. In addition to the distortions from the ideal perovskite unit cell which can be determined from the Bragg reflexion data, disorder displacements of atoms, correlated along  $\langle 100 \rangle$  axes, exist in NaNbO<sub>3</sub>. The similarity of the diffuse scattering in relplanes of NaNbO<sub>3</sub> and that which was found for KNbO<sub>3</sub> leads one to think of a 'chain structure', which besides minor modi-

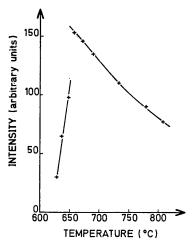


Fig. 4. Variation of the intensity of the scattering restricted to reciprocal axes as a function of temperature (measured at the relpoint h=0.1,  $k=\frac{3}{2}$ ,  $l=\frac{1}{2}$ ).

fications related to the existence of the multiple-cell structure, should be nearly identical to that described for KNbO<sub>3</sub> (Comès et al., 1970a). The fact that the scattering intensity along one plane (along a diffuse line of the pattern) does not show any modulation suggests it is only one type of atom that, in first approximation, is responsible for this scattering. The strong intensity of the scattering and the possibility of observing the diffuse planes at rather large angles, seem to indicate that the linear disorder is mainly attributable to displacements of the niobium atoms. The general considerations about the structures of NaNbO3 mentioned previously, and the variation of diffuse scattering intensity with temperature leads to the same conclusions. It is precisely in the same temperature range, from room temperature to 500°C, that the value of the long-range ordered off-centre displacements of the niobium atom is found (from Bragg reflexion data) to decrease; also, diffuse scattering intensity in the fundamental (100) relplanes is found to increase. Both these facts can be explained by an increasing linear disorder involving the niobium atoms.

#### Planar disorder and critical scattering in NaNbO<sub>3</sub>

Critical scattering along reciprocal axes, which is superimposed on diffuse scattering along reciprocal planes, is a completely new phenomenon. Critical X-ray scattering in perovskites in the vicinity of phase transitions has already been found in LaAlO<sub>3</sub> (Plakhty & Cochran, 1968) and KMnF<sub>3</sub> (Minkiewicz, *et al.*, 1970). But despite some information on the scattering anisotropy in KMnF<sub>3</sub>, NaNbO<sub>3</sub> is the first example in which the distribution of the scattering in reciprocal space is known. This allows one to deduce some direct information about the type of atomic displacements responsible for it.

The critical scattering in NaNbO<sub>3</sub> is restricted to  $\langle 100 \rangle$  reciprocal axes. This means that the atomic displacements responsible for it are correlated in {100} lattice planes. In other words, collective displacements exist in large portions of {100} lattice planes.

Critical scattering is not restricted to the vicinity of the superlattice Bragg spots of the lower-temperature phase; it is continuous along a whole reciprocal rod, which means that there is no correlation of the displacements between parallel and successive {100} planes.

Scattering is found on the reciprocal axes passing through the superlattice node of the lower-temperature phase (phase  $T_2$ , Fig. 1, multiplicity:  $2a \times 2b \times 2c$ ). This indicates that the planar correlation of the atomic displacements involves a local doubling of the unit cell in the cubic phase (multiplicity of the bulk crystal  $a \times a \times a$ ); also, the local order might be related to the structure of the  $T_2$  phase.

From the width of the diffuse lines, it is possible to deduce an order of magnitude for the correlation lengths: while a length of less than 100 Å is found for the linear disorder, the order of magnitude for the planar disorder is 400 Å. This difference supports the idea that the linear and planar disorders have two completely different origins. The X-ray patterns reveal that the scattering intensity along the relrods decreases at a much quicker rate when the angle of reflexion increases, than does the intensity of the scattering in relplanes; this might indicate that the bigger (though lighter) oxygen atoms are responsible for it. Considering that the linear disorder has been found to be mainly due to the niobium atoms, these facts suggest that the oxygen atoms are those that are mainly responsible for the critical scattering on relrods.

Unfortunately, the structure of the  $T_2$  phase of NaNbO<sub>3</sub> is not known in detail, but it is possible to make reasonable suggestions about it. We have already mentioned that the departure from the ideal perovskite structure of the  $T_2$  phase is likely to involve only tilts of the oxygen octahedra. The optical observations made in the  $T_2$  phase are coherent with a tetragonal symmetry, which has also been suggested from X-ray diffraction measurements. Thus, it is likely that the  $T_2$  phase of NaNbO<sub>3</sub> has a structure similar to that of the tetragonal phases of SrTiO<sub>3</sub> or KMnF<sub>3</sub>, with space group I4/mcm  $(D_{4h}^{18})$ . This structure has a multiplicity  $2a \times 2b \times 2c$  (a=b) as is found for NaNbO<sub>3</sub>. Its departure from the ideal perovskite structure is due to rotations of the oxygen (or fluorine in the case of KMnF<sub>3</sub>) octahedra about their tetrad axes parallel to c, [Fig. 5(a)] in which the successive layers perpendicular to the c axes correspond to alternate rotations in the opposite sense.

This type of structure provides a possible picture of the atomic displacements in the cubic phase that are responsible for the diffuse scattering along reciprocal axes, because it involves a correlation of the atomic displacements in (001) planes. To give a qualitative account for the diffuse scattering, one has only to consider a local order in the {001} planes involving the same type of tilts, *i.e.* rotations of the oxygen octahedra about the cube axes. The differences with the  $T_2$  phase are that:

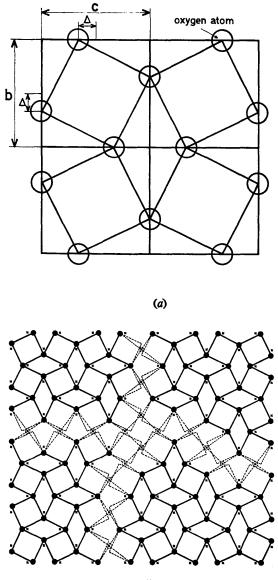
(a) In a given  $\{001\}$  plane, the rotations of the octahedra are only coherent in regions of about 400 Å diameter, giving a sort of microdomain structure [Fig. 5(b)].

(b) Such a planar correlation of the atomic displacements exists in the three sets of  $\{100\}$  planes of the cubic phase.

(c) The alternate sense of rotation of the successive layers is destroyed, giving a bulk unit-cell multiplicity of 1 and an average cubic symmetry.

With such a structure each (100) plane (or portion of such a plane) scatters partly independent of the others, giving a diffuse scattering along whole reciprocal axes.

The oxygen displacements associated with the scattering on *one* set of relrods, for a given single cubic unit cell are given in Fig. 6(a). Final displacements, assuming that each unit cell contributes simultaneously to the scattering on the three sets of reciprocal axes, are given in Fig. 6(b). Simultaneous rotations of the octahedra occur about the three tetrad axis. At the scale of one unit cell such a description is identical with the atomic displacements of a triply degenerate  $\Gamma_{25}$  optic phonon mode (Cowley, 1964); this mode has been suggested as being responsible for the 110°K phase transi

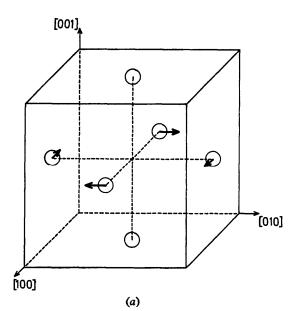


(b)

Fig. 5. Atom displacement and planar correlations. (a) Displacement in a (100) plane of the oxygen atoms involved with rotations of the oxygen octahedra about the tetrad axis parallel to [100]. (b) Planar correlations limited to microdomains of coherent rotations of the octahedra; approximate dimension of such regions is 400 Å. The structure of the borders of the microdomains is not known; dotted lines are drawn just to show that the coherence of the alternate rotations of the successive octahedra is broken. Crosses show the average periodic lattice.

tion in SrTiO<sub>3</sub> (Fleury, Scott & Worlok, 1968) and the 184°K phase transition in KMnF<sub>3</sub> (Minkiewicz & Shirane, 1969). The difficulty of a similar phonon description for the scattering reported here lies in the extension of the diffuse scattering in reciprocal space, which restricts the correlations of these displacements to one plane while a *simple* phonon description should involve correlations in a certain volume.

In a general sense, it is not very clear to us how a thermal-vibration mode can account for displacements correlated in each  $\{100\}$  plane, without any correlation



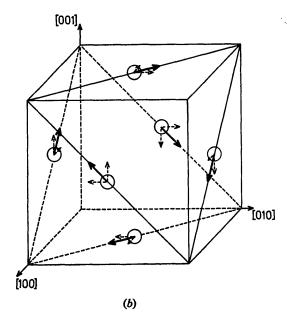


Fig. 6. Displacements of the oxygen atoms in one unit cell; (a) for a rotation of the octahedra about one [100] axis, (b) for simultaneous rotations about the three {100} axes.

between the displacements in the successive parallel planes.

The qualitative considerations describing the atomic displacements can be confirmed by a simplified calculation in which only one set of correlation planes is considered, e.g. the (100) planes. For further simplicity we consider only the four oxygen atoms of each single unit cell which are displaced by the rotation. We assume a crystal with  $N_1$  unit cells in the **a** direction ([100]),  $N_2$  in the **b** direction ([010]) and  $N_3$  in the **c** direction ([001]). In the planes perpendicular to [100] the oxygen octahedra are rotated as shown in Fig. 5; this results in the oxygen atoms being displaced from their ideal symmetric position of  $\varepsilon \Delta c$  along [001] or  $\varepsilon \Delta \mathbf{b}$  along [010], where  $\varepsilon = \pm 1$  according to the atom considered, and  $\Delta$  is the displacement parameter. The sense of rotation of the successive octahedra along the [100] direction is at random, either positive or negative, giving two types of (100) planes distributed at random along [100]. With such a structure total correlation exists in each (100) plane, and no correlation (as far as the displacements are concerned occurs between the different (100) planes. The calculation of the diffracted intensity by such a crystal gives two terms:

(a) The contribution, to the Bragg reflexion, of the oxygen atoms considered:

$$16f_o^2 \left(\frac{\sin \pi N_1 h}{\sin \pi h}\right)^2 \left(\frac{\sin 2\pi N_2 k}{\sin 2\pi k}\right)^2 \left(\frac{\sin 2\pi N_3 l}{\sin 2\pi l}\right)^2$$

 $\times \cos^2 \pi k \cos^2 \pi l(\cos \pi k \cos 2\pi \Delta l + \cos \pi l \cos 2\pi \Delta k)^2$ , which shows that the local doubling of the unit cell does not result in a long-range doubling; the average multiplicity is still 1 as the above expression is different from zero only for *h*, *k*, *l* integers.

(b) The diffuse scattering term:

$$16f_o^2 N_1 \left(\frac{\sin 2\pi N_3 l}{\sin 2\pi l}\right)^2 \left(\frac{\sin 2\pi N_2 k}{\sin 2\pi k}\right)^2$$

 $\times \sin^2 \pi k \sin^2 \pi l (\sin \pi l \sin 2\pi \Delta k - \sin \pi k \sin 2\pi \Delta l)^2$ in which the first line shows that the diffuse scattering is localized on [100] reciprocal axes; the second line gives the extinctions and the relative intensities of the scattering along the different axes: (1) no scattering along the axes passing through the Bragg spots of the cubic phase (l and k integers), (2) no scattering for  $l=n+\frac{1}{2}$  and  $k=n'+\frac{1}{2}$  if n=n' and (3) the most intense scattering is observed along the axes with  $l=n+\frac{1}{2}$ , k= $n'+\frac{1}{2}$  and l+k odd, and a weaker scattering along those with l+k even.

The above calculation is over-simplified. A complete interpretation must consider the simultaneous correlation of the three sets of  $\{100\}$  planes to account for the three sets of reciprocal axes where the diffuse scattering is observed. Also, the calculation should probably allow for small contributions from the niobium and sodium atoms. Nevertheless, the general agreement is found to be good as evidenced by the appearance of the three important features mentioned above [(1), (2) and (3)] in Fig. 2(c).

#### Conclusion

The choice of a crystal such as NaNbO<sub>3</sub>, whose structure is not well known, in most of its phases, to perform such experiments, might at first seem surprising, SrTiO<sub>3</sub>, which has been extensively studied with neutrons. would be more appropriate in yielding awaited data; but the available X-ray wavelengths are not suited to study weak phenomena such as diffuse scattering with SrTiO<sub>3</sub> samples. The Mo K $\alpha$  radiation ( $\lambda = 0.710$  Å) excites the fluorescence of strontium with  $\lambda = 0.88$  Å which is impossible to eliminate, and the Cu Ka radiation ( $\lambda = 1.54$  Å) is heavily absorbed by the titanium atoms. NaNbO3 and most of the other niobates correspond to the best experimental conditions for two reasons. First, the absorbtion of the Mo Ka radiation is very small which allows the use of bigger samples and thus more scattering atoms. Second, the heavy atom, which has the highest scattering factor, is in the strategic position of the single unit-cell centre (its displacement is directly related to the electrical properties). This explains the very intense scattering in relplanes with NaNbO3 as well as with KNbO3, and the fact that it was possible to observe diffuse scattering from oxygen atoms. It is perhaps possible to confirm the similarity of the 641 °C phase transitions of NaNbO3 and the 110°K phase transitions of SrTiO<sub>3</sub> which is suggested here, by studying the diffuse scattering in the vicinity of the 184°K phase of KMnF<sub>3</sub>.\*

The qualitative results and interpretations reported here should be considered as preliminary. A detailed long-run study of the diffuse scattering in NaNbO<sub>3</sub> above room temperature, as well as in the low-temperature ferroelectric phase, is now in process. Precise interpretations will need more complete information about the mean structures of the different phases of NaNbO<sub>3</sub> which are presently being studied in Cambridge Cavendish Crystallographic Laboratory.

We are deeply indebted to Dr Helen D. Megaw for introducing us to the complex structures of NaNbO<sub>3</sub>, and grateful to L. Deschamps for his technical assistance. This work was partly sponsored by the French 'Direction des Recherches et Moyens d'Essais' under contract No. 70.34.045.00.470.75.01.

#### References

- ALEFELD, B. (1969). Z. Phys. 222, 155.
- ANDERSSON, G. (1963). Acta Chem. Scand. 7, 154.
- AXE, J. D. & SHIRANE, G. (1969). Phys. Rev. 183, 820.
- BECKMAN, O. & KNOX, K. (1961). Phys. Rev. 121, 376.
- BOUILLAUD, Y. (1968). Thesis, Bordeaux (France).
- COMÈS, R., LAMBERT, M. & GUINIER, A. (1968). Solid State Commun. 6, 715
- COMÈS, R., LAMBERT, M. & GUINIER, A. (1970a). Acta Cryst. A 26, 244.
- COMÈS, R., LAMBERT, M. & GUINIER, A. (1970b). J. Phys. Soc. Japan, 28 (Suppl.), 195 (see discussion).
- COWLEY, R. A. (1964). Phys. Rev. 134, A981.
- FLEURY, P. A., SCOTT, J. F. & WORLOK, J. M. (1968). Phys. Rev. Letters. 21, 16.
- HARADA, J. & HONJO, G. (1967). J. Phys. Soc. Japan, 22, 45.
- ISMAILZADE, I. G. (1963). Sov. Phys. Cryst. 8, 284.
- LEFKOWITZ, I., LUKASZEWICZ, K. & MEGAW, H. D. (1966). Acta Cryst. 20, 670.
- LYTLE, F. W. (1964). J. Appl. Phys. 35, 2212.
- MEGAW, H. D. (1968). Acta Cryst. A24, 589.
- MEGAW, H. D. & Wells, M. (1958). Acta Cryst. 11, 858.
- MINKIEWICZ, V. J. FUJII, Y. & YAMADA, Y. (1970). J. Phys. Soc. Japan, 28, 443.
- MINKIEWICZ, V. J. & SHIRANE, G. (1969). J. Phys. Soc. Japan, 26, 674.
- Müller, K. A. (1958). Helv. Phys. Acta 31, 173.
- Müller, A. (1969). Solid State Commun. 7, 589.
- PLAKHTY, V. & COCHRAN, A. (1968). Phys. stat. sol. 29, K81.
- SAKOWSKI-COWLEY, A. C., LUKASZEWICZ, K. & MEGAW, H. D. (1969). Acta Cryst. B25, 851.
- SHIRANE, G., AXE, J. D. & HARADA, J. (1970). To be published.
- SHIRANE, G., AXE, J. D. HARADA, J. & REMEIKA, J. P. (1970). *Phys. Rev. B*, **2**, 155.
- SHIRANE, G., NATHANS, R. & MINKIEWICZ, V. J. (1967). Phys. Rev. 157, 396.
- SHIRANE, G., NEWNHAM, R. & PEPINSKY, R. (1954). Phys. Rev. 96, 581.
- SHIRANE, G. & YAMADA, Y. (1969). Phys. Rev. 177, 858.
- SOLOV'EV, S. P., VENEVTSEV, Y. N. & ZHANOV, G. S. (1961). Sov. Phys. Cryst. 6, 171.
- UEDA, R. & KOBAYASHI, J. (1963). Phys. Rev. 91, 1565.
- UNOKI, H. & SAKUDO, T. (1967). J. Phys. Soc. Japan, 23, 546.
- VOUSDEN, P. (1951). Acta Cryst. 4, 545.
- WOOD, E. (1951). Acta Cryst. 4, 353.
- YAMADA, Y. & SHIRANE, G. (1969). Phys. Rev. 177, 848.

<sup>\*</sup> Note added in proof: The experiment has been carried out and the results are described in *Physics Letters*.