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Concentration Wave Approach to the Pairwise Interaction Model for Predicting the Atomic Structure of Ceramics, II

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The concentration wave approach is applied to Ti and V oxides with noninteger variable valences. This approach enables both the composition and the structure of the homologous series of Magneli phases Ti_nO_{2n-1} and V_nO_{2n-1} to be predicted in the composition range between Ti_2O_3 and TiO_2. © 1986 Academic Press, Inc.

1. The Structure of Homologous Series of Chemical Compounds

The concentration wave approach and, particularly, the maximal amplitude principle has earlier been applied for the theoretical prediction of the structure of chemical compounds (oxides in particular) with metal atoms having fixed integer valences (*1*). In this scheme the compounds were regarded as a superstructure in which metal atoms are located in octahedral interstices of the bcc host lattice formed by oxygen atoms. It has been shown that stable structures with fixed stoichiometry are generated only by dominant concentration waves, with wave vectors given by 0, $\frac{1}{2}\mathbf{H}$, $\frac{1}{3}\mathbf{H}$ and $\frac{1}{4}\mathbf{H}$ ($\mathbf{H}$ is an arbitrary reciprocal lattice vector of the phase in which ordering occurs). The term "dominant concentration wave" refers to the eigenfunction which corresponds to the minimal eigenvalue of the matrix $W_{pq}(\mathbf{R} - \mathbf{R}')$ describing the pairwise interaction energies of interstitial atoms at the interstices (p, $\mathbf{R}$) and (q, $\mathbf{R}'$). The indices p and q label the interstices related to the nearest host lattice sites designated by the reference vectors $\mathbf{R}$ and $\mathbf{R}'$, respectively. The maximal amplitude principle mentioned above refers to the requirement that the sum of the modulus squared of the dominant wave amplitudes should attain the maximal possible value.

In following up on the above it is natural to pose the question as to what would happen if the wave vector, $\mathbf{k}_0$, of the dominant wave does not meet the above-mentioned limitation that it be given by 0, $\frac{1}{2}\mathbf{H}$, $\frac{1}{3}\mathbf{H}$, $\frac{1}{4}\mathbf{H}$, i.e., if $\mathbf{k}_0$ corresponds to a more general point of the reciprocal lattice. As has been shown, the dominant waves then produce nondominant waves whose wave vectors are multiples of $\mathbf{k}_0$. Together the dominant and nondominant concentration waves generate layered superstructure (*1*). The occupation probabilities, $n(p, \mathbf{R})$ to find an interstitial atom at the interstice (p, $\mathbf{R}$) for such a layer superstructure is

$$n(p, \mathbf{R}) = \sum_{s=0}^{s_1-1} a_p(s\mathbf{k}_0)e^{i2\pi s\mathbf{k}_0\mathbf{R}} \qquad (1)$$

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where s_1 is the minimal integer meeting the equality

$$s_1\mathbf{k}_0 = \mathbf{H} \tag{2}$$

(See Eqs. (13) and (12) in (*1*)). **H** entering the definition (2) is the smallest reciprocal lattice vector formed by multiplying the vector $\mathbf{k}_0$ by an integer. It is, however, not necessarily equal to the smallest reciprocal lattice vector $\mathbf{H}_0$ in the direction of $\mathbf{k}_0$ but may differ from it by an integer multiple of s_0; i.e., $\mathbf{H} = s_0\mathbf{H}_0$. Hence, bearing in mind (2), we obtain

$$\mathbf{k}_0 = \frac{1}{s_1} \cdot \mathbf{H} = \frac{s_0}{s_1}\mathbf{H}_0. \tag{3}$$

Accordingly, the equation for the m^{th} plane normal to the vector $\mathbf{k}_0$ has the form

$$\mathbf{H}_0\mathbf{R} = m, \quad m = 0, \pm 1, \pm 2, \ldots . \tag{4}$$

By definition, the waves $a_p(\mathbf{k}_0)e^{i2\pi\mathbf{k}_0\mathbf{R}}$ and $a_p((s_1 - 1)\mathbf{k}_0)e^{i2\pi(s_1-1)\mathbf{k}_0\mathbf{R}} = a_p(-\mathbf{k}_0)e^{-i2\pi\mathbf{k}_0\mathbf{R}}$ in the sum (1) involve $s = 1$ and $s = s_1 - 1$ in describing the dominant waves.

The substitution of (3) into (1) yields

$$n(p, \mathbf{R}) = n(p, m) = \sum_{s=0}^{s=s_1-1} a_p(s)e^{i2\pi(s_0/s_1)sm} \tag{5}$$

where $a_p(s)$ stands for $a_p(s\mathbf{k}_0)$ and $n(p, m)$ is the probability that a site of the m^{th} plane in the p^{th} sublattice is occupied by an interstitial atom.

To determine the structure of a layer phase we should: (i) find the sequence of occupied and vacant parallel planes within the interstice sublattices of the host lattice frame, (ii) find the indices of the plane forming this sequence, and (iii) find the mutual position of the layered distribution of interstitial atoms in the various sublattices. More accurate structure determinations also require the calculation of small displacements of host atoms produced by the ordered distribution of interstitial atoms.

Below we shall show that the first step, i.e., the determination of the sequence of occupied and vacant layers, can be made by application of the maximal amplitude principle. According to this principle, the minimization of binding energy is possible only through a choice of the special distribution of filled and vacant layers in the layer superstructure (5) which provides for the maximal amplitudes of the dominant wave, at the expense of minimizing the amplitudes of the nondominant waves.

The amplitude of concentration waves of a layer superstructure is related to the $n(p, m)$ probabilities (here the plane number, m, plays the part of the coordinate **R**) by the inverse Fourier transform of Eq. (5):

$$a_p(s) = \frac{1}{s_1}\sum_{m=0}^{s_1-1} n(p, m)\exp\left(-i\frac{2\pi s_0}{s_1}sm\right). \tag{6}$$

The variable $n(p, m)$ is equal either to unity (if the m^{th} plane of the p^{th} sublattice is filled with interstitial atoms) or to zero (if the plane is vacant). The integer s_1 in Eq. (6) is a period expressed in terms of the number of planes comprising the superstructure translational motif. This is the reason why the number of occupied planes m_0 may be easily related to the stoichiometric "occupancy" of the p^{th} sublattice, c_p:

$$c_p = m_0/s_1. \tag{7}$$

As $n(p, m)$ is either 1 or 0, the sum in (6) is simply a sum of m_0 exponents, $\exp(-i(2\pi s_0/s_1)sm')$, taken over the number of occupied planes, i.e.,

$$a_p(s) = \frac{1}{s_1}\sum_{m'} \exp\left(-i2\pi\frac{s_0}{s_1}sm'\right) \tag{8}$$

where m' are the numbers of occupied planes.

By definition, the amplitude of the dominant wave with the wave vector $\mathbf{k}_0$ corresponds to $s = 1$. Hence

$$a_p(1) = \frac{1}{s_1} \sum_{m'} \exp\left(-i2\pi \frac{s_0}{s_1} m'\right). \qquad (9)$$

To make the modulus of the amplitude (9) maximal at a given number of filled planes, m_0, we must choose the index numbers of filled layers, m', such that the modulus of the sum of exponents in (9) be maximal. This requires that the difference between the phases of the exponents, $\exp(-2\pi(s_0/s_1)m')$, related to these layers, be minimal. Each term in (9) may be represented graphically in a circular diagram as a radius-vector of the unit circle in the complex plane which makes an angle of $\varphi(m') = 2\pi(s_0/s_1)m'$ with the real axis (here m' is the number of the layers to which the radius vector corresponds).

Consider first the case of $s_0 = 1$ and $s_1 = 9$ (Fig. 1a). The number drawn near each radius-vector in that figure is the index number m' of layers making up the crystallographic pattern comprising $s_1 = 9$ planes; the angles between these vectors and the real axis are equal to the phase angles, $\varphi(m') = 2\pi(1/9)m'$, of the corresponding planes. It is easy to see that the maximal value of the modulus of the vector sum of m_0 unit vectors is attained when we choose m_0 nearest vectors that make the smallest angles with each other, equal to $2\pi/s_1 = 2\pi/9$. The maximal amplitude of the dominant concentration wave $a_p(1)$ at a given $c_p = m_0/s_1$ is thus determined by expression (9) where the summation is carried out from 0 to $m_0 - 1$. The corresponding sum forms a geometric progression and may easily be calculated. The result for the amplitude of the dominant concentration wave is

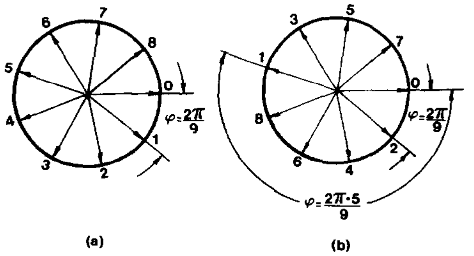

FIG. 1. Vector diagram for the determination of the sequence of alternating vacant and filled planes in superstructures of homologous phases (see text): (a) the case $s_0 = 1$ and $s_1 = 9$; (b) the case $s_0 = 5$ and $s_1 = 9$.

$$a_p(1) = \frac{\sin \pi c_p}{s_1 \sin(\pi/s_1)} \cdot e^{-i\pi(s_0/s_1)(m_0-1)}. \qquad (10)$$

Similar expressions are obtained for the amplitudes of other waves:

$$a_p(s) = \frac{\sin \pi s c_p}{s_1 \cdot \sin(s\pi/s_1)} \cdot e^{-i\pi(s_0/s_1)(m_0-1)}. \qquad (11)$$

Hence the squares of amplitude moduli are given by

$$|a_p(1)|^2 = \frac{\sin^2 \pi c_p}{s_1^2 \sin^2 \frac{\pi}{s_1}},$$

$$|a_p(s)|^2 = \left(\frac{\sin \pi s c_p}{s_1 \cdot \sin \pi s/s_1}\right)^2. \qquad (12)$$

With $s_0 > 1$, each exponential may still be related to the radius-vector making an angle of $\varphi(m') = 2\pi(s_0/s_1)m'$ with the real axis. This situation is illustrated by Fig. 1b for $s_1 = 9$ and $s_0 = 5$. As in Fig. 1a, the numbers drawn near the vectors are the plane index numbers of filled planes, m', and the angles made by the vectors and the real axis are equal to $\varphi(m') = 2\pi(s_0/s_1)m'$. It follows from Fig. 1b that, within an accuracy related to the numbering of unit vectors, their mutual arrangement at $s_0 = 5$ remains the same as with $s_0 = 1$. Therefore, as with $s_0 = 1$, the maximal value of the modulus of the sum of m_0 unit vectors shown in Fig. 1b is attained when neighboring vectors making angles of $\varphi = 2\pi/9$ with each other are chosen. The calculation formulae remain the same as before. For instance, if the concentration c_p is equal to 5/9, i.e., 5 of 9 planes should be filled, it follows from Fig. 1a that in the case $s_0 = 1$ the numbers of occupied planes should be 0, 1, 2, 3, 4. The corresponding sequence of filled and vacant planes is M M M M □ □ □ □ □ M M M. . . . Figure 1b displays that for the case $s_0 = 5$, the numbers of occupied planes are 0, 2, 4, 6, 8 with the sequence of filled and vacant planes M □ M □ M □ M □ M M □ . . . , where M and □ are symbols designating occupied and vacant planes.

According to the maximal amplitude principle, the squared amplitude of the dominant wave, $|a_p(1)|^2$, may be utilized to estimate stabilities of superstructures. Equation (12) for $|a_p(1)|^2$ has the larger value the smaller the translational motif period s_1 so that the structure with the smaller period will be more stable at a given "occupancy" c_p of the p^{th} sublattice. The formation of superstructures having the smallest period consistent with the fraction of filled planes, m_0, is therefore energetically favored. Simple fractions $c_p = m_0/s_1$ with s_1 quantities as denominators make up a discrete series of values. Figure 2 shows the dependence of $|a_p(1)|^2$ on c_p in the c_p range 0 to 0.5 for s_1 varying from 2 to 19. The other part of the plot corresponding to the c range of 0.5 to 1 should, according to (12), be symmetric with respect to the first one. To obtain that part, one must substitute $1 - c_p$ for c_p. The dependence in Fig. 2 reflects the contribution to the internal energy from the smallest eigenvalue $\lambda_{\varphi 0}(\mathbf{k}_0)$ and therefore, characterizes relative stabilities of superstructures. The maxima of the plot correspond to series of homologous compositions $c_p = n/2n - 1 = \frac{2}{3}, \frac{3}{5}, \frac{4}{7}$, etc., for c_p above $\frac{1}{2}$ and $c_p = n/2n + 1 = \frac{1}{3}, \frac{2}{5}, \frac{3}{7}$, etc., for c_p below $\frac{1}{2}$. The respresentatives of those series should therefore be more stable than compounds of other compositions. Both series correspond essentially to the same superstructures. These superstructures are antiisomorphic with respect to each other, i.e., superstructures of one series may be obtained from those of the other by replacing interstitial atoms with vacancies and vice versa. In both cases, the so-called structures of homologous compounds arise. Taking into account (7) and the composition series obtained, one can see that $s_1 = 2n - 1$, i.e., the translational motif of homologous phases always consists of an odd number of planes.

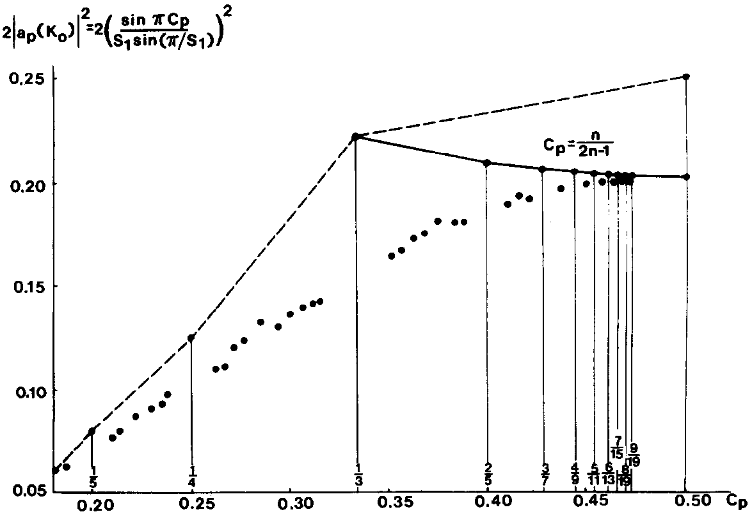

FIG. 2. Squared amplitude, $|a_p(\mathbf{k}_0)|^2$, of the concentration wave of the dominant superstructure vector $\mathbf{k}_0$ vs the stoichiometric composition c_p for layered superstructures. The solid line passes through points corresponding to the homologous series $c_p = n/2n - 1$.

2. Homologous Series of Magnéli Phases, Ti_nO_{2n-1} and V_nO_{2n-1}

A large number of phases having compositions intermediate between TiO_2 and Ti_2O_3 occur in the Ti–O and V–O systems. These were first described and studied in detail by Magnéli and co-workers (*2*); they became known as "Magnéli phases." Since TiO_2 and Ti_2O_3 with rutile and corundum structures, respectively, are formed by ordering of Ti atoms over octahedral interstices of the oxygen bcc lattice, it is natural to assume that intermediate phases should also be represented as interstitial superstructures based on the bcc host lattice.

The compositions and atomic structures of these phases may easily be explained and as a rule, may be predicted, within the thermodynamic theory of ordering in solid solutions as described above. The construction of superstructures with period, s_1, not equal to 2, 3, and 4 requires the addition of several other concentration waves into the density function $n(p, \mathbf{R})$; otherwise, we would not be able to render this function equal to either 0 or 1 at all crystal lattice sites. According to the maximal amplitude principle, the stable superstructure should involve alternating filled and vacant parallel planes (a layer superstructure); the amplitude of the dominant wave attains its maximal value by decreasing amplitudes of all nondominant waves. As shown in Section 1, the maximal value of the dominant amplitude may be attained in the series of homologous compositions $c_p = n/2n - 1$ where $n = 2, 3, 4, \ldots$, with the superstructure period, expressed through the number of layers, $s_1 = 2n - 1$ forming the translational motif. For that reason the configurational energy of such superstructures is lowered, and the superstructure will be comparatively stable.[1]

Consider compositions intermediate between MO_2 and M_2O_3. Intermediate phases should be treated as resulting from tertiary ordering in a nonstoichiometric secondary ordered phase of the type $(M\,\square)_{1/2} \cdot (M\,\square)_{1/2}\,O = MO$ (distribution (36) in (*1*)) in which metal atoms occupy half of "permitted" O_x and O_y interstices with $p = 1$ and $p = 2$ in the oxygen bcc host lattice. We designate these with indices $\{p, \mathbf{r}\}$. As in the cases considered above, the dominant wave amplitude becomes maximal if the function $n(p, \mathbf{r})$ may be represented in a form which includes the only "polarization" of the dominant wave. It has been shown in (*1*) that with odd $s_1 = 2n - 1$, the $n(p, \mathbf{r})$ function may be constructed using the dominant wave with one polarization if condition (47) of Ref. (*1*) is met. In that case the dominant wave yields the same distribution of interstitial atoms in both "permitted" sublattices of the nonstoichiometric structure MO. We may then apply the results of the theory of homologous series valid for the case of one sublattice to each of the two "permitted" sublattices of the nonstoichiometric structure MO. In particular, $n/(2n - 1)$ "permitted" sites should be occupied in each sublattice. Relating that number to the total number of O_x or O_y sites we obtain $c_p = \frac{1}{2} \cdot n/(2n - 1)$ (we have taken into consideration that the number of "permitted" sites in the secondary superstructure MO is smaller by a factor of $\frac{1}{2}$ than the number of O_x and O_y sites in the bcc lattice). This yields the stoichiometric formula

$$\left[M_{\frac{n}{2n-1}}\,\square_{\frac{n-1}{2n-1}}\right]_{\frac{1}{2}}\left[M_{\frac{n}{2n-1}}\,\square_{\frac{n-1}{2n-1}}\right]_{\frac{1}{2}}O$$

$$= M_{\frac{n}{2n-1}}O \quad \text{i.e.,}\ M_nO_{2n-1}$$

In other words, we have obtained the well established stoichiometric formula of the homologous Magnéli phases, Ti_nO_{2n-1} and V_nO_{2n-1}. We next have to determine the se-

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[1] It should be mentioned here that such layer structures are less stable than the favorable structures with $s_1 = 2, 3, 4$ considered in (*1*), since the foregoing have nonzero amplitudes of nondominant waves.

quence of filled and vacant planes in layer phases M_nO_{2n-1}. As an example, we analyze the homolog of composition Ti_5O_9. Eq. (84b) in (*1*) shows that the dominant superstructure vector may be written

$$\mathbf{k}_1 = \frac{n}{2n-1}\mathbf{H}_r = \frac{5}{9}\mathbf{H}_r \qquad (13)$$

where

$$\mathbf{H}_r = 2\mathbf{k}_r + 2\mathbf{H} \qquad (14)$$

$$\mathbf{k}_r = (\tfrac{1}{2}\,\tfrac{1}{2}\,0) \qquad (15)$$

and **H** is the reciprocal lattice vector of the secondary superstructure $(\mathrm{M}\,\square)_{1/2}\,(\mathrm{M}\,\square)_{1/2}\,\mathrm{O}$. The **H** vectors include the vector $(\tfrac{1}{2}\,\tfrac{\bar{1}}{2}\,0)$ and all other vectors which differ from $(\tfrac{1}{2}\,\tfrac{\bar{1}}{2}\,0)$ by a reciprocal lattice vector of the bcc host lattice (*1*).

As shown above (Fig. 1b) the maximal dominant amplitude value is provided with the following sequence of $s_1 = 9$ filled and vacant planes in each of the O_x and O_y octahedral sublattices "permitted" in the secondary structure:

Ti □ Ti □ Ti □ Ti □ Ti Ti
□ Ti □ Ti □ Ti □ Ti Ti □ . . . . (16)

Thus, filled and vacant planes should alternate in the stable Ti_5O_9 structure, with faults occurring in each ninth plane (the fault is shown in (16) by dashed line). The latter feature may be interpreted as an interstitial defect: two filled planes are not separated by a vacant one. A similar modulation pattern is observed in other homologs of the series.

Lastly, we must determine the direction of modulation of atomic planes to complete the description of the structural pattern of Magnéli phases (as mentioned above, this description is accurate within small displacements of oxygen atoms). This is the most ambiguous point in our discussion because the choice of modulation direction $\mathbf{k}_1$ requires more detailed information about interatomic interactions. Within the approximate model we can only determine the most probable modulation direction which coincides with the direction of the reciprocal lattice vector $\mathbf{H}_r$ (see Eq. (13)). It has been shown (*1*) that the maximal amplitude principle implies the following restriction on the components of the vector $\mathbf{H}_r = (H_{rx}\ H_{ry}\ H_{rz})$:

$$-\cos\frac{\pi(H_{rx}-H_{ry})}{2(2n-1)}\exp\left(-\frac{i\pi}{2}(H_{rx}-H_{ry})\right) = 1. \qquad (17)$$

Since $\mathbf{k}_r = (\tfrac{1}{2}\,\tfrac{1}{2}\,0)$, it follows from definition (14) that $H_{rx} - H_{ry}$ is an even number for all vectors $\mathbf{H}_r$. The condition (17) is met in two cases, namely when

$$H_{rx} - H_{ry} < 2n - 1 \quad \text{at } H_{rx} - H_{ry} = 4l + 2 \qquad (18a)$$

or when

$$H_{rx} - H_{ry} > 2n - 1 \quad \text{at } H_{rx} - H_{ry} = 4l \qquad (18b)$$

where l is an arbitrary integer.

To select the correct vector $\mathbf{H}_r$ more information is needed about the interatomic interaction of interstitial atoms. The short-range repulsive interaction model assumed in (*1*) leads to the stable rutile structure generated by the dominant wave with the wave vector $\mathbf{k}_r = \tfrac{1}{2}\mathbf{H}_r$ within the accuracy of reciprocal lattice vector **H** (*1*). This means that the absolute minimum of the spectrum $\bar{\lambda}_{(-)}(\mathbf{k})$ of eigenvalues of the interaction matrix $W_{pq}(\mathbf{r} - \mathbf{r}')$ defined on the "permitted" sites of the secondary superlattice $[\mathrm{M}\,\square]_{1/2}\,[\mathrm{M}\,\square]_{1/2}\,\mathrm{O}$ occurs at $\mathbf{k}_1 = \tfrac{1}{2}\mathbf{H}_r$. Further refinement of the interaction by introduction of the additional long-range interaction caused, for example, by conducting electrons or strain-induced interaction (*3*) may shift the absolute minimum of $\bar{\lambda}_{(-)}(\mathbf{k})$ by the vector $\boldsymbol{\tau}$ away from $\tfrac{1}{2}\mathbf{H}_r$. The sole assumption about the additional interaction which will be made is that this shift vector $\boldsymbol{\tau}$ is small, i.e.,

$$\mathbf{k}_1 = \tfrac{1}{2}\mathbf{H}_r + \boldsymbol{\tau} \qquad (19)$$

where $\boldsymbol{\tau} \ll \mathbf{k}_r$. According to Eq. (64) from (*1*)

$$\boldsymbol{\tau} = \frac{1}{2(2n-1)}\mathbf{H}_r. \qquad (20)$$

It follows from (20) that small $\boldsymbol{\tau}$ corresponds to the case of small reciprocal lattice vector $\mathbf{H}_r$ and a large n. Both latter conditions, small $\mathbf{H}_r$ and large n, are consistent with the case (18a). To provide the small value $|\mathbf{H}_r|$ we should choose $l = 0$. Therefore the vectors $\mathbf{H}_r$ should be selected from Table 1 in (*1*) so that they would meet the condition

$$H_{rx} - H_{ry} < 2n - 1 \text{ at } H_{rx} - H_{ry} = 2$$

or, equivalently,

$$H_{rx} - H_{ry} = 2 \text{ and } 2n - 1 > 2. \quad (21)$$

The selection of all low index vectors $\mathbf{H}_r$ (to provide small $|\mathbf{H}_r|$) from Table 1 in Ref. (*1*) which meet the condition (18a) yields the series

$$\mathbf{H}_r = (200),\ (1\bar{1}2),\ (312) \qquad (22)$$

where the crystal lattice plane indices (H_{rx} H_{ry} H_{rz}) are related to the bcc host lattice. Being related to the rutile axes, these planes have indices $(110)_{\text{rut}}$, $(101)_{\text{rut}}$ and $(121)_{\text{rut}}$, respectively. Indices in the bcc and rutile representation are connected by the equations

$$\tfrac{1}{2}(H_x^{\text{bcc}} - H_y^{\text{bcc}}) = H_x^{\text{rut}},$$
$$\tfrac{1}{2}(H_x^{\text{bcc}} + H_y^{\text{bcc}}) = H_y^{\text{rut}},$$
$$\text{and } \tfrac{1}{2}H_z^{\text{bcc}} = H_z^{\text{rut}}.$$

According to (13) the wave vectors corresponding to the series (22) are

$$\mathbf{k}_1 = \frac{n}{2n-1}(200),\ \frac{n}{2n-1}(1\bar{1}2),$$
$$\text{and } \frac{n}{2n-1}(312). \quad (23)$$

The wave vector of the dominant wave generating the most stable superstructure provides the minimal eigenvalue $\bar{\lambda}_{(-)}(\mathbf{k}_1)$ (*1*). This minimum condition determines wave vector of the dominant wave from (23). To date we do not have enough information about interatomic interactions and, thus, cannot calculate $\bar{\lambda}_{(-)}(\mathbf{k})$ with sufficient accuracy to select unambigiously the wave vector $\mathbf{k}_1$ from (23). Nevertheless, the result (23) is consistent with the X-ray determination (*4*) of the Magnéli phase structures. The Magnéli phases Ti_nO_{2n-1} and V_nO_{2n-1} are generated by the $(312)_{\text{bcc}}$ plane (i.e., $(121)_{\text{rut}}$ plane) for $4 \leq n \leq 10$. The bcc lattice plane $(1\bar{1}2)$ (i.e., the $(101)_{\text{rut}}$ plane) which also enters in (23) generates the corundum structure for Ti_2O_3, at $n = 2$.

If the value n proves to be too large (the case of very small $\boldsymbol{\tau}$), the difference between corresponding $\bar{\lambda}_{(-)}(\mathbf{k}_r + \boldsymbol{\tau})$ becomes very small since $\bar{\lambda}_{(-)}(\mathbf{k}_r + \boldsymbol{\tau}) \to \bar{\lambda}_{(-)}(\mathbf{k}_r)$ at $n \to \infty$. In this situation the selection of the vector $\mathbf{H}_r$ or $\mathbf{k}_1 = (n/2n-1)\mathbf{H}_r$ becomes especially difficult.

To complete the structure determination of the Magnéli phases the mutual positions of the interstitial atom distributions in the O_x and O_y sublattices should be found. As shown in (*1*), the structure of stable phase is always determined by the dominant concentration wave

$$v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}} \qquad (24)$$

where $v_{(-)}(p, \mathbf{k}_1)$ describes the contributions of the dominant wave to the distribution of interstitial atoms in O_x interstices when $p = 1$ and in O_y interstices when $p = 2$. Eq. (40b) from (*1*) yields

$$v_{(-)}(p, \mathbf{k}_1) = \frac{1}{\sqrt{2}}(1, e^{-i\pi(k_{1x}-k_{1y})})$$
$$= \frac{1}{\sqrt{2}}(1, e^{-i2\pi\mathbf{k}_1(\mathbf{a}_1-\mathbf{a}_2)/2}) \quad (25)$$

where $\mathbf{a}_1$ and $\mathbf{a}_2$ are unit reference vectors along the [100] and [010] bcc lattice directions, respectively. Substitution of (25) into (24) yields

$$v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}} = \begin{cases} \dfrac{1}{\sqrt{2}}\, e^{i2\pi\mathbf{k}_1\mathbf{r}} & \text{if } p = 1 \\ \dfrac{1}{\sqrt{2}}\, e^{-i2\pi\mathbf{k}_1(\mathbf{a}_1-\mathbf{a}_2)/2}e^{i2\pi\mathbf{k}_1\mathbf{r}} & \text{if } p = 2. \end{cases} \tag{26}$$

Equation (26) may be identically rewritten as

$$v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}} = \begin{cases} \dfrac{1}{\sqrt{2}}\, e^{i2\pi\mathbf{k}_1\mathbf{r}} & \text{if } p = 1 \\ \dfrac{1}{\sqrt{2}}\, e^{+i2\pi\mathbf{k}_1(\mathbf{r}+\mathbf{T})} & \text{if } p = 2 \end{cases} \tag{27}$$

where

$$\mathbf{T} = n \cdot (\mathbf{a}_2 - \mathbf{a}_1). \tag{28}$$

In (27) we took into consideratioin the relations (28), $\mathbf{k}_1 = (n/2n - 1)\mathbf{H}_r$ and $\mathbf{H}_r(\mathbf{a}_1 - \mathbf{a}_2)/2 = 2l + 1$ (see Eq. 18a)) where l is an integer to prove the identity

$$e^{-i2\pi\mathbf{k}_1(\mathbf{a}_1-\mathbf{a}_2/2)+\mathbf{T})} \equiv 1.$$

Equation (27) shows that the dominant wave (24) generates the same ordered distribution in O_x and O_y interstices; however, the distribution in O_y interstices is shifted rigidly by the reference vector $\mathbf{T}$ given in (28). In other words, if an O_x interstice related to the host lattice site $\mathbf{r}$ is occupied by a Ti atom, a Ti atom also occupies the O_y interstice related to the $\mathbf{r} + \mathbf{T}$ host lattice site. This condition, combined with the known sequence of the occupied and vacant planes within the O_x and O_y sublattices, enables us to construct the complete atomic structure of the Magnéli phase.

As an example consider the Ti_5O_9 structure. Comparison of (3) and (13) shows that this case corresponds $s_0 = n = 5$ and $s_1 = 2n - 1 = 9$. When the layered structure is generated by the alternating planes $(312)_{bcc} = (121)_{rut}$, the reciprocal lattice of this structure is described by the superlattice diffraction spots which divide all $\mathbf{H}_r = (312)$ reciprocal lattice vectors by nine equidistant segments. Figure 3 displays the reciprocal lattice and atomic lattice of the Ti_5O_9 phase which results from the present consideration. One may easily recognize in Fig. 3 the orientational relations between the bcc host lattice frame and the lattice of the Ti_5O_9 superstructure. The size of the

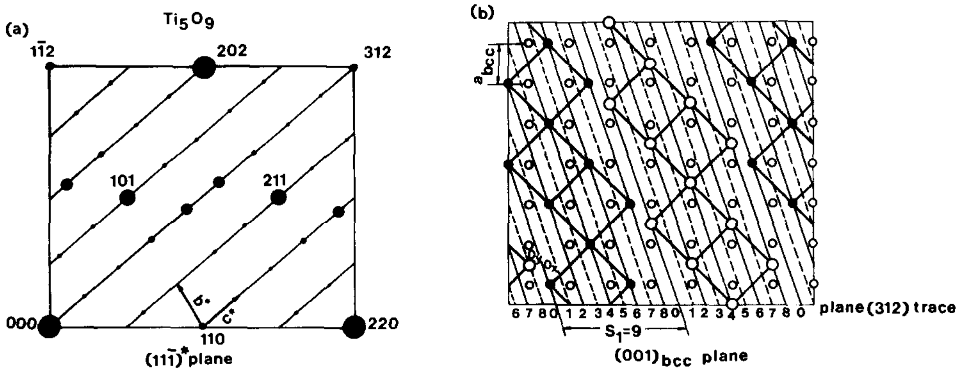

FIG. 3. Structure of the Ti_5O_9 phase: (a) Reciprocal lattice in the $(\bar{1}\bar{1}1)^*$ plane. Reciprocal lattice point size is proportional to the calculated intensity. The fundamental reciprocal lattice points referred to the bcc host lattice are indexed. (b) Atomic lattice. Solid lines are traces of the planes fitted by Ti atoms. Dashed lines are traces of vacant planes. Circles are Ti atoms situated in a (001) plane of the bcc host lattice. The rutile unit cells are shown by the solid line.

TABLE I

POWDER DIFFRACTION PATTERN OF Ti_5O_9

No.	d (Å)	Conventional indices $(H_x\ H_y\ H_z)^a_{\text{homolog}}$	Reflection indices related to the reciprocal lattice of the bcc host crystal	Harmonic s of the wave vector $\mathbf{k} = \frac{5}{9}(312)_{\text{bcc}}$	Relative intensity	
					Experim. (5)	Calulation
1	7.81	$0\,0\,1$	$\frac{1}{3}\ \frac{1}{9}\ \frac{1}{9}$	2	vw	2.8
2	5.19	$1\,0\,\bar{1}$	$\bar{\frac{1}{2}}\ \frac{1}{6}\ \frac{1}{3}$	3	w	10
3	4.71	$1\,0\,0$	$\frac{1}{6}\ \frac{5}{18}\ \frac{5}{9}$	4	vw	4.2
4	4.03	$1\,0\,\bar{2}$	$\bar{\frac{5}{6}}\ \frac{1}{18}\ \frac{1}{9}$	1	st	83
5	3.42	$1\,0\,1$	$\frac{1}{6}\ \frac{7}{18}\ \frac{7}{9}$	2	vw	2.8
6	3.36	$1\,\bar{2}\,0$	$\bar{\frac{1}{6}}\ \frac{7}{18}\ \frac{7}{9}$	1	vst	83
7	3.34	$0\,2\,\bar{1}$	$\bar{\frac{1}{3}}\ \bar{\frac{7}{9}}\ \frac{4}{9}$	4	vw	4.2
8	3.23	$0\,2\,0$	$0\ \bar{\frac{2}{3}}\ \frac{2}{3}$	3	w	10
9	3.12	$\bar{1}\,2\,1$	$\frac{1}{2}\ \bar{\frac{5}{6}}\ \frac{1}{3}$	3	w	10
10	3.07	$1\,\bar{2}\,1$	$\frac{1}{6}\ \frac{19}{18}\ \frac{1}{9}$	1	vst	83
11	2.94	$0\,2\,\bar{2}$	$\bar{\frac{2}{3}}\ \bar{\frac{8}{9}}\ \frac{2}{9}$	2	w	10
12	2.91	$1\,0\,\bar{3}$	$\bar{\frac{7}{6}}\ \bar{\frac{1}{18}}\ \bar{\frac{1}{9}}$	1	vst	83
13	2.72	$0\,2\,1$	$\frac{1}{3}\ \bar{\frac{5}{9}}\ \frac{8}{9}$	1	m	83
14	2.60	$2\,0\,\bar{1}$	$\bar{\frac{2}{3}}\ \frac{4}{9}\ \frac{8}{9}$	1	st	83
15	2.58	$\bar{1}\,2\,2$	$\frac{5}{6}\ \bar{\frac{13}{18}}\ \frac{5}{9}$	4	vw	4.2

$$^a\ (H_x\ H_y\ H_z)_{\text{homolog}} = \begin{pmatrix} \bar{1} & 1 & 1 \\ 0 & \bar{2} & 1 \\ \frac{5}{2} & \frac{1}{2} & \frac{1}{2} \end{pmatrix} \times \begin{pmatrix} H_x \\ H_y \\ H_z \end{pmatrix}_{\text{bcc}}$$

reciprocal lattice point is proportional to the calculated intensities of the X-ray spots. Table I enables us to compare the relative intensities of the diffraction spots obtained on the powder diffraction pattern (5) and intensities measured in arbitrary units which follow from the proposed model. Table I demonstrates the good agreement between X-ray data and calculations despite the fact that displacements of oxygen atoms have not been taken into consideration. The same agreement is observed between the proposed model and the single crystal X-ray data.

Summing up the foregoing, the theoretical determination based on the maximal amplitude principle combined with the simple short-range interaction model results in the correct prediction of the structure of the Magnéli phases:

(i) it yields the layered structure in O_x and O_y sublattices with the correct sequence of filled and vacant planes of the type of (16);

(ii) it provides the correct mutual location of these sequences in the O_x and O_y sublattices; and

(iii) it specifies the short list of the most probable planes whose alternation generates the layered structure, the planes $(1\bar{1}2)$ and (312) observed for the Magnéli phases contained in this list.

The proposed interpretation of the Magnéli phases differs from the conventional one based on the crystallographic shear mechanism (4). According to the latter, a Magnéli phase is produced from the rutile structure by the shear along the parallel regularly spaced shear planes, the Miller indices of the shear planes coinciding with above-mentioned alternating filled and vacant planes.

Although the atomic structures of the Magnéli phases based on both interpretations are the same, the proposed thermodynamic approach, proceeding from the fact that the Magnéli phases are long-period interstitial layer superstructures in the bcc host oxygen lattice, seems to be more realistic. Actually, according to our consideration, mutual transformations between rutile, α-PbO_2 structure, corundum, and Magnéli phases are reduced to mere redistributions of Ti atoms within octahedral interstices of the same bcc host lattice composed of O atoms. It does not require the artificial introduction of crystallographic shear which is difficult to justify. Furthermore, the proposed theory enables us to predict the atomc structure of phases arising in the Ti–O system using a simple model of interatomic interactions.

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