Structural distortions in the low-temperature phase of NbO_2†

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At about 810°C niobium dioxide undergoes an apparently second-order transition between a high-temperature (HT) rutile structure and a low-temperature (LT) phase whose structure is slightly distorted from rutile. The primary order parameters of the transition are the amplitudes of sinusoidal displacement waves with wave vectors $\vec{q}_p \equiv (1/4, \pm 1/4, 1/2)$. These waves give rise to a series of superlattice reflections in diffraction patterns obtained with the LT phase. Additional superlattice reflections occur at wave vectors which are related by the rutile point group to $\vec{q}_m \equiv (1/2,1/2,0)$ and $\vec{q}_x \equiv (1/2,0,0)$. The latter reflections may be diffraction harmonics or they may represent the presence of secondary distortions in the LT phase. A detailed neutron diffraction study at room temperature has allowed the LT structure to be determined and has demonstrated that both primary and secondary distortions are required for an adequate description of this phase. The general symmetry properties of the primary distortion are discussed and this distortion is discribed in terms of a simple model involving dimerization of c-axis chains of Nb atoms.

I. INTRODUCTION

Niobium dioxide undergoes a structural phase transition[1] at a temperature of about 810 °C. Close to the transition, which experiment indicates to be of a continuous nature, there are anomalous changes in both electrical resistivity and magnetic susceptibility.[2,3] X-ray experiments have shown that, in the high-temperature (HT) phase, NbO_2 crystallizes with a rutile structure[1] (cf. Fig. 1). In the low-temperature (LT) phase the structure is slightly distorted and a series of superlattice reflections appear on x-ray photographs.[4] While the x-ray measurements have succeeded in identifying the space group to which the LT structure belongs (C_{4h}^6), they have not provided an accurate determination of all atomic positions in this phase. In particular, the deviation of the positions of oxygen atoms from the ideal rutile sites have been determined with uncertainties which are equal to or greater than the deviations themselves.[4]

The vectors $\vec{a}_i^T$ which define the body-centered tetragonal unit cell of the LT phase are related to the unit-cell dimensions $\vec{a}_i^0$ of the HT rutile cell by

$$\vec{a}_1^T = 2(\vec{a}_1^0 - \vec{a}_2^0), \quad \vec{a}_2^T = 2(\vec{a}_1^0 + \vec{a}_2^0), \quad \vec{a}_3^T = 2\vec{a}_3^0 . \tag{1a}$$

For convenience we choose an (unconventional) LT primitive unit cell bounded by the vectors $\vec{a}_i$, where

$$\vec{a}_1 = 2(\vec{a}_1^0 - \vec{a}_2^0), \quad \vec{a}_2 = 2(\vec{a}_1^0 + \vec{a}_2^0), \quad \vec{a}_3 = 2\vec{a}_1^0 + \vec{a}_3^0 . \tag{1b}$$

These transformations imply that the reciprocal lattices of the high- and low-temperature phases are related by

$$\vec{\tau} = \vec{\tau}_0 + \vec{q}_s . \tag{2}$$

Here $\vec{\tau}_0$ and $\vec{\tau}$ are reciprocal-lattice vectors of the high- and low-temperature phases and $\vec{q}_s$ may be any member of the sets

$$\{\vec{q}_p\} \equiv \{\tfrac{1}{4}, \tfrac{1}{4}, \tfrac{1}{2}\}, \quad \{\vec{q}_x\} \equiv \{\tfrac{1}{2}, 0, 0\}, \quad \{\vec{q}_m\} \equiv \{\tfrac{1}{2}, \tfrac{1}{2}, 0\}, \quad \vec{q}_\Gamma \equiv (0,0,0), \tag{3}$$

where $\vec{\tau}_0 \equiv (h,k,l)$ and h,k,l are integers. In Eq. (3) the quantity $\{\vec{q}_s\}$ denotes all wave vectors in the "star" of $\vec{q}_s$, that is, all wave vectors which can be generated from $\vec{q}_s$ by operation of the point group of the HT phase.

Superlattice reflections of the P, M, and X types were studied in the recent neutron scattering experiment of Shapiro *et al.*[5] These authors found that the intensities of M- or X-type reflections and the squares of the intensities of P-type reflections showed the same dependence on sample temperature. The X and M reflections were however

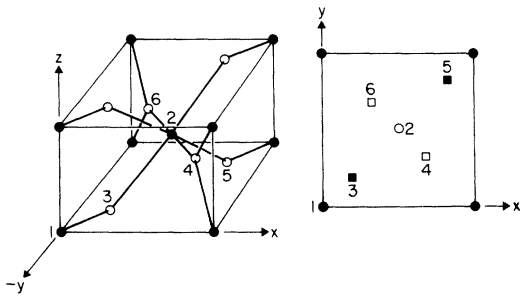

FIG. 1. (a) Unit cell of the high-temperature rutile phase of NbO_2. ● : Nb, ○: Oxygen. The numbers beside the atoms are the values of k in, for example, Eqs. (4), (12), etc. (b) Projection of the high-temperature unit cell on the $x-y$ plane. Filled symbols are at $z=0$ while open symbols are at $z=\frac{1}{2}c$. Niobium atoms are denoted by circular symbols while oxygens are squares.

invariably much weaker than those of the P type. In addition, critical scattering was observed around $\{\vec{q}_p\}$ at temperatures slightly above the phase transition temperature T_c while no such scattering was observed in the neighborhoods of the X- or M-type reflections. From these observations it was concluded[5] that the intensities of the P-type reflections provide a measure of the primary order parameter associated with the structural transformation in NbO_2. In order to explain the behavior of the X- and M-type reflections Shapiro *et al.* noted that any wave vector in the stars of $\vec{q}_x$ and $\vec{q}_m$ can be written as a linear combination of two wave vectors in $\{\vec{q}_p\}$. Thus the observed temperature dependence of the X- and M-type reflections may be explained if these reflections are diffraction harmonics obtained from a rutile structure modulated only by sinusoidal distortions with wave vectors $\{\vec{q}_p\}$. The X- and M-type reflections may also be obtained from a LT phase in which the rutile structure is modulated by distortions of wave vectors $\{\vec{q}_x\}$ and $\{\vec{q}_m\}$ in addition to the P-type modulations. These two situations are of course different physically; on the one hand the X and M reflections are a manifestation of the manner in which the neutron probes the lattice structure while on the other hand these reflections are related to an actual distortion of the rutile structure. In the latter case the X- and M-type refelctions would be a measure of secondary, induced order parameters similar in origin to the ferroelectric polarization which appears in improper ferroelectrics.[6] Phase transitions in systems which display secondary order parameters of this type have recently received theoretical attention from Achiam and Imry[7] and from Murata.[8]

In order to determine the relative significance of the two explanations of the X and M reflections discussed above, accurate structural data for the LT phase are required. The existing x-ray data are not of sufficient accuracy to determine whether or not a secondary distortion is present in NbO_2. It was in an attempt to answer this question that the experiment described in this paper was performed.

In addition to the foregoing considerations our desire to thoroughly understand the low-temperature phase of NbO_2 is a natural preliminary to the study of the static and dynamic critical phenomena associated with the structural phase transition in this material. Renewed interest in these phenomena has recently been generated by Mukamel[9] who has pointed out that NbO_2 is an example of a system with a four-component order parameter.[10] Mukamel has used renormalization-group theory to estimate the critical exponents of such a system and has found them to be markedly different from the mean-field values which appear to describe most structural transitions so far studied.

The remainder of this paper is divided into five sections. In Sec. II the neutron scattering cross section for the LT phase of NbO_2 is derived for the case in which only primary distortions exist. The analysis, which is applicable with minor modification to a large class of problems concerned with structural phase transitions, demonstrates the manner in which X and M reflections are produced as diffraction harmonics. The constraints which symmetry imposes upon the nature of the primary distortions are considered in Sec. III. Section IV, which contains a discussion of the secondary order parameters which may occur in NbO_2, completes the discoursive part of the paper. Experimental data obtained by neutron diffraction with a LT sample of NbO_2 are described in Sec. V and analyzed in Sec. VI.

II. SCATTERING CROSS SECTION WITH PRIMARY DISTORTION ONLY

The qualitative features of x-ray data[4] for NbO_2 show that the low-temperature phase may be obtained by superposing on the HT rutile structure sinusoidal distortions with wave vectors $\{\vec{q}_p\}$, $\{\vec{q}_m\}$, $\{\vec{q}_x\}$, and $\vec{q}_\Gamma$. Thus if $\vec{r}^{\,0}_{lk}$ denotes the position of the kth atom (cf. Fig. 1) in the lth unit cell of the rutile phase and if $\vec{r}_{lk}$ denotes the position of the same atom in the LT phase one may write

$$\vec{r}_{lk}=\vec{r}^{\,0}_{lk}+\vec{u}_{lk}\equiv\vec{x}^{\,0}_l+\vec{r}^{\,0}_k+\vec{u}_{lk}\ , \tag{4}$$

where $\vec{x}^{\,0}_l$ is the position of the origin of the lth rutile cell and the displacement $\vec{u}_{lk}$ is given by

$$\vec{u}_{lk}=\sum_{q_s} Q_s(T)\,\vec{E}_k(\vec{q}_s)\exp(i\vec{q}_s\cdot\vec{x}^{\,0}_l)\ . \tag{5}$$

In this equation $Q_s(T)$, which is the amplitude of the modulation of wave vector $\vec{q}_s$, may be considered as a temperature- (T) dependent order parameter. The unit vector $\vec{E}_k(\vec{q}_s)$ describes the lattice distortions which result from the presence of the modulation of wave vector $\vec{q}_s$.

While Eq. (5) provides the most general description of the LT phase the actual situation may, as was discussed in the Introduction, be somewhat simpler in that only one order parameter Q_p may be finite. In this case one may rewrite Eq. (5) in the form

$$\vec{u}_{lk}=\sum_{i=1,2}[\vec{a}(k\vec{q}_i\,|\,T)\cos(\vec{q}_i\cdot\vec{x}^{\,0}_l) + \vec{b}(k\vec{q}_i\,|\,T)\sin(\vec{q}_i\cdot\vec{x}^{\,0}_l)]\ , \tag{6}$$

where

$$\vec{q}_1\equiv(\tfrac{1}{4},\tfrac{1}{4},\tfrac{1}{2})\ ,\quad \vec{q}_2\equiv(\tfrac{1}{4},-\tfrac{1}{4},\tfrac{1}{2}) \tag{7}$$

and $\vec{a},\vec{b}$ are real, temperature-dependent amplitudes. In obtaining Eq. (6) from the general re-

sult given by Eq. (5) the wave vectors $-\vec{q}_1$ and $-\vec{q}_2$ have been eliminated by demanding that $\vec{u}_{lk}$ be real, and other wave vectors belonging to $\{\vec{q}_p\}$ have been omitted because they differ from $\vec{q}_1$ or $\vec{q}_2$ by a rutile reciprocal-lattice vector $\vec{\tau}_0$.

In order to obtain expressions for the intensities of the superlattice reflections which result from a distortion of the type given by Eq. (6) it is necessary to evaluate the neutron scattering cross section $d\sigma/d\Omega$ defined by

$$\frac{d\sigma}{d\Omega} \propto |\rho(\vec{Q})|^2 ,$$

where

$$\rho(\vec{Q}) = \sum_{lk} b_k \exp(i\vec{Q}\cdot\vec{r}_{lk}) , \tag{8}$$

Here b_k is the bound coherent scattering length (with a Debye-Waller factor included) of the kth atomic species and $\vec{Q}$ is the neutron scattering vector. Equation (8) may be evaluated by substituting for $\vec{r}_{lk}$ from Eqs. (4) and (6) and by making use of the identity[11]

$$e^{iz\sin\phi} = \sum_{n=-\infty}^{\infty} J_n(z)\, e^{in\phi} , \tag{8a}$$

where $J_n(z)$ is a cylindrical Bessel function. The result is

$$\rho(\vec{Q}) = \sum_l \sum_k \sum_{nm} \sum_{\mu\nu} b_k\, e^{i\vec{Q}\cdot\vec{r}_k^0} e^{i\vec{Q}\cdot\vec{x}_l^0} J_n(\vec{Q}\cdot\vec{a}_{1k}) e^{in(\vec{q}_1\cdot\vec{x}_l^0+\pi/2)} J_m(\vec{Q}\cdot\vec{a}_{2k})\, e^{im(\vec{q}_2\cdot\vec{x}_l^0+\pi/2)}$$
$$\times J_\nu(\vec{Q}\cdot\vec{b}_{1k})\, e^{i\nu\vec{q}_1\cdot\vec{x}_l^0} J_\mu(\vec{Q}\cdot\vec{b}_{2k})\, e^{i\mu\vec{q}_2\cdot\vec{x}_l^0} , \tag{9}$$

where $\vec{a}_{ik}$ and $\vec{b}_{ik}$ have been written for $\vec{a}(k\vec{q}_i|T)$ and $\vec{b}(k\vec{q}_i|T)$, respectively. Carrying out the sum over l yields

$$\rho(\vec{Q}) = \sum_k \sum_{mn} \sum_{\mu\nu} b_k\, e^{i\vec{Q}\cdot\vec{r}_k^0} e^{in\pi/2} J_n(\vec{Q}\cdot\vec{a}_{1k}) J_\nu(\vec{Q}\cdot\vec{b}_{1k})\, e^{im\pi/2} J_m(\vec{Q}\cdot\vec{a}_{2k}) J_\mu(\vec{Q}\cdot\vec{b}_{2k})\, \delta(\vec{Q}+(n+\nu)\vec{q}_1+(m+\mu)\vec{q}_2-\vec{\tau}_0) . \tag{10}$$

In order to simplify Eq. (10) one may make use of the identity

$$J_p(w)\, e^{ip\chi} = \sum_n J_n(u) J_{p+n}(v)\, e^{in\pi/2} ,$$

with $w^2 = u^2 + v^2$, $v = w\cos\chi$, and $u = w\sin\chi$. Applying this result both to the product involving n and ν and the product involving m and μ in Eq. (10) one finds, after a little simple algebra, the result

$$\rho(\vec{Q}) = \sum_k \sum_n \sum_m b_k\, e^{i\vec{Q}\cdot\vec{r}_k^0} J_n(w_{1k}) J_m(w_{2k})$$
$$\times e^{in\chi_{1k}} e^{im\chi_{2k}} \delta(\vec{Q}+n\vec{q}_1+m\vec{q}_2-\vec{\tau}_0) , \tag{11}$$

where

$$w_{ik}^2 = [\vec{Q}\cdot\vec{a}(k\vec{q}_i|T)]^2 + [\vec{Q}\cdot\vec{b}(k\vec{q}_i|T)]^2 ,$$

$$\vec{Q}\cdot\vec{b}(k\vec{q}_i|T) = w_{ik}\cos\chi_{ik} , \quad \vec{Q}\cdot\vec{a}(k\vec{q}_i|T) = w_{ik}\sin\chi_{ik} .$$

Equation (11) is a perfectly general result which describes the intensities of Bragg reflections in any material in which a basic structure is modulated by two sinusoidal waves with (arbitrary) wave vectors $\vec{q}_1$ and $\vec{q}_2$. However, for NbO_2, in which $\vec{q}_1$ and $\vec{q}_2$ are simple submultiples of reciprocal-lattice vectors $\vec{\tau}_0$ of the parent structure, further simplification of Eq. (11) is possible. In this commensurate situation only certain combinations of m and n are allowed in Eq. (11) for any given value of $\vec{Q}$. Consider, for example, the case of $\vec{Q} = \vec{q}_1$; n may take values $\pm(2p+1)$, where p is a positive integer or zero. For even values of p, m may take values $\pm(4r+2)$ while for odd values of p, m takes values $\pm 4r$; once again r is a positive integer or zero. Once the terms which contribute in Eq. (11) have been identified the equation may be summed by making use of the expansions of trigonometric functions in terms of Bessel functions.[11] After some simple but painfully long-winded manipulations one finds the results

$$\rho(\vec{Q}) = \frac{1}{2}\sum_k e^{i\vec{Q}\cdot\vec{r}_k^0}\Big((i)^{n+m} \begin{matrix}\sin\\ \cos\end{matrix}[\vec{Q}\cdot\vec{a}(k\vec{q}_1|T)] \begin{matrix}\sin\\ \cos\end{matrix}[\vec{Q}\cdot\vec{a}(k\vec{q}_2|T)]$$
$$+(-1)^{n+m} \begin{matrix}\sin\\ \cos\end{matrix}[\vec{Q}\cdot\vec{b}(k\vec{q}_1|T)] \begin{matrix}\sin\\ \cos\end{matrix}[\vec{Q}\cdot\vec{b}(k\vec{q}_2|T)]\Big) \qquad \text{for } \vec{Q} = \vec{\tau}_0 + n\vec{q}_1 + m\vec{q}_2 . \tag{12}$$

In Eq. (12) the cosine (sine) function is to be used as the first term of each product if n is even (odd) and the cosine (sine) function is to be used as the second term of each product if m is even (odd). Notice then Eq. (12) now applies specifically to a system in which the combinations $4\vec{q}_1$, $4\vec{q}_2$ and $2\vec{q}_1$

$\pm 2\vec{q}_2$ are equal to reciprocal-lattice vectors of the high-temperature phase.

Equation (12) may be used to calculate the relative temperature dependences on the intensities of the P-, M-, and X-type reflections. Setting both $\vec{a}(k\vec{q}_i \mid T)$ and $\vec{b}(k\vec{q}_i \mid T)$ proportional to an order parameter $Q_p(T)$, one finds to leading order in $Q_p(T)$ that

$$\begin{aligned} &P \text{ type, } (n+m) \text{ odd, } \quad \rho(\vec{Q}) \sim Q_p(T) \ ; \\ &M \text{ type, } n=0, \ m=2 \text{ or vice versa,} \\ &\qquad\qquad \rho(\vec{Q}) \sim [Q_p(T)]^2 \ ; \\ &X \text{ type, } n \text{ and } m \text{ odd, } \quad \rho(\vec{Q}) \sim [Q_p(T)]^2 \ . \end{aligned} \tag{13}$$

Thus, as Shapiro *et al.*[5] noted, a single-order-parameter model is sufficient to account for the qualitative behavior of the P, M, and X reflections.

III. SYMMETRY CONSTRAINTS AND SINGLE-ORDER-PARAMETER MODEL

In Sec. II the vectors $\vec{a}(k\vec{q}_i \mid T)$ and $\vec{b}(k\vec{q}_i \mid T)$ which describe the lattice distortion of the LT phase [cf. Eq. (6)] were considered to be arbitrary. However a number of constraints are placed on these vectors by the symmetry of the high-temperature, rutile phase. To determine these constraints one may note, following Landau,[12] that, if the transition is of second order, the distortion introduced in the low-temperature phase must transform according to one of the irreducible representations of the HT group of the wave vector $\vec{q}_p$.

The consequences of this fact have been worked out in the language of phonon coordinates by a number of authors. In this paper we shall adopt the methods developed by Maradudin and Vosko.[13] In order to parallel their calculation in detail it is

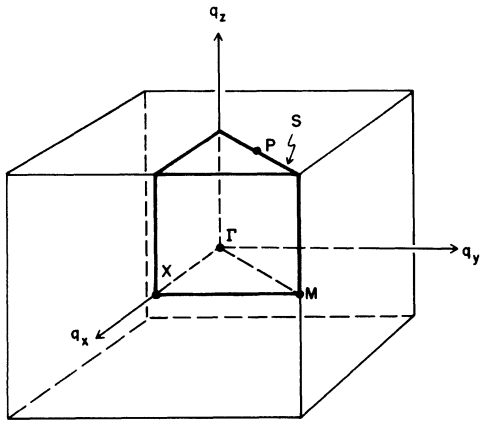

FIG. 2. First Brillouin zone of the rutile structure showing the location of the P, X, M, and Γ points. The point P has the same symmetry as any point on the line denoted S.

convenient to work with Eq. (5) in the form

$$\vec{u}_{lk} = \mathrm{Re}[\vec{E}_k(\vec{q}_1)\, e^{i\vec{q}_1\cdot\vec{x}_l^0} + \vec{E}_k(\vec{q}_2)\, e^{i\vec{q}_2\cdot\vec{x}_l^0}] \ , \tag{14}$$

where $\vec{E}_k(\vec{q}_i)$ is analogous to the usual (unnormalized) phonon polarization vector.

Following the prescription of Maradudin and Vosko one first finds[14] the multiplier representation for the group of the wave vector $\vec{q}_1$. In NbO_2 this wave vector lies on the symmetry line conventionally denoted by the letter S (see Fig. 2) and the group of $\vec{q}_1$ has four one-dimensional irreducible representations[15] S_1 through S_4. Projection operators which generate basis functions for these representations may be obtained from the multiplier representations by the methods described by Maradudin and Vosko.[13] Using these operators one finds

$$\begin{aligned} \vec{E}^{(1)}(\vec{q}_1) &= (a, a, 0; 0, 0, b; \mu, \mu, 0; 0, 0, c; \\ &\quad -\mu^*, -\mu^*, 0; 0, 0, c) \ , \\ \vec{E}^{(2)}(\vec{q}_1) &= (0, 0, 0; a, -a, 0; 0, 0, 0; \mu, -\mu^*, 0; \\ &\quad 0, 0, 0; \mu^*, -\mu, 0) \ , \\ \vec{E}^{(3)}(\vec{q}_1) &= (a, -a, 0; 0, 0, 0; \mu, -\mu, 0; 0, 0, \mu; \\ &\quad -\mu^*, \mu^*, 0; 0, 0, -\nu) \ , \\ \vec{E}^{(4)}(\vec{q}_1) &= (0, 0, a; b, b, 0; 0, 0, \mu; \nu, \nu^*, 0; \\ &\quad 0, 0, -\mu^*; \nu^*, \nu, 0) \ , \end{aligned} \tag{15}$$

where $\vec{E}^{(n)}(\vec{q}_1)$ is a basis vector for the irreducible representation S_n. In Eq. (15) roman letters represent real quantities and greek letters complex quantities. On each line, the kth set of three symbols are the Cartesian components of the polarization vector for the kth atom (cf. Fig. 1) of the rutile cell. Basis vectors for the irreducible representations of the group of the wave vector $\vec{q}_2$ can be found by using the transformation laws given by Maradudin and Vosko.[13] The polarization vectors [Eq. (15)] determined from the group-theoretical analysis may in general be multiplied by arbitrary phase factors. Whence the most general form for Eq. (14) is

$$\vec{u}_{lk} = \mathrm{Re}[e^{i\phi_1}\vec{E}_k^{(n)}(\vec{q}_1)\, e^{i\vec{q}_1\cdot\vec{x}_l^0} + e^{i\phi_2}\vec{E}_k^{(n)}(\vec{q}_2)\, e^{i\vec{q}_2\cdot\vec{x}_l^0}] \ . \tag{16}$$

This generalization, which may at first sight appear pedantic or irrelevant, actually contains some essential physics. It corresponds to acknowledging the fact that in the LT structure the phases of the sinusoidal modulations which are superposed on the rutile structure are measurable quantities. The phases ϕ_1 and ϕ_2 introduce a complication; until they are specified it is not possible to determine the space group to which the LT phase will belong even if one knows which of the $\vec{E}^{(n)}(\vec{q}_p)$ is correct. In the case of NbO_2, general values of ϕ_1 and ϕ_2 produce a low-temperature

structure which is orthorhombic whereas the x-ray results[4] indicate that the structure is in fact tetragonal with symmetry C_{4h}^6. If one accepts that the LT space group is indeed tetragonal[16] one finds from Eqs. (6), (12), (15), and (16) that

$$|\phi_1| = |\phi_2| = \tfrac{1}{4}\pi \ . \tag{17}$$

While the above result has been presented here as a consequence of the assumed tetragonal symmetry of the LT phase it may actually be predicted theoretically. Anticipating a result which will be discussed in Sec. IV, one may write a Landau-like free energy for NbO_2 in the form [cf. Eq. (22)]:

$$F = \sum_{i=1,2} \{A|Q(\vec{q}_i)|^2 + C[Q(\vec{q}_i)^4 + Q(-\vec{q}_i)^4] + C'[Q(\vec{q}_1)^2 + Q(-\vec{q}_1)^2][Q(\vec{q}_2)^2 + Q(-\vec{q}_2)^2] + \cdots\} , \tag{18}$$

where $Q(\vec{q}_i)$ is the complex amplitude of a distortion of wave vector $\vec{q}_i$ and A, C, C' are constants. Writing $Q(\vec{q}_s) = \eta_s e^{i\phi_s}$ and minimizing the free energy with respect to ϕ_1 and ϕ_2 leads to the condition $|\phi_1| = |\phi_2| = \frac{1}{4}\pi$ which is identical to Eq. (17). This simple calculation demonstrates the important fact that in a commensurate transition the phases of the distortions are determined by higher-order terms in an expansion of the free energy.

Once the phases ϕ_1 and ϕ_2 have been determined one may use Eqs. (12) and (15) to make a number of deductions concerning the symmetry of the LT phase. Each of the $\vec{E}^{(n)}$ imply certain constraints on the superlattice reflections which can be observed. These constraints are most easily expressed in terms of the Miller indices of the LT reciprocal lattice in which each reflection is described by indices (HKL) which are integers. Thus one has

$$\vec{\tau}_{HKL} \equiv H(\tfrac{1}{4}, \tfrac{1}{4}, 0) + K(\tfrac{1}{4}, -\tfrac{1}{4}, 0) + L(0, 0, \tfrac{1}{2}) \ , \tag{19}$$

where $\vec{\tau}_{HKL}$ is a reciprocal-lattice vector of the LT structure and the vectors on the right-hand side of Eq. (19) are written with respect to the rutile reciprocal lattice. With these definitions one finds that distortions described by *any* $\vec{E}^{(n)}$ given in Eq. (15) imply that

$$\begin{aligned} &H + K + L = 2m \quad \text{for } (HKL) \text{ reflections,} \\ &L = 4m \quad \text{for } (00L) \text{ reflections,} \\ &H = 2m; \quad K = 2m \quad \text{for } (HK0) \text{ reflections,} \end{aligned} \tag{20}$$

where m is an integer. These conditions are in fact precisely those determined by Marinder[4] from his x-ray results and are sufficient to specify the LT space group as C_{4h}^6. In addition to the conditions given above, distortions described by $\vec{E}^{(2)}$ and $\vec{E}^{(3)}$ both imply that

$$H = 2m \quad \text{for } (H0L) \text{ reflections,} \tag{21}$$

a condition which contradicts both Marinder's experiment and the data presented in this paper. Thus it is possible on the basis of qualitative observations to assert that the distortion which occurs in the LT phase cannot transform as a linear combination of S_2 and S_3 alone.

Although the space group C_{4h}^6 can represent a distortion which transforms as any linear combination of all S_n, experiment (cf. Secs. V and VI) shows that S_1 is the relevant representation. The vectors $\vec{a}(k\vec{q}_i \mid T)$ and $\vec{b}(k\vec{q}_i \mid T)$ which apply to this representation are given in Table I. The lattice distortions which these vectors imply are shown in Fig. 3. The essential features are displayed more clearly in part (c) of this figure in which the atomic displacements in (110) and $(1\bar{1}0)$ planes are reproduced. Notice that the displacements shown are approximately those one would expect if the Niobium "chains" along the [001] axis were to be dimerized and all other atomic motions were to be determined by keeping the length of the niobium-oxygen bonds [cf. Figs. 3(a) and 3(b)], constant.[17] Distortions with wave vector $\vec{q}_1$ cause dimerization of one sublattice of Nb atoms while distortions with wave vector $\vec{q}_2$ dimerize the other sublattice.

IV. SECONDARY-ORDER PARAMETERS

In this section we shall use a Landau theory[12] to demonstrate the mechanism which may introduce secondary distortions in the LT phase of NbO_2. Following Kwok and Miller[18] we first write a general expression for the Helmholtz free energy in the form

$$F = F_0 + \frac{1}{2!}\sum_{qq'} A(\vec{q}, \vec{q}')\, Q_q Q_{q'}\, \delta(\vec{q} + \vec{q}' - \vec{\tau}_0) + \frac{1}{3!}\sum_{qq'q''} B(\vec{q}, \vec{q}', \vec{q}'')\, Q_q Q_{q'} Q_{q''}\, \delta(\vec{q} + \vec{q}' + \vec{q}'' - \vec{\tau}_0) + \frac{1}{4!}\sum_{qq'q''q'''} C(\vec{q}, \vec{q}', \vec{q}'', \vec{q}''')\, Q_q Q_{q'} Q_{q''} Q_{q'''}\, \delta(\vec{q} + \vec{q}' + \vec{q}'' + \vec{q}''' - \vec{\tau}_0) \ . \tag{22}$$

Here Q_q is the thermal expectation value of the (complex) amplitude[19] of a sinusoidal modulation of wave vector $\vec{q}$ and A, B, C are coefficients. The presence of the momentum conserving δ functions in Eq. (22) is an expression of the fact that F must be invariant under the translational subgroup of the HT phase. Since the primary distortion in NbO_2 has a wave vector in $\{\vec{q}_p\}$ the important second-order term in Eq. (22)

will be associated with this wave vector. In addition, third- and fourth-order coupling terms will only be of interest here if they involve $\vec{q}_p$. Thus the important contributions to the free energy can be written

$$F = F_0 + \frac{1}{2!}\left(\sum_p A_p |Q_p|^2 + \sum_m A_m |Q_m|^2 + \sum_x A_x |Q_x|^2 + A_\Gamma |Q_\Gamma|^2\right) + \frac{1}{3!}\left(\sum_{pm} A_{pm} Q_p Q_p Q_m + \sum_{pp'x} A_{px} Q_p Q_{p'} Q_x + \sum_p A_{p\Gamma} Q_p Q_p^* Q_\Gamma\right) + \frac{1}{4!}\left(\sum_{pp'} C_{pp'} Q_p^2 Q_{p'}^2 + \cdots\right) . \quad (23)$$

In this equation Q_s has been written for Q_{q_s} and $\sum_s$ is intended to imply that the sum extends over all vectors in the star of $\vec{q}_s$ which satisfy the appropriate momentum conserving δ function.

The free energy given in Eq. (23) may be used to describe a system in which there is a second-order transition with Q_p as the order parameter. For such a transition to occur one requires[12] that A_p change sign at the transition temperature and that A_m, A_x, A_Γ be positive. In order to specify the behavior of the LT phase of the system described by Eq. (23), the free energy must be minimized with respect to Q_p, Q_x, Q_m, and Q_Γ. In particular, this minimization leads to the relations

$$\frac{\partial F}{\partial Q_m} = \tfrac{1}{6} A_{pm} Q_p Q_p + A_m Q_m = 0 , \quad (24)$$

$$\frac{\partial F}{\partial Q_x} = \tfrac{1}{6} A_{px} Q_p Q_{p'} + A_x Q_x = 0 , \quad (25)$$

$$\frac{\partial F}{\partial Q_\Gamma} = \tfrac{1}{6} A_{p\Gamma} Q_p Q_p^* + A_\Gamma Q_\Gamma = 0 , \quad (26)$$

which give Q_m, Q_x, and Q_Γ in terms of Q_p. From these equations one sees that a finite value of Q_p will in general induce finite values of Q_m, Q_x, and and Q_Γ. Thus the latter quantities behave as secondary induced order parameters in the LT phase. One may show rigorously[20] that the introduction of a secondary distortion does not lower the symmetry of the low-temperature phase once the distortion characterized by Q_p has appeared.

From the foregoing analysis [cf. Eqs. (24)–(26)] it is not difficult to appreciate that in NbO_2 the intensities of X- and M-type reflections will show the same dependence on sample temperature as the square of the intensities of P-type reflections even if all X and M intensity were to occur as a result of induced secondary distortions (which according to Sec. II cannot be the case). Thus both the induced-order-parameter and diffraction-harmonic arguments predict the same relative temperature dependences of the X-, M-, and P-type reflections. In point of fact *any* argument (including multiple scattering) which relates the intensities of these reflections must give the same result!

TABLE I. General forms of the vectors $\vec{a}(k,\vec{q})$ and $b(k,\vec{q})$ for the primary wave vectors $\vec{q}_1 = (\frac{1}{4},\frac{1}{4},\frac{1}{2})$ and $\vec{q}_2 = (\frac{1}{4},\frac{1}{4},\frac{1}{2})$ deduced from lattice symmetry. The symbols a, b, and c represent the same quantities as the identical symbols in Eq. (15) while μ' and μ'' are the real and imaginary parts of the μ of Eq. (15). S_i and C_i are abbreviations for $\sin\phi_i$ and $\cos\phi_i$, respectively [cf. Eq. (16)].

$\vec{q}$	k	$\vec{a}(k,\vec{q})$			$\vec{b}(k,\vec{q})$		
$(\frac{1}{4},\frac{1}{4},\frac{1}{2})$	1	aC_1	aC_1	0	$-aS_1$	$-aS_1$	0
	2	0	0	bC_1	0	0	$-bS_1$
	3	$\mu'C_1-\mu''S_1$	$\mu'C_1-\mu''S_1$	0	$-\mu''C_1-\mu'S_1$	$-\mu''C_1-\mu'S_1$	0
	4	0	0	cC_1	0	0	$-cS_1$
	5	$-\mu'C_1-\mu''S_1$	$-\mu'C_1-\mu''S_1$	0	$-\mu''C_1+\mu'S_1$	$-\mu''C_1+\mu'S_1$	0
	6	0	0	cC_1	0	0	$-cS_1$
$(\frac{1}{4},-\frac{1}{4},\frac{1}{2})$	1	0	0	bS_2	0	0	$-bC_2$
	2	aC_2	$-aC_2$	0	$-aS_2$	aS_2	0
	3	0	0	$-cS_2$	0	0	$-cC_2$
	4	$\mu'C_2-\mu''S_2$	$-\mu'C_2+\mu''S_2$	0	$-\mu''C_2-\mu'S_2$	$\mu''C_2+\mu'S_2$	0
	5	0	0	$-cS_2$	0	0	$-cC_2$
	6	$\mu'C_2+\mu''S_2$	$-\mu'C_2-\mu''S_2$	0	$\mu''C_2-\mu'S_2$	$-\mu''C_2+\mu'S_2$	0

V. EXPERIMENTAL DETAILS

A. Crystal

The single-crystal sample was in the form of a rectangular prism cut from the large crystal used and described by Shapiro *et al.*[5] The sample dimensions were $3\times3\times6.5$ mm^3, and the largest two faces were parallel to $(001)_L$ and $(100)_L$ planes. Here, as in much of the remainder of this paper, Miller indices are given with respect to the crystallographic axes of the low-temperature phase (cf. Fig. 4). As a remainder of this fact the subscript L is appended to these indices. A least-squares fit of the scattering angles for a number of easily identifiable reflections yielded values of $a = 13.66 \pm 0.01$ Å and $c = 5.964 \pm 0.005$ Å for the lattice constants of the sample at room temperature. These results agree tolerably well with those found by Marinder.[4]

B. Data collection and reduction

The neutron-diffraction data were obtained at room temperature with an automated four-circle diffractometer at the Brookhaven High Flux Beam Reactor. Intensities of reflections were measured with a $\theta - 2\theta$ scanning technique with about 40 measured points per scan.

Background corrections were made in a manner[21] which separates the peak and background such that $\sigma(I)/I$ is minimized. Here I is the integrated intensity of a peak and $\sigma(I)$ is the estimated standard deviation of I calculated on the basis of counting statistics. Squared structure factors $F^2 = I\sin2\theta$ (2θ is the scattering angle at the sample) were obtained and corrected for absorption by a Gaussian integration method with 512 sampling points.

Values of F^2 were found to be consistent with a Laue symmetry of $4/m$ and hence reflections of the types $(hkl)_L$, $(\bar{h}kl)_L$, $(hk\bar{l})_L$, and $(\bar{h}\bar{k}l)_L$ were averaged to give a quantity denoted $\overline{F}^2$. The standard deviation of the latter was determined from

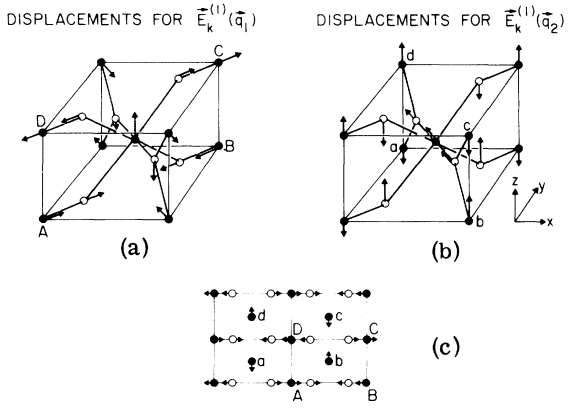

FIG. 3. Parts (a) and (b) of this figure show the atomic displacements associated with sinusoidal distortions of wave vectors $\vec{q}_1$ and $\vec{q}_2$ [$\vec{q}_1 \equiv (\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ and $\vec{q}_2 \equiv (\frac{1}{4}, \frac{\bar{1}}{4}, \frac{1}{2})$] which transform according to the representation S_1. Part (c) of the figure shows the essential ingredients of the distortions. Parts (a) and (c) and parts (b) and (c) can be put into the correct relation to one another by observing the labeled corners of the unit cells.

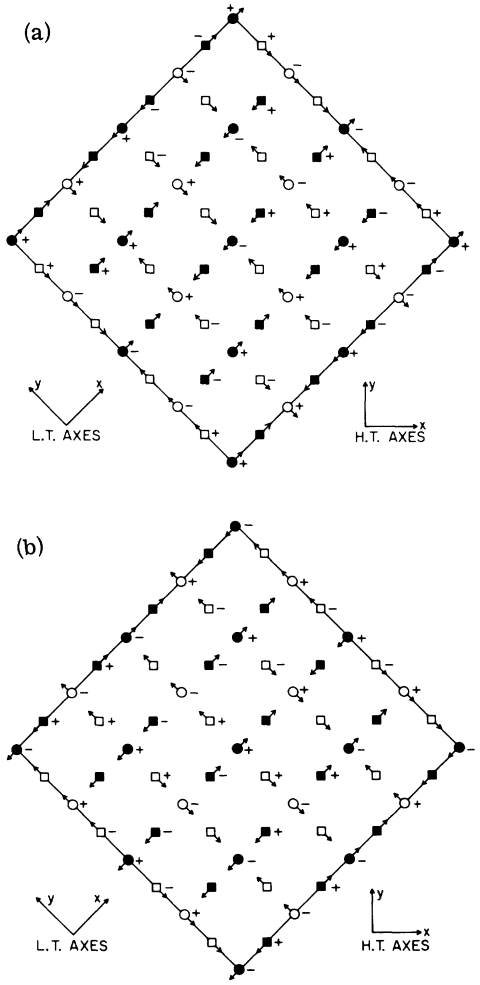

FIG. 4. Projections of the low-temperature structure of NbO_2 onto the $x-y$ plane. Part (a) shows atoms in the planes $z = 0$ (filled symbols) and $z = \frac{1}{2}c$ (open symbols), while part (b) shows atoms in planes $z = c$ (filled symbols) and $z = \frac{3}{2}c$ (open symbols). Here c is the rutile lattice parameter in the z direction. In both parts of the figure circular symbols denote niobium atoms and squares are oxygen atoms. The arrows and + or − signs indicate the direction of displacement of an atom from its ideal rutile site. For the niobium atoms displacements in the $x-y$ plane are $\sim 0.03a$ (a is the rutile lattice parameter) while z displacements (denoted + or −) are $\sim 0.05c$. Oxygen atoms are displaced by $\sim 0.015a$ in the $x-y$ plane and by $\sim 0.01c$ in the z direction. Some oxygen atoms [O(2) and O(3) in table II] move by $\sim 0.001c$ in the z direction; no + or − sign is associated with these atoms.

the spread of the individual observations. While this method differs from that often used (in which only counting statistics are considered) it appears to be the most appropriate in this case. In measurements of weak superlattice reflections multiple scattering contamination was found to be a severe problem. Since this difficulty cannot be entirely avoided it is best to minimize the effect by averaging over many observations of equivalent reflections. Such averaging is, however, only useful if equivalent reflections were affected differently by multiple scattering processes. In practice this was achieved by ensuring that the crystal was mounted in such a way that no major crystallographic direction coincided with any of the instrumental axes about which the crystal was rotated during the data collection.

During the experiment the integrated intensities of 1078 reflections were recorded. Systematically absent reflections are not included in this number although a check was made of the validity of the criteria given by Eq. (20) for the determination of the indices of nonexistent reflections. After the averaging procedure described above 154 values of $\overline{F}^2$ were obtained. As a measure of the quality of the data (or alternatively of the problems caused by multiple scattering) the over-all agreement factor $R = \sum |F^2 - \overline{F}^2| / \sum F^2$ was found to be $R = 0.09$. While this value is somewhat large it should be noted that it is totally unadulterated; no observations have been rejected for "statistical" reasons.

VI. STRUCTURE REFINEMENT

The simplest method of including both primary and secondary distortions in the description of the low-temperature structure of NbO_2 is to fit the diffraction data to a general crystal structure belonging to the space group C_{4h}^6. This may be accomplished by using one of the programs available in the crystallographers' arsenal. In the present case the full-matrix, least-squares program FLINUS was used to minimize the quantity $\sum w(\overline{F}^2 - |F_c|^2)^2$, where $|F_c|^2$ is the calculated value of a squared structure factor and w is a weighting factor. The latter was chosen to be the inverse of the sample variance discussed in the previous section.

In order to use FLINUS one must specify both the positions of nonequivalent atoms and the symmetry operations which relate the positions of equivalent atoms. Let us denote the position of an atom with respect to the low-temperature coordinate system (cf. Fig. 4) by (x, y, z). For general atomic positions commensurate with the space group C_{4h}^6 the coordinate (x, y, z) is a member of the symmetry related set[22]

$$\begin{aligned}&(0,0,0) \text{ and } (\tfrac{1}{2},\tfrac{1}{2},\tfrac{1}{2}) \text{ plus}\\ &(x,y,z);\ (-x,\tfrac{1}{2}-y,z);\ (\tfrac{3}{4}-y,\tfrac{1}{4}+x,\tfrac{1}{4}+z);\\ &(\tfrac{1}{4}+y,\tfrac{1}{4}-x,\tfrac{1}{4}+z)\,(-x,-y,-z);\ (x,\tfrac{1}{2}+y,-z);\\ &(\tfrac{1}{4}+y,\tfrac{3}{4}-x,\tfrac{3}{4}-z);\ (\tfrac{3}{4}-y,\tfrac{3}{4}+x,\tfrac{3}{4}-z)\,.\end{aligned} \tag{27}$$

The specification of the coordinates of two niobium atoms and four oxygen atoms is sufficient to describe the positions of the 96 atoms contained in the body-centered tetragonal LT unit cell. In the case that the LT phase results from a distortion of the rutile phase which transforms according to S_1 one may show that the atomic coordinates [the (x, y, z) above] are

$$\begin{aligned}&\text{Nb(1)},\ (0.125\,x'',\ 0.125,\ 0.5\,z'');\\ &\text{Nb(2)},\ (0.125\,x'',\ 0.125,\ z'');\\ &\text{O(1)},\ (0.975-x'-y',\ 0.125,\ z');\\ &\text{O(2)},\ (0.975+x'+y',\ 0.125,\ 0.5-z');\\ &\text{O(3)},\ (0.275-x'+y',\ 0.125,\ 1.0+z');\\ &\text{O(4)},\ (0.275+x'-y',\ 0.125,\ 0.5-z').\end{aligned} \tag{28}$$

Here the quantities x'', z'', x', y', and z' are displacements related to the constants given in Table I and the undisplaced oxygen positions are those of rutile itself[1] (oxygen parameter $u = 0.3$).

In our attempts to fit the low-temperature structure various sets of trial atomic coordinates were input to FLINUS. Each set of input parameters was obtained from Eq. (28) above by changing both the magnitudes and signs of the displacements. Calculations based on many of the initial parameter sets refused to converge; those calculations which

TABLE II. Final fitted parameters for the low-temperature phase of NbO_2. The quantities listed are the atom label, the neutron scattering length (in 10^{-12} cm), the atomic coordinates [cf. Eq. (27)], and the thermal factors. In terms of the latter factors the Debye-Waller factor which multiplies the structure factor of the (HKL) reflection is $\exp(-\beta_{11}H^2 - \beta_{22}K^2 \cdots - 2\beta_{12}HK - \cdots)$. Estimated standard deivations ($\times 10^4$) are shown in parentheses.

Atom	b	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb(1)	0.711	0.1155(3)	0.1249(2)	0.4746(8)	0.0008(7)	0.0015(6)	0.0146(31)	0.0001(4)	0.0000(3)	−0.0001(4)
Nb(2)	0.711	0.1356(3)	0.1250(2)	0.0267(7)	0.0005(6)	0.0024(6)	0.0119(28)	0.0000(3)	0.0002(4)	−0.0007(3)
O(1)	0.5803	0.9866(5)	0.1262(6)	−0.0046(5)	0.0009(10)	0.0029(8)	0.0137(26)	0.0007(5)	−0.0008(3)	−0.0006(4)
O(2)	0.5803	0.9749(5)	0.1252(6)	0.5000(5)	0.0023(11)	0.0024(8)	0.0133(26)	0.0005(4)	0.0004(4)	0.0008(4)
O(3)	0.5803	0.2739(5)	0.1245(6)	0.9998(5)	0.0020(11)	0.0027(8)	0.0098(25)	0.0008(4)	−0.0004(4)	−0.0008(4)
O(4)	0.5803	0.2631(6)	0.1241(6)	0.5043(5)	0.0017(9)	0.0017(8)	0.0111(24)	0.0011(5)	−0.0004(4)	0.0006(5)

TABLE III. Vectors $\vec{a}(k,\vec{q})$ and $b(k,\vec{q})$ for $\vec{q}_1=(\frac{1}{4},\frac{1}{4},\frac{1}{2})$ and $\vec{q}_2=(\frac{1}{4},\bar{\frac{1}{4}},\frac{1}{2})$ obtained from the fitted structure. Standard deviations ($\times 10^4$) are shown in parentheses.

$\vec{q}$	k	$a_1(k,\vec{q})$	$a_2(k,\vec{q})$	$a_3(k,\vec{q})$	$b_1(k,\vec{q})$	$b_2(k,\vec{q})$	$b_3(k,\vec{q})$
$(\frac{1}{4},\frac{1}{4},\frac{1}{2})$	1	−0.0199(3)	−0.0201(3)	0	−0.0199(3)	−0.0201(3)	0
	2	0	0	−0.0522(5)	0	0	−0.0522(5)
	3	−0.0105(6)	−0.112(6)	0	−0.0106(6)	−0.0127(6)	0
	4	0	0	0.0045(3)	0	0	0.0047(4)
	5	0.0106(6)	0.0127(6)	0	0.0105(6)	0.0112(6)	0
	6	0	0	0.0047(4)	0	0	0.0045(3)
$(\frac{1}{4},-\frac{1}{4},\frac{1}{2})$	1	0	0	−0.0522(5)	0	0	0.0522(5)
	2	−0.0201(3)	0.0199(3)	0	−0.0201(3)	0.0199(3)	0
	3	0	0	0.0045(3)	0	0	−0.0047(4)
	4	−0.0112(6)	0.0105(6)	0	−0.0127(6)	0.0106(6)	0
	5	0	0	0.0047(4)	0	0	−0.0045(3)
	6	−0.0127(6)	0.0106(6)	0	−0.0112(6)	0.0105(6)	0

did converge yielded a unique set of atomic coordinates. In the final cycles of the refinement 36 anisotropic thermal parameters (Debye-Waller factors), one scale factor, and an isotropic extinction parameter was varied in addition to the 18 positional parameters described earlier. The final agreement factors were

$$R=\sum\left|\bar{F}^2-|F_c|^2\right|\Big/\sum|\bar{F}|^2=0.058\ ,$$
$$R_w=\left(\sum|w\bar{F}^2-|F_c|^2|^2\Big/\sum w\bar{F}^4\right)^{1/2}=0.098\ . \tag{29}$$

In view of the spread of values of F^2 contained within the original data set (cf. Sec. V B) these R factors would appear to be satisfactory. The parameters obtained in the final fitting procedure are displayed in Table II.

The parameters listed in Table II include both primary and secondary (induced) distortions. In order to separate these distortions the vectors $\vec{a}(k,\vec{q}_s)$ and $\vec{b}(k,\vec{q}_s)$ have been obtained for P, M, X, and Γ wave vectors and are displayed in Tables III and IV. It was found that if the oxygen parameter of TiO_2 ($u=0.3$) was used in this calculation, the $\vec{q}_\Gamma$ distortion involved a relatively large component which transformed as the identity representation A_{1g}. This contribution probably does not represent a secondary distortion associated with the structural transition, but rather a deviation of the HT oxygen positions from those found in TiO_2. The A_{1g} distortion may be suppressed by choosing the oxygen parameter as $u=0.2878$ and this has been done in preparing Table IV.

Tables III and IV demonstrate that the finite components of $\vec{a}(k,\vec{q}_s)$ for $\vec{q}_s=(\frac{1}{2},0,0)$, $\vec{q}_s=(\frac{1}{2},\frac{1}{2},0)$ and $\vec{q}_s=(0,0,0)$ are significantly different from zero even though all components of $\vec{b}(k,\vec{q}_s)$ vanish at X, M, and Γ by symmetry. It is also apparent from a comparison of the tables that the amplitudes of the secondary distortions are considerably smaller than those of the primary, P-type distortions. It should be noted that to within the experimental uncertainty, the vectors listed in Table III transform as S_1 (cf. Table I). Although the space group C_{4h}^6 allows for distortions which transform as any linear combination of the S_n the conventional theory[12] of second-order phase transitions asserts that only a single irreducible representation of the group of $\vec{q}_p$ can be involved. For this reason the fact that our data yield a P-type distortion which transforms as S_1 is gratifying.

The pattern of atomic displacements implied by the fitted parameters is displayed in Fig. 4. For the niobium atoms these displacements are of the

TABLE IV. Vectors $\vec{a}(k,\vec{q})$ [$\vec{b}(k,\vec{q})$ is identically zero in these cases] for X, M, and Γ points. Table entries have been obtained from the fitted structure. Standard deviations ($\times 10^4$) are given in parentheses. For $q=0$ a rather large distortion which transforms as A_{1g} has been suppressed. This distortion corresponds to changing the oxygen parameter of the HT phase from $u=0.3$ to $u=0.2878$.

$\vec{q}$	k	$a_1(k,\vec{q})$	$a_2(k,\vec{q})$	$a_3(k,\vec{q})$
$(\frac{1}{2},0,0)$	1	0	0	0
	2	0	0	0.0013(4)
	3	0	0	0.0043(2)
	4	0	0	−0.0003(2)
	5	0	0	0.0043(2)
	6	0	0	−0.0003(2)
$(\frac{1}{2},\frac{1}{2},0)$	1	0.0012(2)	0.0010(2)	0
	2	0.0010(2)	−0.0012(2)	0
	3	−0.0007(4)	−0.0008(4)	0
	4	−0.0008(4)	0.0007(4)	0
	5	−0.0007(4)	−0.0008(4)	0
	6	−0.0008(4)	0.0007(4)	0
(0,0,0)	1	0	0	0
	2	0	0	0
	3	0.0014(4)	−0.0014(4)	0
	4	−0.0014(4)	0.0014(4)	0
	5	−0.0014(4)	0.0014(4)	0
	6	0.0014(4)	−0.0014(4)	0

TABLE V. Fitted parameters for the low-temperature phase of NbO_2 obtained with a domain model (see text). The quantities listed are the same as those given in Table II.

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Nb(1)	0.1149(4)	0.1250(2)	0.4749(10)	0.0015(8)	0.0022(7)	0.0109(36)	0.0002(4)	−0.0008(4)	0.0005(4)
Nb(2)	0.1362(4)	0.1251(3)	0.0268(9)	0.0007(7)	0.0032(8)	0.0097(33)	0.0001(4)	0.0002(4)	−0.0010(4)
O(1)	0.9873(6)	0.1285(8)	−0.0045(6)	0.0022(12)	0.0030(9)	0.0110(31)	−0.0005(6)	−0.0002(4)	−0.0002(5)
O(2)	0.9747(6)	0.1271(7)	0.5003(6)	0.0029(14)	0.0020(9)	0.0146(30)	−0.0008(5)	0.0002(4)	0.0008(5)
O(3)	0.2739(6)	0.1225(7)	0.9993(6)	0.0030(14)	0.0022(9)	0.0107(30)	−0.0005(5)	0.0000(4)	−0.0013(5)
O(4)	0.2629(7)	0.1220(7)	0.5050(5)	0.0031(12)	0.0017(9)	0.0066(27)	0.0001(5)	−0.0006(4)	0.0012(6)

form which one would deduce from the discussion of Sec. III if a distortion transforming as S_1 were to occur. To a large extent the oxygen displacements also obey this rule, with the notable exception that certain of this species of atom (denoted 02 and 03 in Table II) obstinately refuse to be displaced at all.

In the foregoing discussion it has been assumed that the NbO_2 sample comprises a single domain. However, it is entirely likely that domains, related by a 180° rotation about the ⟨110⟩ rutile axis, are present. Since the (*hkl*) and (*khl*) reflections are not of equal intensity for a crystal belonging to the space group C_{4h}^6, such a combination of domains could, in principle, seriously affect the analysis of diffraction data. In order to investigate this problem we have used the observed intensities of (*hkl*) and (*khl*) reflections in conjunction with various assumed domain concentrations to calculate "true" structure factors for all reflections. These true structure factors have been fitted in the manner described earlier and the "goodness-of-fit" parameters for various relative domain concentrations have been compared. The somewhat surprising result is that the calculated atomic parameters are very little effected by the domain concentration and that it is essentially impossible to determine the latter. As evidence of this result we display in Table V the fitted parameters for a situation in which only 60% of the sample is in the domain assumed by the fit given in Table II. Comparison of Tables II and V shows that the fitted parameters are insensitive to domain population and thus the results described earlier in this section cannot be substantially improved by including this extra degree of freedom.

The Debye-Waller parameters β_{ij} displayed in Tables II and V are both anisotropic and large. In particular, the values of β_{33} imply atomic distributions along the c axis which have rms spreads of about 0.15 (± 0.03) Å. This value is of the same order as the distance between LT and HT sites. However, it is possible that the large values of β_{33} are a fortuitous result of the data analysis. It was found to be impossible to obtain reasonable temperature factors when an (isotropic) extinction parameter was included in the fitting of the data. In fact the fitting procedure had to be carried out for several fixed values of the extinction parameter and a "best value" of the latter selected. Although this procedure is reasonable the strong correlation of the β_{ij} and the extinction parameter casts some doubt on the values obtained for the temperature factors. This suspicious circumstance does not, we hasten to add, affect any of the positional parameters determined by the fit.

If the Debye-Waller parameters in Tables II and V are not an artifact of the fitting procedure they are both noteworthy and consistent with observations[23] made in VO_2. McWhan *et al.*[23] have found that the Debye-Waller factors relevant to the rutile phase of VO_2 are anisotropic and much larger than those found for rutile (TiO_2) itself. Since VO_2 undergoes a structural phase transition while TiO_2 does not, it may be tempting to postulate[24] the existence of low-lying phonon states in VO_2. While we cannot comment on the case of VO_2 we caution against a soft-phonon picture for NbO_2. Additional experiments (to be reported elsewhere) have failed to reveal any low-frequency phonon branches and have also shown that the temperature dependence of Bragg intensity is much too small for the β_{ij} of Tables II and V to be entirely of dynamical origin. It is not possible on the basis of our experiments to date to rule out the possibility that the large, fitted Debye-Waller factors result from some unresolved, "static" positional disorder. Evidently such a concept is less than satisfying since it poses more questions than it answers.

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