

## The Concentration Wave Approach to the Pairwise Interaction Model for Predicting the Crystal Structures of Ceramics, I

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The structures of chemical compounds are predicted on the basis of energy calculations with the help of the concentration wave approach. The method predicts both the structures of the most stable oxides with fixed valencies and the structures of the so-called homologous series of Magnéli phases. To exemplify the procedure, the atomic structures of the Ti and V oxides are considered. The rutile and  $\alpha$ -PbO<sub>2</sub> structures are shown to be the most stable ones for tetravalent cations while the corundum structure is most stable for trivalent cations. © 1986 Academic Press, Inc.

It is known (see, for example, (1)) that many metal oxides, halogenides, fluorides, and other compounds may be treated as completely ordered solid solutions. This fact enables us to use the Ising model to analyze the structure and stability of chemical compounds (at least to within small atomic displacements caused by ordering). We may then employ the concentration wave method (2-4) to combine the symmetry and thermodynamic aspects of the problem and predict the structures of the most stable chemical compounds. This new approach is developed for the structures of the titanium and vanadium oxides which, as will be shown, can be considered as a completely ordered interstitial solution on a body-centered cubic host lattice of oxygen atoms.

### 1. Conditions for the Formation of Stable Oxides

We will now describe the basic concepts

of the concentration wave approach as it is applied to fully ordered atomic distributions in substitutional and interstitial systems. For specificity we shall confine the discussion to binary interstitial solid solutions. The principal results given below are, however, applicable to substitutional solid solutions and can be extended to multicomponent solutions.

Let atoms of a certain kind be distributed over crystal lattice sites that are specified by the indices  $(p, \mathbf{R})$ , where  $\mathbf{R}$  denotes the position of the origin of the unit cell of the host lattice and  $p$  labels the atom positions within the unit cell. We shall assume that all the atom positions ( $p = 1, \dots, g$ , where  $g$  is the position multiplicity) are crystallographically equivalent, i.e., that they can be brought into coincidence with one another by applying the host lattice symmetry operations. The atomic distribution over the sites  $\{p, \mathbf{R}\}$  is then described by the probability,  $n(p, \mathbf{R})$ , of finding a solute atom in the position  $(p, \mathbf{R})$ .

In a fully ordered interstitial solid solution (or chemical compound) the function  $n(p, \mathbf{R})$  describes a specific distribution of atoms; it has the value 1 if the position  $(p, \mathbf{R})$  is occupied by an interstitial atom and is 0 if the position is vacant. As shown in references (2-4) such a distribution can be written as a superposition of static concentration waves:

$$\begin{aligned} n(p, \mathbf{R}) &= \sum_{\mathbf{k}} a_p(\mathbf{k}) \exp[2\pi i \mathbf{k} \cdot \mathbf{R}] \\ &= c_p + \sum_{\mathbf{k}}' a_p(\mathbf{k}) \exp[2\pi i \mathbf{k} \cdot \mathbf{R}] \quad (1) \end{aligned}$$

where  $a_p(0) = c_p$  is the "occupancy" of the  $p$ th sublattice,  $a_p(\mathbf{k})$  is the amplitude of the plane concentration wave that modulates the distribution of interstitial atoms over the  $p$ th sublattice formed by all positions of the type  $p$ ,  $2\pi\mathbf{k}$  is the superstructure wave vector determined in the first Brillouin zone of the host lattice, and the prime on the second summation on the right hand side means that the term corresponding to  $\mathbf{k} = 0$  is omitted. Since the function  $n(p, \mathbf{R})$  assumes only the two values 0 and 1, it retains its value after being raised to any power,  $m$ :

$$[n(p, \mathbf{R})]^m = n(p, \mathbf{R}). \quad (2)$$

The properties of the function  $n(p, \mathbf{R})$  impose the following two restrictions on the concentration waves entering Eq. (1): (a) the sum of any two wave vectors entering Eq. (1) must equal either one of the superstructure vectors entering this distribution or zero, to within an additive reciprocal lattice vector,  $\mathbf{H}$ ; (b) the squares of the concentration wave amplitudes satisfy the summation rule

$$\sum_{\mathbf{k}} |a_p(\mathbf{k})|^2 = c_p \quad (3)$$

irrespective of the type of the atomic distribution.

The pairwise interaction model gives the following equation for the configurational

energy of interaction of the interstitial atoms (2-4):

$$E = \frac{1}{2} \sum_p \sum_q \sum_{\mathbf{R}, \mathbf{R}'} W_{pq}(\mathbf{R} - \mathbf{R}') n(p, \mathbf{R}) n(q, \mathbf{R}') \quad (4)$$

where the indices  $p$  and  $q$  label the  $g$  atom sites, the summations over  $\{p, \mathbf{R}\}$  and  $\{q, \mathbf{R}'\}$  are carried out over all crystal interstices, and  $W_{pq}(\mathbf{R} - \mathbf{R}')$  is the pairwise interaction energy between the interstitial atoms occupying the sites  $(p, \mathbf{R})$  and  $(q, \mathbf{R}')$ .

The distribution function,  $n(p, \mathbf{R})$ , can be expressed in terms of normal concentration waves,  $v_\sigma(p, \mathbf{k}) \exp(2\pi i \mathbf{k} \cdot \mathbf{R})$ :

$$n(p, \mathbf{R}) = \sum_{\sigma} \sum_{\mathbf{k}} \gamma_{\sigma}(\mathbf{k}) v_{\sigma}(p, \mathbf{k}) \exp(2\pi i \mathbf{k} \cdot \mathbf{R}) \quad (5)$$

where the  $v_{\sigma}(p, \mathbf{k})$ ,  $\sigma = 1, \dots, g$ , are orthogonal unit "polarization vectors" that are the eigenvectors of the pairwise interaction energy and the  $\gamma_{\sigma}(\mathbf{k})$  are amplitudes. The  $g$  polarization vectors are determined by the equation

$$\sum_q V_{pq}(\mathbf{k}) v_{\sigma}(q, \mathbf{k}) = \lambda_{\sigma}(\mathbf{k}) v_{\sigma}(p, \mathbf{k}) \quad (6)$$

where  $V_{pq}(\mathbf{k})$  is the Fourier transform of the pairwise interaction energy,

$$V_{pq}(\mathbf{k}) = \sum_{\mathbf{R}} W_{pq}(\mathbf{R}) \exp[-2\pi i \mathbf{k} \cdot \mathbf{R}] \quad (7)$$

and the  $\lambda_{\sigma}(\mathbf{k})$  are the eigenvalues of  $V_{pq}(\mathbf{k})$ . The substitution of Eqs. (5) and (6) into Eq. (4) gives

$$E = (N/2) \sum_{\sigma} \sum_{\mathbf{k}} \lambda_{\sigma}(\mathbf{k}) |\gamma_{\sigma}(\mathbf{k})|^2 \quad (8)$$

where the summation over  $\mathbf{k}$  is carried out over the first Brillouin zone and  $N$  is the total number of unit cells.

This paper treats structures that remain fully ordered up to the crystal melting

point. It follows that (at least in the modified Ising model) the relative stability of the various possible superstructures is governed by the internal energy. The most stable superstructure is that which has the lowest energy per interstitial, i.e., the minimum binding energy. The binding energy can be evaluated from Eq. (8):

$$E_{\text{int}} = E/N_{\text{int}} = \frac{1}{2} \sum_{\sigma, \mathbf{k}} \lambda_{\sigma}(\mathbf{k}) |\gamma_{\sigma}(\mathbf{k})|^2 / c \quad (9)$$

where

$$c = \sum_p c_p = N_{\text{int}}/N$$

and  $N_{\text{int}}$  is the total number of interstitial atoms. Using the orthogonality of the eigenfunctions of the Hermetian matrix  $V_{pq}(\mathbf{k})$  and the fact that  $n(p, \mathbf{R})$  is equal to either 0 or 1 the following summation rule follows from Eq. (3):

$$\sum_{\sigma, \mathbf{k}} |\gamma_{\sigma}(\mathbf{k})|^2 / c = 1. \quad (10)$$

Each coefficient  $|\gamma_{\sigma}(\mathbf{k})|^2 / c$  determines the partial contribution (weight) of the eigenvalue  $\lambda_{\sigma}(\mathbf{k})$  to the binding energy, Eq. (9).

The binding energy,  $E_{\text{int}}$ , has its minimum value when the major contribution to the sum on the right hand side of Eq. (9) is made by the smallest eigenvalue,  $\lambda_{\sigma^0}(\mathbf{k}^0)$  [ $\min \lambda_{\sigma}(\mathbf{k}) = \lambda_{\sigma^0}(\mathbf{k}^0)$ ]. Since there may be several wave vectors in the star of  $\mathbf{k}^0$ , the distribution function  $n(p, \mathbf{R})$  may include several concentration waves that are related to the smallest eigenvalue,  $\lambda_{\sigma^0}(\mathbf{k}^0)$ . We shall call these "dominant waves." The partial contribution of the smallest eigenvalue is

$$P = (1/c) \sum_j |\gamma_{\sigma^0}(\mathbf{k}_j^0)|^2$$

where  $j$  is the index number of the wave vectors of dominant waves in the star  $\{\mathbf{k}^0\}$ . It is easy to see that the energy (9) is minimized if the sum of the squares of the am-

plitudes associated with the dominant concentration waves,  $\sum_j |\gamma_{\sigma^0}(\mathbf{k}_j^0)|^2$ , assumes its maximum possible value for the given concentration,  $c$ . According to Eq. (10) this occurs when the squares of the nondominant waves that are related to the larger eigenvalues,  $\lambda_{\sigma}(\mathbf{k})$ , are reduced to a minimum. The condition that a maximum of the sum  $\sum_j |\gamma_{\sigma^0}(\mathbf{k}_j^0)|^2$  minimizes the configurational energy will be referred to as the *maximum amplitude principal*.

It follows from Eq. (10) that the energetically most favorable case is realized when the amplitudes of all nondominant waves vanish. The sum of the squared moduli of the dominant wave amplitudes then assumes the maximum value possible for a given composition, i.e., the maximum amplitude principal is fulfilled as completely as possible.

The minimal set of dominant concentration waves always includes at least two waves,  $(\sigma^0, \mathbf{k}^0)$  and  $(\sigma^0, -\mathbf{k}^0)$ , ( $j = 1, 2$ ). The presence of the conjugate wave,  $(\sigma^0, -\mathbf{k}^0)$ , with the amplitude  $\gamma_{\sigma^0}^*(\mathbf{k}^0)$ , follows immediately from the reality of the density function,  $n(p, \mathbf{R})$ . The only case in which the conjugate vector need not explicitly appear is when the vectors  $\mathbf{k}^0$  and  $-\mathbf{k}^0$  differ from one another by a reciprocal lattice vector,  $\mathbf{H}$ , i.e., if  $\mathbf{k}^0 = \mathbf{H}/2$ . When the density function depends on two conjugate dominant waves it has the form

$$n_{\text{dom}}(p, \mathbf{R}) = c/g + \frac{1}{2} \{ \gamma_{\sigma^0}(\mathbf{k}^0) v_{\sigma^0}(p, \mathbf{k}^0) \exp[2\pi i \mathbf{k} \cdot \mathbf{R}] + \gamma_{\sigma^0}^*(\mathbf{k}^0) v_{\sigma^0}^*(p, \mathbf{k}^0) \exp[-2\pi i \mathbf{k} \cdot \mathbf{R}] \} \quad (11)$$

where  $g$  is the number of sublattices available for the interstitial atoms.

Equation (11) provides the simplest representation of an interstitial distribution based on dominant concentration waves. But it does not always satisfy the condition that the function  $n(p, \mathbf{R})$  be equal to 0 or 1 at every atom site. If it does not we must introduce additional concentration waves,

$(\sigma, \mathbf{k})$ , into (11) while trying to keep their number as small as possible to maximize the partial fraction of the minimal eigenvalue in the sum (9).

The most favorable modification of Eq. (11) to permit appropriate values at the interstitial atom positions is almost always the addition of concentration waves with wave vectors equal to  $s\mathbf{k}^0$ , where  $s$  is an integer that varies from 0 to  $s^1 - 1$ ,  $s^1$  is the smallest integer that satisfies the equality

$$s^1 \mathbf{k}^0 = \mathbf{H}, \quad (12)$$

and  $\mathbf{H}$  is a reciprocal vector of the host lattice. This choice of additional wave vectors satisfies the requirement that the sum of any two vectors in the distribution also appear in the distribution. The function  $n(p, \mathbf{R})$  may then be written

$$n(p, \mathbf{R}) = \sum_{s=0}^{s^1-1} a_p(s\mathbf{k}^0) \exp[2\pi i s \mathbf{k}^0 \cdot \mathbf{R}] \quad (13)$$

where

$$a_p(s\mathbf{k}^0) = \sum_{\sigma} \gamma_{\sigma}(s\mathbf{k}^0) v_{\sigma}(p, s\mathbf{k}^0). \quad (14)$$

Since all the wave vectors  $s\mathbf{k}^0$  entering Eq. (13) are collinear, the distribution function (13) yields a layered structure with alternate planes of filled and vacant interstices normal to the vector  $\mathbf{k}^0$ .

The common preference for layered superstructures follows directly from the maximum amplitude principle.

The distribution function given in Eq. (11) generates a layered superstructure because, of all the dominant waves, only the two conjugate parallel waves  $(\sigma^0, \mathbf{k}^0)$  and  $(\sigma^0, -\mathbf{k}^0)$  were utilized. The vectors of the star  $\{\mathbf{k}^0\}$  that were not parallel to the first two were omitted. This choice of vectors for constructing the distribution function conforms to the maximal amplitude principle. The maximal value of the sum of the squares of the amplitudes of the dominant waves is achieved when the distribution involves the minimum number of additional

concentration waves. To see this, let the distribution function include noncollinear dominant waves from the star  $\{\mathbf{k}^0\}$ . The sums of these wave vectors, which must also appear in the distribution, would generate two- and three-dimensional networks of nondominant wave vectors in reciprocal space.

The distribution function (13) was constructed from Eq. (11) to provide the flexibility needed to ensure an occupancy of 0 or 1 at each atom site. The distribution function (13) generates a one-dimensional network whose points divide the reciprocal lattice vector,  $\mathbf{H}$ , into  $s^1$  segments of equal length. In the usual case this division introduces a much smaller number of nondominant waves than would appear if noncollinear vectors were included. The energetic preference for layered superstructures is violated only rarely, when the star  $\{\mathbf{k}^0\}$  that provides a minimum of  $\lambda_{\sigma}(\mathbf{k})$  contains only vectors that sum to a vector of the same star or to zero.

Now let us consider the most favorable case when a superstructure is generated by the dominant waves alone. This case allows the maximum amplitude principle to be fulfilled as completely as possible.

The simplest distribution has  $s^1 = 2$ . Then

$$\mathbf{k}^0 = \mathbf{H}/2.$$

(Here and below the vector  $\mathbf{k}^0$  need not necessarily lie within the first Brillouin zone.) The sublattices,  $p$ , that are occupied by interstitial atoms have the distribution

$$\begin{aligned} n(p, \mathbf{R}) &= \frac{1}{2} + \frac{1}{2} \exp[2\pi i \mathbf{k} \cdot \mathbf{R}] \\ &= \frac{1}{2} + \frac{1}{2} \exp[\pi i \mathbf{H} \cdot \mathbf{R}] \end{aligned} \quad (15)$$

Since, by the definition of the reciprocal lattice, the product,  $\mathbf{H} \cdot \mathbf{R}$ , is an integer for any lattice translation,  $\mathbf{R}$ , the function (15) is equal to 0 or 1 for every lattice translation. The distribution (15) corresponds to  $c_p = \frac{1}{2}$ ; one-half of the interstitial sites on the  $p$ th sublattice are occupied.

A second favorable case is that of  $s^1 = 3$  when

$$\mathbf{k}^0 = \mathbf{H}/3$$

and  $2\mathbf{k}^0 = -\mathbf{k}^0$  to within  $\mathbf{H}$ . The distribution of atoms over the occupied interstitial sublattices is then given by

$$\begin{aligned} n(p, \mathbf{R}) &= \frac{1}{3} + \frac{2}{3} \cos[2\pi\mathbf{k}^0 \cdot \mathbf{R}] \\ &= \frac{1}{3} + \frac{2}{3} \cos[2\pi\mathbf{H} \cdot \mathbf{R}/3]. \end{aligned} \quad (16)$$

This function also assumes the values 0 and 1 for lattice translations,  $\mathbf{R}$ . The distribution (16) describes a layered structure having the occupancy  $c_p = \frac{1}{3}$ . Every third interstitial plane normal to  $\mathbf{H}$  is filled.

A third simple case has  $s^1 = 4$ ,  $\mathbf{k}^0 = \mathbf{H}/4$ . The corresponding distribution function,

$$\begin{aligned} n(p, \mathbf{R}) &= \frac{1}{2} + \frac{1}{2} \{ \cos[\pi\mathbf{H} \cdot \mathbf{R}/2] \\ &\quad + \sin[\pi\mathbf{H} \cdot \mathbf{R}/2] \} \end{aligned} \quad (17)$$

also takes the values 0 and 1, but does not contain concentration waves with the multiple vector  $2\mathbf{k}^0$ . The occupancy of the  $p$ th interstitial lattice is  $c_p = \frac{1}{2}$ .

The procedure outlined above leads to the determination of the dominant concentration waves that generate the primary superstructure. This procedure is the starting point for the determination of the stable oxide structures. But the primary superstructure has a natural stoichiometry that usually will not correspond to the oxide stoichiometry that satisfies valence constraints. It is then necessary to remove a certain number of the interstitial atoms to achieve a composition match.

The resulting vacancies on the interstitial sublattice can undergo a secondary ordering to decrease the configurational energy further. The superstructure formed in the secondary ordering can be determined in the same way as was the primary superstructure. The only difference is that the matrices,  $W_{pq}(\mathbf{r} - \mathbf{r}')$ , their eigenvalues,  $\lambda_\sigma(\mathbf{k})$ , and densities,  $n(p, \mathbf{r})$ , should not be determined at all the host lattice interstices

$\{p, \mathbf{R}\}$ , but only on the subset of "permitted" interstices,  $\{p, \mathbf{r}\}$ .

This procedure should be applied repeatedly, through sequential interstitial ordering reactions, until a superstructure is achieved whose natural occupancy satisfies the valency rule. This superstructure is the minimum-energy structure of the oxide.

## 2. Interstitial Superstructures Based on the bcc Lattice in the Ti-O System

The procedure for identifying the stable oxide phases will be illustrated below and applied to determine the oxide structures formed by ordering metal atoms over octahedral interstices in a bcc host lattice formed by oxygen atoms. The system Ti-O is used as a specific example.

There are three octahedral interstices for each site in the bcc structure. These are usually designated  $O_x$ ,  $O_y$ , and  $O_z$ . They are displaced by the vectors  $[a/2, 0, 0]$ ,  $[0, a/2, 0]$ , and  $[0, 0, a/2]$  from the bcc host lattice sites, where  $a$  is the lattice parameter of the bcc cell. Each of these interstices generates a bcc sublattice of interstices under the lattice translations of the bcc structure. The three sublattices will be labelled by the indices  $p = 1, 2, 3$ . Each octahedral interstice has four nearest-neighbor interstices that are removed from it by the distance,  $r_1 = a/2$ , eight interstices in a second coordination shell at  $r_2 = a/2^{1/2}$ , eight interstices in the third coordination shell at  $r_3 = 3^{1/2}a/2$ , and six interstices in the fourth coordination shell at  $r_4 = a$ .

The interaction between ions placed on neighboring interstices is expected to be repulsive, and should be the sum of the direct repulsion due to the overlap of electron clouds and the Coulomb repulsion due to the interaction of like charges. The direct repulsion should be the dominant interaction between typical metal ions placed in adjacent interstitial sites. Since the distance  $r_1$  is less than the atomic diameter of most

metals, this repulsion should be very strong. Since the direct repulsion decreases rapidly with distance, the dominant interaction between metal ions placed on second- and higher-neighbor sites should be the Coulomb repulsion. However, the Coulomb interaction is screened by the polarization of the oxygen atoms on the host lattice, and should become negligible when the ions are separated by several lattice distances.

These considerations lead us to select a model in which the interaction is nonzero only out to the fourth coordination shell. The repulsion between interstitial ions in the nearest-neighbor positions is assumed large, and that between ions in the second, third, and fourth shells is assumed to be given approximately by the Coulomb interaction. Hence

$$\begin{aligned} W_1 &\gg W_2 > W_3 > W_4 > 0 \\ W_i &\sim e^2/r_i \quad (i = 2, 3, 4) \\ W_i &\sim 0 \quad (i > 4) \end{aligned} \quad (18)$$

where  $W_i$  represents the repulsive interaction energies of pairs of atoms that are separated by the distance  $r_i$  and  $i$  designates the  $i$ th coordination shell.

We shall consider examples of titanium oxide with titanium valency in the range 3 to 4. The oxides with the limiting Ti valencies +3 and +4 have the stoichiometric compositions  $Ti_2O_3$  and  $TiO_2$ , respectively. Oxides that include Ti with intermediate valence have compositions between these limits. The Ti/O ratio in the phases under consideration thus lies in the range

$$\frac{1}{2} \leq \text{Ti/O} \leq \frac{2}{3}. \quad (19)$$

The  $V_{pq}(\mathbf{k})$  matrix for the three sublattices pertaining to the octahedral interstices (OI) in the bcc lattice has the form

$$V_{pq}(\mathbf{k}) = \begin{pmatrix} V_{11}(\mathbf{k}) & V_{12}(\mathbf{k}) & V_{13}(\mathbf{k}) \\ V_{12}^*(\mathbf{k}) & V_{22}(\mathbf{k}) & V_{23}(\mathbf{k}) \\ V_{13}^*(\mathbf{k}) & V_{23}^*(\mathbf{k}) & V_{33}(\mathbf{k}) \end{pmatrix}. \quad (20)$$

The  $V_{pq}(\mathbf{k})$  matrix components may easily be expressed in terms of the interaction energies  $W_1, W_2, W_3, W_4$  by substituting the coordinates of the OIs from the first, second, and third coordination shells into (7). This yields

$$V_{11}(\mathbf{k}) = 8W_3 \cdot \cos \pi k_x \cdot \cos \pi k_y \cdot \cos \pi k_z + 2W_4 \cdot (\cos 2\pi k_x + \cos 2\pi k_y + \cos 2\pi k_z)$$

$$V_{12}(\mathbf{k}) = (2W_1 \cdot \cos \pi k_z + 4W_2 \cdot \cos \pi k_x \cdot \cos \pi k_y) \cdot \exp(i\pi(k_x - k_y)), \quad (21)$$

where  $\mathbf{k} = k_x \mathbf{a}_1^* + k_y \mathbf{a}_2^* + k_z \mathbf{a}_3^*$ ,  $\mathbf{a}_1^*, \mathbf{a}_2^*, \mathbf{a}_3^*$  are the basis vectors of the reciprocal bcc crystal lattice along the directions [100], [010], and [001], respectively. The other elements of the matrix (20) may be derived from (21) by cyclic permutation.

In a bcc-based interstitial alloy, the principle of maximum amplitude generates two types of dominant waves which could produce the ordered distribution without additional nondominant waves. The first is the wave

$$\begin{aligned} v_1(p, \mathbf{k}_0) e^{i2\pi \mathbf{k}_0 \mathbf{R}} \\ = (v_1(1, \mathbf{k}_0), v_1(2, \mathbf{k}_0), v_1(3, \mathbf{k}_0)) e^{i2\pi \mathbf{k}_0 \mathbf{R}} \\ = \frac{1}{\sqrt{3}} (1, 1, 1) e^{i2\pi \mathbf{k}_0 \mathbf{R}} \end{aligned} \quad (22)$$

corresponding to the wave vector  $\mathbf{k}_0 = (111)$ , with the corresponding eigenvalue

$$\begin{aligned} \lambda_1(\mathbf{k}_0) &= V_{11}(\mathbf{k}_0) + 2V_{12}(\mathbf{k}_0) \\ &= -4W_1 + 8W_2 - 8W_3 + 6W_4 < 0. \end{aligned}$$

For brevity, here and below we shall use the designations  $\mathbf{k} = (k_x, k_y, k_z)$  and  $\mathbf{H} = (H_x, H_y, H_z)$  in place of the correct  $\mathbf{k} = (1/a)(k_x, k_y, k_z)$  and  $\mathbf{H} = (1/a)(H_x, H_y, H_z)$ .

The second dominant wave which generates the superstructure is

$$\begin{aligned} v_2(p, 0) &= (v_2(1, 0), v_2(2, 0), v_2(3, 0)) \\ &= \frac{1}{\sqrt{6}} (\bar{1}, \bar{1}, 2). \end{aligned} \quad (23)$$

It corresponds to the wave vector  $\mathbf{k}_0 = 0$  and to the eigenvalue

$$\lambda_2(0) = V_{11}(0) - V_{12}(0) \\ = -2W_1 - 4W_2 + 8W_3 + 6W_4 < 0.$$

Both eigenvalues  $\lambda_2(0)$  and  $\lambda_1(\mathbf{k}_0)$  are negative because of the assumed relation (18a). Therefore, the formation of the superstructures via both dominant waves reduces the configurational energy.

Consider first the dominant wave (22). According to (11), it generates the distribution

$$n_0(p, \mathbf{R}) = \frac{1}{3}c + \gamma_1(\mathbf{k}_0) \cdot v_1(p, \mathbf{k}_0)e^{i2\pi\mathbf{k}_0\mathbf{R}} \quad (24)$$

where  $v_1(p, \mathbf{k}_0)e^{i2\pi\mathbf{k}_0\mathbf{R}}$  is given by (22). The function (24) assumes the two values, 0 and 1, only if  $c = c_{st} = \frac{2}{3}$ ,  $\gamma_1(\mathbf{k}_0) = \sqrt{3}/2$ , for which Eq. (24) yields

$$n_0(1, \mathbf{R}) = n_0(2, \mathbf{R}) = n_0(3, \mathbf{R}) \\ = \frac{1}{2} + \frac{1}{2}e^{i2\pi(x+y+z)}, \quad (25)$$

where  $\mathbf{k}_0\mathbf{R} = x + y + z$ , since

$$\mathbf{R} = x\mathbf{a}_1 + y\mathbf{a}_2 + z\mathbf{a}_3. \quad (26)$$

Here  $\mathbf{a}_1$ ,  $\mathbf{a}_2$ , and  $\mathbf{a}_3$  are unit vectors of the bcc lattice along [100], [010], and [001] directions, respectively;  $(x, y, z)$  are bcc lattice site coordinates (for instance, (100),  $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ ,  $(\frac{3}{2}\frac{1}{2}\frac{1}{2})$ , and so on). The Ti atoms are placed at octahedral sites where  $n_0(p, \mathbf{R}) = 1$ .

The distribution (25) corresponds to the ratio  $c_{st} = \text{Ti/O} = \frac{2}{3}$ . This ratio lies outside the range (19). To shift the Ti/O ratio into the range (19) one should remove a fraction of the Ti atoms. There is additional reduction in the configurational energy produced by secondary ordering of vacancies over

the "permitted" OI formed by the removal of the Ti atoms. The secondary ordering along  $\{p, \mathbf{r}\}$  sites "permitted" by the distribution (25) can be generated solely by the dominant wave of the form

$$v_1(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{R}} = \frac{1}{\sqrt{3}}(1, 1, 1) \cdot e^{i2\pi\mathbf{k}_1\mathbf{r}} \quad (27)$$

where  $\mathbf{k}_1 = (kkk)$ . Otherwise, the distributions of Ti atoms would be different in  $O_x$ ,  $O_y$ , and  $O_z$  interstices and we would then have to introduce the additional wave (23) which controls the redistribution of Ti atoms between  $O_x$ ,  $O_y$ , and  $O_z$  sublattices.

To find the eigenvalue corresponding to the eigenvector  $v_1(p, \mathbf{k}_1) = (1/\sqrt{3})(1, 1, 1)$  we should calculate the matrix  $\bar{V}_{pq}(\mathbf{k})$  defined at the "permitted" interstices  $\{p, \mathbf{r}\}$ . It may be readily shown that in this case the eigenvector (27) of the dominant wave corresponds to the eigenvalue

$$\bar{\lambda}_1(\mathbf{k}_1) = \bar{V}_{11}(\mathbf{k}_1) + 2\bar{V}_{12}(\mathbf{k}_1) \\ = 6W_4 \cos 2\pi k_1 + 8W_2 \cos^2 \pi k.$$

Since the inequality  $W_4 < W_2$  is assumed,  $\bar{\lambda}_1(\mathbf{k}_1) > 0$ , so that the development of the secondary superstructure generated by the dominant wave (27) would increase the configurational energy. In such a case the secondary superstructures meeting the maximal amplitude principle cannot be formed.

Therefore we should give up consideration of secondary superstructures based on the distribution (25) and should consider only the primary superstructure generated by the dominant wave (23). According to (11), the corresponding distribution is

$$n_0(p, \mathbf{R}) = \frac{1}{3}c + \gamma_2(0)v_2(p, \mathbf{0}) = \begin{cases} \frac{1}{3}c - \gamma_2(0)\frac{1}{\sqrt{6}} & \text{at } p = 1 \\ \frac{1}{3}c - \gamma_2(0)\frac{1}{\sqrt{6}} & \text{at } p = 2 \\ \frac{1}{3}c + 2\gamma_2(0)\frac{1}{\sqrt{6}} & \text{at } p = 3, \end{cases} \quad (28)$$

since  $\nu = 3$ . The distribution (28) assumes two values, 0 and 1, in two cases only: (i) if  $\frac{1}{3}c = \frac{1}{3}$ ,  $\gamma_2(0) = \sqrt{6}/3$ , and (ii) if  $\frac{1}{3}c = \frac{2}{3}$ ,  $\gamma_2(0) = -(\sqrt{6}/3)$ . In the first instance

$$n_0(1, \mathbf{R}) = n_0(2, \mathbf{R}) = 0, n_0(3, \mathbf{R}) = 1 \quad (29a)$$

and we have the superstructure where all  $O_z$  interstices are occupied and all  $O_x$  and  $O_y$  interstices are vacant (Ti/O = 1). In the second case

$$n_0(1, \mathbf{R}) = n_0(2, \mathbf{R}) = 1, n_0(3, \mathbf{R}) = 0. \quad (29b)$$

Since the Ti/O ratio for both structures (29a) and (29b) is outside the range (19), we must remove a fraction of Ti atoms from the relevant stoichiometric superstructures. An additional energy decrease may be attained by secondary ordering of vacancies formed after removal of excess Ti atoms. The ordering should involve "permitted" Ti octahedral interstices, i.e., interstices  $\{p, \mathbf{r}\}$  for which  $n_0(p, \mathbf{R}) \equiv 1$ .

The two primary superstructures (29a,b) are thus "predecessors" of two families of secondary superstructures formed by ordering nonstoichiometric vacancies over the primary superstructures. In all superstructures derived from (29a) interstitial atoms occupy one  $O_z$  sublattice with  $p = 3$  only. This causes considerable tetragonal

extension along the  $[001]_{\text{bcc}}$  axis of the bcc host lattice. Because of the large radius of interstitial Ti atoms, the tetragonal distortion is very strong and produces an instability in the bcc host lattice which should, for that reason, undergo a transformation to an fcc lattice (one should bear in mind that the fcc lattice is merely a tetragonal bcc lattice having the tetragonal axial ratio  $c/a = \sqrt{2} \approx 1.41$ ). The bcc to fcc host lattice rearrangement of the structure described by Eq. (29a) produces the classical NaCl-type structure (Fig. 1a), one of the most frequently encountered structures, as in divalent oxides (MgO, CaO etc.). Therefore, all secondary superstructures arising from the nonstoichiometric primary superstructure (29a) should be secondary superstructures of the NaCl structure type. Bearing this in mind, we shall analyze ordering in the bcc host lattices in conformity with the primary superstructure (29b) only.

As in the primary structure (29b), only the  $O_x$  and  $O_y$  sublattices are permitted ( $p = 1$  and  $p = 2$ ); the  $V_{pq}(\mathbf{k})$  matrix has the simplified form

$$V_{pq}(\mathbf{k}) = \begin{pmatrix} V_{11}(\mathbf{k}) & V_{12}(\mathbf{k}) \\ V_{12}^*(\mathbf{k}) & V_{11}(\mathbf{k}) \end{pmatrix}, \quad (30)$$

where the matrix components are specified by (21).

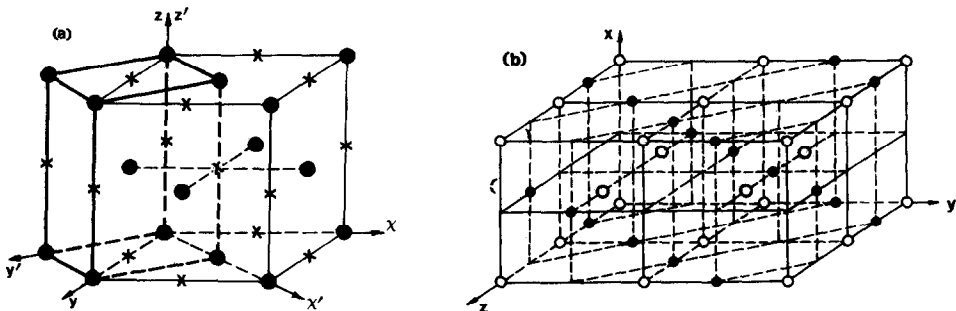


FIG. 1. (a) Primary superstructure (Eq. (29a)) resulting in the NaCl structure. The bcc unit cell is contoured by the solid line. Axes  $x, y, z$  are related to the fcc unit cell, axes  $x', y', z'$  to the fcc unit cell;  $\bullet$ —host atom;  $\times$ —interstitial atom. (b) NiAs-type secondary superstructure (Eq. (36)):  $\circ$ —host atom;  $\bullet$ —interstitial atom.



The lower branch of eigenvalues of the matrix (30) is

$$\begin{aligned} \lambda_{(-)}(\mathbf{k}) = & 8W_3 \cos \pi k_x \cdot \cos \pi k_y \cdot \cos \pi k_z \\ & + 2W_4(\cos 2\pi k_x + \cos 2\pi k_y + \cos 2\pi k_z) \\ & - |2W_1 \cos \pi k_z + 2W_2 \cos \pi k_x \cdot \cos \pi k_y|. \end{aligned} \quad (31)$$

As mentioned above, a stable secondary superstructure should be generated by the sole dominant wave to satisfy the maximal amplitude principle. It has been shown that the latter condition is only satisfied if the wave vectors of the dominant wave are  $\frac{1}{2}\mathbf{H}$ ,  $\frac{1}{3}\mathbf{H}$ , and  $\frac{1}{4}\mathbf{H}$  and also if  $\mathbf{k} = 0$ . Being reduced into the first Brillouin zone of the bcc host lattice all such vectors produce the series of stars:

$$\{k_x k_y k_z\} = \{000\}, \{100\}, \{\frac{1}{2}\frac{1}{2}0\}, \{\frac{1}{2}\frac{1}{2}\frac{1}{2}\}, \{\frac{1}{4}\frac{1}{4}0\}, \{\frac{1}{3}00\}, \{\frac{2}{3}00\}, \{\frac{1}{3}\frac{1}{3}0\}, \{\frac{2}{3}\frac{2}{3}\frac{2}{3}\}. \quad (32)$$

Substitution of the vectors  $\mathbf{k}$  from (32) in (31) yields the spectrum of eigenvalues. If the dependence

$$W_i \sim \frac{e^2}{r_i} \quad (2 \leq i \leq 4), \text{ i.e.,}$$

$$W_2 : W_3 : W_4 \sim \sqrt{2} : \frac{2}{\sqrt{3}} : 1$$

is assumed, we may readily see that the lowest eigenvalue of the resulting spectrum is

$$\lambda_{(-)}(\mathbf{k}_0) = -2W_1 - 2W_4. \quad (33)$$

It is realized at a value

$$\mathbf{k}_0 = (\frac{1}{2}\frac{1}{2}0) \quad (34a)$$

and corresponds to the eigenvector of the matrix (30),

$$\begin{aligned} v_{(-)}(p, \mathbf{k}_0) = & (v_{(-)}(1, \mathbf{k}_0), v_{(-)}(2, \mathbf{k}_0)) \\ = & \frac{1}{\sqrt{2}}(1, 1). \end{aligned} \quad (34b)$$

Using the maximal amplitude principle, we may construct the secondary distribution  $n_1(p, \mathbf{R})$  generated by the wave  $v_{(-)}(p,$

$\mathbf{k}_0)e^{i2\pi\mathbf{k}_0\mathbf{R}}$  where  $\mathbf{k}_0$  and  $v_{(-)}(p, \mathbf{k}_0)$  are given by (34). According to (11), this distribution is

$$n_1(p, \mathbf{R}) = \frac{c}{\nu} + \gamma_{(-)}(\mathbf{k}_0)v_{(-)}(p, \mathbf{k}_0) \cdot e^{i2\pi\mathbf{k}_0\mathbf{R}} \quad (35)$$

Substituting  $\gamma_{(-)}(\mathbf{k}_0) = 1/\sqrt{2}$ ,  $\nu = 2$ , and  $c/\nu = c/2 = \frac{1}{2}$  into (35) to set  $n_1(p, \mathbf{R})$  equal to either 1 or 0, we have

$$n_1(p, \mathbf{R}) = \begin{cases} n_1(1, \mathbf{R}) = \frac{1}{2} + \frac{1}{2}e^{im(x-y)} \\ n_1(2, \mathbf{R}) = \frac{1}{2} + \frac{1}{2}e^{im(x-y)} \end{cases} \quad (36)$$

where  $\mathbf{k}_0\mathbf{R} = x - y$ . Since  $c/\nu = c/2 = \frac{1}{2}$ , we have  $c = \text{Ti/O} = 1$ ; thus, the stoichiometric formula is TiO. Placing Ti atoms at the "permitted" sites  $(p, \mathbf{R})$  where  $n_1(p, \mathbf{R}) \equiv 1$  we obtain the superstructure shown in Fig. 1b.

It is noteworthy that with  $O_x$  and  $O_y$  sublattices having the same occupancies, a tetragonal distortion of the bcc lattice takes place: the lattice undergoes the same uniform extension along the [100] and [010] directions. At the same time, according to the crystal lattice statics theory, the ordered distribution of atoms within the sublattices produces a displacement of each second (110) plane of the oxygen bcc host lattice in the [110]<sub>bcc</sub> direction (5). If the tetragonal axial ratio is equal to  $\sqrt{2/3} = 0.816$ , and the displacement along the [110]<sub>bcc</sub> axis is equal to 1/12 of the [110]<sub>bcc</sub> translation, the bcc host lattice becomes the hcp one, and the structure (36) is transformed into the NiAs-type structure (6). The NiAs structure is widely encountered among the binary metal chalcogenides.

Distribution (36) corresponds to Ti/O = 1 which falls beyond the range of Ti/O stoichiometries (19). For that reason, some fraction of the Ti atoms should again be removed, and the resulting nonstoichiometric vacancies should be ordered over the "permitted" interstices of structure (36) in a manner that provides the maximal reduc-

tion of configurational energy. To express the elements of the  $\bar{V}_{pq}(\mathbf{k})$  matrix at the sites "permitted" in the secondary superstructure (36) through the interaction constants  $W_i$  the relation

$$\bar{V}_{pq}(\mathbf{k}) = \sum_{\mathbf{r}} W_{pq}(\mathbf{r}) e^{-i2\pi\mathbf{k}\cdot\mathbf{r}} = \frac{1}{2} V_{pq}(\mathbf{k}) + V_{pq}(\mathbf{k} - \mathbf{k}_0) \gamma_{(-)}(\mathbf{k}_0) v_{(-)}(q, \mathbf{k}_0) \quad (37)$$

has to be used (see section 2.7 of (4)). The coefficients  $\gamma_{(-)}(\mathbf{k}_0) = 1/\sqrt{2}$  and  $v_{(-)}(q, \mathbf{k}_0) = (1/\sqrt{2})(1, 1)$  in (37) are taken from (34b), (35), and (36) describing the positions of "permitted" sites in the secondary superstructure. Substitution of these parameters into (37) yields

$$V_{pq}(\mathbf{k}) = \begin{pmatrix} \bar{V}_{11}(\mathbf{k}) & \bar{V}_{12}(\mathbf{k}) \\ \bar{V}_{12}^*(\mathbf{k}) & \bar{V}_{11}(\mathbf{k}) \end{pmatrix} \quad (38)$$

where

$$\begin{aligned} \bar{V}_{11}(\mathbf{k}) &= 4W_3 \cos \pi(k_x + k_y) \cdot \cos \pi k_z \\ &\quad + 2W_4 \cos 2\pi k_z \\ \bar{V}_{12}(\mathbf{k}) &= 2W_2 \cos \pi(k_x - k_y) \\ &\quad \exp(i\pi(k_x - k_y)). \end{aligned} \quad (39)$$

The lower branch of eigenvalues of matrix (38) is

$$\begin{aligned} \bar{\lambda}_{(-)}(\mathbf{k}) &= \bar{V}_{11}(\mathbf{k}) - |\bar{V}_{12}(\mathbf{k})| \\ &= 4W_3 \cos \pi(k_x + k_y) \\ &\quad \cos \pi k_z + 2W_4 \cos 2\pi k_z \\ &\quad - 2W_2 |\cos \pi(k_x - k_y)|. \end{aligned} \quad (40a)$$

This eigenvalue corresponds to the eigenvector

$$v_{(-)}(p, \mathbf{k}) = \frac{1}{\sqrt{2}} (1, -\bar{V}_{12}(\mathbf{k})/|\bar{V}_{12}(\mathbf{k})|). \quad (40b)$$

The minimal value of  $\bar{\lambda}_{(-)}(\mathbf{k})$  is  $-4W_3 - 2W_2 + 2W_4$ , which is attained at  $\mathbf{k}_r = (\frac{1}{2}\frac{1}{2}0)$ . According to (40b) the corresponding eigenvector is given by

$$v_{(-)}(p, \mathbf{k}_r) = \frac{1}{\sqrt{2}} (1, \bar{1}). \quad (41)$$

The wave  $v_{(-)}(p, \mathbf{k}_r) e^{i2\pi\mathbf{k}\cdot\mathbf{r}}$  generates the stoichiometric distribution

$$\begin{aligned} n^{(2)}(p, \mathbf{r}) &= \frac{1}{2} + \frac{1}{\sqrt{2}} v_{(-)}(p, \mathbf{k}_r) e^{i2\pi\mathbf{k}\cdot\mathbf{r}} \\ &= \begin{cases} \frac{1}{2} + \frac{1}{2} e^{i2\pi\mathbf{k}\cdot\mathbf{r}} & \text{at } p = 1 \\ \frac{1}{2} - \frac{1}{2} e^{i2\pi\mathbf{k}\cdot\mathbf{r}} & \text{at } p = 2 \end{cases} \end{aligned} \quad (42)$$

where  $\mathbf{r}$  represents the "permitted" site coordinates of the primary superstructure (36) and where  $n_1(p, \mathbf{R}) = 1$ . To write out the distribution (42) in terms of arbitrary bcc site coordinates  $\mathbf{R}$ , i.e., to introduce the host lattice sites  $\mathbf{R}$  instead of the secondary structure sites  $\mathbf{r}$ , Eq. (42) should be transformed into

$$\begin{aligned} n_2(p, \mathbf{R}) &= n_1(p, \mathbf{R}) \cdot n^{(2)}(p, \mathbf{R}) \\ &= \begin{cases} n^{(2)}(p, \mathbf{r}) & \text{at } \mathbf{R} = \mathbf{r} \\ 0 & \text{at } \mathbf{R} \neq \mathbf{r}. \end{cases} \end{aligned} \quad (43)$$

Equation (43) holds because, by the definition (36), the function  $n(p, \mathbf{R}) = 1$  on the "permitted" secondary superstructure sites when  $\mathbf{R} = \mathbf{r}$ , and vanishes on all the other sites when  $\mathbf{R} \neq \mathbf{r}$ . The substitution of (42) and (36) into (43) yields

$$n_2(p, \mathbf{R}) = \begin{cases} \frac{1}{4} + \frac{1}{4} e^{i2\pi x} + \frac{1}{4} [e^{i\pi(x+y)} + e^{i\pi(x-y)}] & \text{at } p = 1 \\ \frac{1}{4} - \frac{1}{4} e^{i2\pi x} - \frac{1}{4} [e^{i\pi(x+y)} - e^{i\pi(x-y)}] & \text{at } p = 2. \end{cases} \quad (44)$$

On injecting Ti atoms into interstices  $O_x$  and  $O_y$  of the first and second sublattices of the oxygen bcc host lattice on which the

$n_2(p, \mathbf{R})$  function given by (44) is equal to unity, and leaving the other interstices vacant, we obtain the atomic structure shown

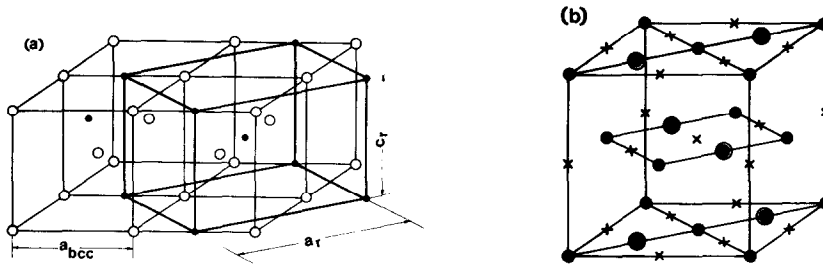


FIG. 2. Rutile tertiary superstructure; (a) Atomic lattice:  $\circ$ —oxygen atoms composing the bcc host lattice;  $\bullet$ —Ti atoms in octahedral interstices,  $O_x$  and  $O_y$ . The conventional unit cell of the rutile structure is shown by the solid line; (b) Reciprocal lattice pattern:  $\bullet$ —fundamental reciprocal lattice points related to the bcc host lattice;  $\circ$ —superlattice points of the secondary superstructure (36) generated by the wave vector  $\mathbf{k}_0 = (\frac{1}{2}\frac{1}{2}0)$  of the dominant concentration wave resulting in the NiAs structure;  $\times$ —superlattice points generated by the tertiary ordering resulting in the rutile structure.

in Fig. 2. This structure corresponds to the stoichiometric formula  $\text{TiO}_2$  and therefore corresponds to the Ti valency state +4. The structure so determined is thus the most stable structure for the stoichiometric composition  $\text{TiO}_2$ . The atomic distribution shown in Fig. 2 is actually encountered to within the small displacements caused by ordered distribution of interstitial atoms in the rutile structure (7). The rutile structure is the most widely spread oxide structure based on the bcc lattice, as, for example, in  $\text{TiO}_2$ ,  $\text{VO}_2$ ,  $\text{CrO}_2$ ,  $\text{MnO}_2$ ,  $\text{SiO}_2$ -stishevite,  $\text{TaO}_2$ ,  $\text{RuO}_2$ ,  $\text{AsO}_2$ ,  $\text{GeO}_2$ ,  $\text{SnO}_2$ ,  $\text{PbO}_2$ , and  $\text{IrO}_2$  and in slightly distorted structures  $\text{WO}_2$ ,  $\text{MoO}_2$ ,  $\text{TeO}_2$ , and  $\text{ReO}_2$ . The rutile structure is also observed in metal fluorides such as  $\text{MgF}_2$ ,  $\text{MnF}_2$ ,  $\text{FeF}_2$ ,  $\text{CoF}_2$ ,  $\text{NiF}_2$ ,  $\text{PdF}_2$ , and  $\text{ZnF}_2$ .

### 3. Alternatives to the Rutile Structure

Within the model of interatomic interactions we have assumed, the rutile structure has the lowest configurational energy and therefore, the largest stability at the composition  $\text{TiO}_2$ ; however, this model is rather approximate, and contributions from long-range potentials may change this conclusion and thereby render one of the alternative structures more stable. It seems clear that the energy of the alternative possible

structure calculated in the frame of the present model should be only slightly higher than that of the rutile structure. Otherwise it would be improbable that slight long-range interactions neglected by the model might outbalance the energy increase in structures far exceeding the rutile structure in energy. We thus arrive at a rather simple procedure for the determination of possible alternative structures without extending the simplest model of interatomic interactions considered above (the latter circumstance is of utmost importance because as a rule, the necessary information for refinement of that model is lacking: we must array alternative structures in order of increasing energy and choose those that follow rutile in the series thus obtained. This procedure will be exemplified below.

To determine structures alternative to rutile one, we must return to ordering of vacancies in the secondary structure described by the distribution (36).

As mentioned in Section 1, the condition of the maximal amplitude for the dominant wave is realized if the structure is produced by the only "polarization" of the dominant concentration wave. For this condition to be met we take advantage of the fact that the  $n(p, \mathbf{r})$  function of a fully ordered distribution remains unaffected by raising it to

any power. Hence, raising the dominant wave,  $v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}}$  that generates the tertiary superstructure to a power of  $s_1 + 1$  should produce the same wave

$$\begin{aligned} v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}}s_1+1 \\ = v_{(-)}^{s_1+1}(p, \mathbf{k}_1)e^{i2\pi\mathbf{H}'\mathbf{r}}e^{i2\pi\mathbf{k}_1\mathbf{r}} \\ = v_{(-)}^{s_1+1}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}} \\ = \beta v_{(-)}(p, \mathbf{k}_1)e^{i2\pi\mathbf{k}_1\mathbf{r}}. \end{aligned} \quad (45)$$

Bearing in mind (46), the above condition may be written as

$$v_{(-)}^{s_1+1}(p, \mathbf{k}_1) = \beta v_{(-)}(p, \mathbf{k}_1) \quad (46)$$

where  $\beta$  is a dimensionless quantity. Using (40b) we find that (46) is satisfied if

$$\left( -\frac{\tilde{V}_{12}^*(\mathbf{k}_1)}{|\tilde{V}_{12}(\mathbf{k}_1)|} \right)^{s_1} = 1. \quad (47)$$

Using (12) and substituting (39) into (47) we obtain

$$\begin{aligned} \left[ -\frac{\cos \pi(k_{1x} - k_{1y})}{|\cos \pi(k_{1x} - k_{1y})|} e^{-i\pi(k_{1x} - k_{1y})} \right]^{s_1} \\ = \left[ -\frac{\cos \pi(k_{1x} - k_{1y})}{|\cos \pi(k_{1x} - k_{1y})|} \right]^{s_1} \cdot e^{-i\pi(H_x - H_y)} = 1. \end{aligned} \quad (48)$$

With the model (18) the spectrum of eigenvalues,  $\bar{\lambda}_{(-)}(\mathbf{k})$ , given by (40a) reaches its minimal value at  $\mathbf{k}_r = (\frac{1}{2}\frac{1}{2}0)$ . Refinement of the model by introduction of additional interactions may shift the minimum of  $\bar{\lambda}_{(-)}(\mathbf{k})$  to the point  $\mathbf{k}_1$ . The shift  $\boldsymbol{\tau}$  in the minimum (supposing the minimum does shift) can be determined according to the assumption that it produces the lowest increase of the eigenvalue  $\bar{\lambda}_{(-)}(\mathbf{k})$ , which may be compensated by "switching on" the additional long-range interaction. Let us introduce the shift vector with its origin at  $(\frac{1}{2}\frac{1}{2}0)$ ,

$$\boldsymbol{\tau} = \mathbf{k}_1 - \mathbf{k}_r, \quad (49)$$

where  $\mathbf{k}_1$  is the sought dominant wave vector of the alternative structure. The substitution of (49) into (40a) yields

$$\begin{aligned} \lambda_{(-)}(\mathbf{k}_r + \boldsymbol{\tau}) = -4W_3 \cos \pi(\tau_x + \tau_y) \cos \pi\tau_z \\ + 2W_4 \cos 2\pi\tau_z - 2W_2 |\cos \pi(\tau_x - \tau_y)|, \end{aligned} \quad (50)$$

where  $1/a$  ( $\tau_x, \tau_y, \tau_z$ ) are the shift vector components. Using (49) in (12) we obtain

$$\boldsymbol{\tau} = \frac{\mathbf{H}}{s_1} - \mathbf{k}_r = \frac{\mathbf{H} - s_1\mathbf{k}_r}{s_1}. \quad (51)$$

If  $s_1$  is an even number, the numerator on the right-hand side of (51) represents a secondary structure reciprocal lattice vector  $\mathbf{H}'$  (because  $\mathbf{k}_r = (\frac{1}{2}\frac{1}{2}0)$ ). The vector  $(\frac{1}{2}\frac{1}{2}0)$ , like any other vector differing by a fundamental reciprocal lattice vector of the bcc crystal is, by definition, the secondary superstructure (36) reciprocal lattice vector. It thus follows from (51)

$$\boldsymbol{\tau} = \mathbf{H}'/s_1 \quad (52a)$$

where

$$\mathbf{H}' = \mathbf{H} - s_1\mathbf{k}_r. \quad (52b)$$

The substitution of (52a) into (50) yields

$$\begin{aligned} \lambda_{(-)}(\mathbf{k}_r + \boldsymbol{\tau}) = -4W_3 \cos \frac{\pi}{s_1} (H'_x + H'_y) \\ \cdot \cos \frac{\pi}{s_1} H'_z + 2W_4 \cos \frac{2\pi}{s_1} H'_z \\ - 2W_2 |\cos \frac{\pi}{s_1} (H'_x - H'_y)|. \end{aligned} \quad (53)$$

The atomic structure of the tertiary superstructure will again be determined using the maximal amplitude principle. As mentioned in Section 1, the maximal concentration wave amplitude corresponds to  $s_1 = 2, 3, \text{ or } 4$ . As we analyze even values of  $s_1$ , we shall consider the cases  $s_1 = 2$  and  $s_1 = 4$ .

To find the vector  $\mathbf{H}'$  and, therefore, the vector  $\mathbf{k}_1$  of the dominant wave, substitute  $\mathbf{k}_1 = \mathbf{k}_r + \boldsymbol{\tau} = \mathbf{k}_r + \mathbf{H}'/s_1$  into (48); this yields

$$\begin{aligned} \left[ -\frac{\cos \pi(H'_x - H'_y)/s_1}{|\cos \pi(H'_x - H'_y)/s_1|} \right]^{s_1} \\ e^{-i\pi(H'_x - H'_y)} = 1. \end{aligned} \quad (54)$$

Equation (54) provides the limiting condition for  $\mathbf{H}'$ . In the case  $s_1 = 2$  and  $s_1 = 4$  Eq. (54) holds when

$$H'_x - H'_y = 2l \quad (55)$$

where  $l$  is an integer. Note that by definition the shift vector  $\tau$  is defined within the first Brillouin zone of the secondary superstructure (36). The latter condition, definition (52b), and condition (55) with  $s_1 = 2$  and  $s_1 = 4$  impose severe limitations on the reciprocal lattice vectors  $\mathbf{H}'$ , only a few of which meet all these limitations:

$$\mathbf{H}' = (\frac{1}{2}\bar{1}), (\bar{1}10), (110), (\frac{3}{2}\bar{1}), (002), (112) \quad \text{at } s_1 = 4 \quad (56a)$$

and

$$\mathbf{H}' = (\frac{1}{2}\bar{1}) \text{ at } s_1 = 2. \quad (56b)$$

The analysis of the spectrum (53) at  $\mathbf{H}'$  listed in (56) under the above-assumed condition  $W_2 > W_3 > W_4$  shows that the mini-

mal eigenvalue is realized at the reciprocal lattice vector  $\mathbf{H}' = (\frac{1}{2}\bar{1})$  and  $s_1 = 4$ , where it is equal to  $\min \lambda_{(-)}(\mathbf{k}_r + \tau) = -2W_2 - 2W_3$ . According to (49) and (52a) the corresponding vector  $\mathbf{k}_1$  is

$$\mathbf{k}_1 = \mathbf{k}_r + \tau = \mathbf{k}_r + \frac{1}{4}H'_{(\frac{1}{2}\bar{1})} = (\frac{1}{2}\bar{1}0) + \frac{1}{4}(\frac{1}{2}\bar{1}) = (\frac{5}{8}\frac{5}{8}\bar{1}). \quad (57)$$

Reduction of  $\mathbf{k}_1$  into the first Brillouin zone of the secondary superstructure by subtracting from (57) the reciprocal lattice vector  $(\frac{1}{2}\bar{1})$  yields

$$\mathbf{k}_1 = (\frac{1}{8}\frac{1}{8}\frac{8}{8}) = \frac{1}{8}(116) = \frac{1}{8}\mathbf{H}_{(116)}. \quad (58)$$

It follows from (40b) and (58) that

$$v_{(-)}(p, \mathbf{k}_1) = \frac{1}{\sqrt{2}}(1, \bar{1}). \quad (59)$$

According to (17) and (59) the sought stoichiometric distribution for  $s_1 = 4$  has the form

$$\begin{aligned} n^{(3)}(p, \mathbf{r}) &= \frac{1}{2} + \frac{1}{2\sqrt{2}} [e^{i\pi/4} v_{(-)}(p, \mathbf{k}_1) e^{i2\pi\mathbf{k}_1\mathbf{r}} + e^{-i\pi/4} v_{(-)}^*(p, \mathbf{k}_1) e^{-i2\pi\mathbf{k}_1\mathbf{r}}] \\ &= \begin{cases} \frac{1}{2} + \frac{1}{2}(\cos 2\pi\mathbf{k}_1\mathbf{r} - \sin 2\pi\mathbf{k}_1\mathbf{r}) & \text{at } p = 1 \\ \frac{1}{2} - \frac{1}{2}(\cos 2\pi\mathbf{k}_1\mathbf{r} + \sin 2\pi\mathbf{k}_1\mathbf{r}) & \text{at } p = 2 \end{cases} \quad (60) \end{aligned}$$

where  $\mathbf{r}$  are the site vectors of bcc lattice sites "permitted" in the secondary superstructure (36).

To write distribution (60) as a function of arbitrary bcc sites  $\mathbf{R}$  Eq. (60) should be represented in a form similar to (43):

resented in a form similar to (43):

$$n_3(p, \mathbf{R}) = n_1(p, \mathbf{R})n^{(3)}(p, \mathbf{R}). \quad (61)$$

The substitution of (60) and (36) into (61) yields

$$n_3(p, \mathbf{R}) = \begin{cases} \frac{1}{4} + \frac{1}{4} e^{i\pi(x-y)} + \frac{1}{4} \left( \cos \frac{\pi}{4} (x+y+6z) - \sin \frac{\pi}{4} (x+y+6z) \right) \\ \quad + \frac{1}{4} \left( \cos \frac{\pi}{4} (5x-3y+6z) - \sin \frac{\pi}{4} (5x-3y+6z) \right) & \text{at } p = 1 \\ \frac{1}{4} + \frac{1}{4} e^{i\pi(x-y)} - \frac{1}{4} \left( \cos \frac{\pi}{4} (x+y+6z) - \sin \frac{\pi}{4} (x+y+6z) \right) \\ \quad - \frac{1}{4} \left( \cos \frac{\pi}{4} (5x-3y+6z) - \sin \frac{\pi}{4} (5x-3y+6z) \right) & \text{at } p = 2 \end{cases} \quad (62)$$

where  $(x, y, z)$  are again the coordinates of bcc lattice sites. Injecting interstitial atoms into the interstices on which  $n_3(p, \mathbf{R}) = 1$  we obtain the atomic configuration shown in Fig. 3. This configuration describes the new polymorph of the  $\text{TiO}_2$  structure accurately to within small displacements of oxygen atoms. This is the so-called  $\alpha\text{-PbO}_2$  structure frequently occurring in oxides of the composition  $\text{MO}_2$  (8).

The theory described above thus predicts the  $\alpha\text{-PbO}_2$  structure as an alternative structure to rutile. The  $\alpha\text{-PbO}_2$  structures are, as a rule, stable under high pressures, whereas the rutile structure is stable under normal pressure conditions. For many synthetic mixed oxides and naturally occurring minerals (in particular, for columbites and tantalites) both polymorphs are known; their transformations to each other are associated with small variations of external thermodynamic parameters.

We now turn to the case of odd  $s_1$  values,

written as  $s_1 = 2n - 1$ , where  $n = 2, 3, 4, \dots$ . Equation (51) may then be cast in the form

$$\tau = \frac{2\mathbf{H} - 2s_1\mathbf{k}_r}{2s_1} = \frac{2\mathbf{H} - 2(2n - 1)\mathbf{k}_r}{2(2n - 1)} \tag{63}$$

Introduce the fundamental reciprocal lattice points  $\mathbf{H}_r$  meeting the condition

$$\frac{1}{2}\mathbf{H}_r = \mathbf{k}_r + \mathbf{H} \tag{64}$$

With accuracy to an arbitrary secondary structure reciprocal lattice vector,  $\mathbf{H}$ ,  $\frac{1}{2}\mathbf{H}_r$  coincides with  $\mathbf{k}_r$ . Equation (64) may also be rewritten in the form

$$\mathbf{H}_r = 2\mathbf{k}_r + 2\mathbf{H} \tag{65}$$

Using (65) we may substitute  $2\mathbf{k}_r$  in (63). The result is

$$\tau = \frac{\mathbf{H}_r - 2(n\mathbf{H}_r + 2\mathbf{H}')}{2(2n - 1)} = \frac{\mathbf{H}_r - 2\mathbf{H}'}{2(2n - 1)} \tag{66}$$

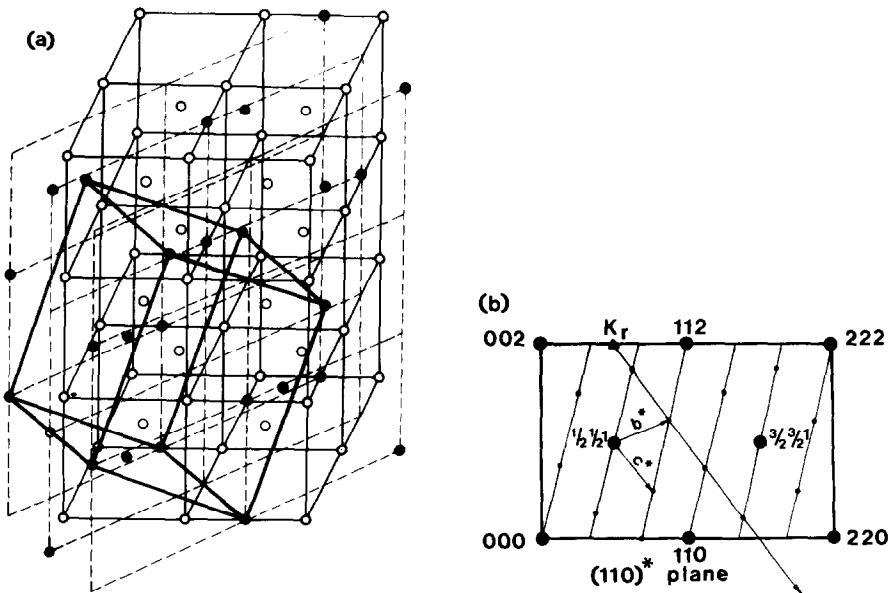


FIG. 3. The  $\alpha\text{-PbO}_2$  tertiary superstructure; (a) Atomic lattice:  $\circ$ —oxygen atoms composing the bcc host lattice;  $\bullet$ —metal atoms in  $O_x$  and  $O_y$  octahedral interstices. The superstructure unit cell is contoured with the solid line. (b) Reciprocal lattice (the  $(110)^*$  plane section); size of the reciprocal lattice points is proportional to their intensities in the diffraction pattern.

TABLE I  
LIST OF RECIPROCAL LATTICE VECTORS  $\mathbf{H}_r$  IN THE bcc HOST LATTICE ARRANGED IN THE ORDER OF  $|\mathbf{H}_r|$  MAGNITUDE

No.	$(H_{rx}H_{ry}H_{rz})$	No.	$(H_{rx}H_{ry}H_{rz})$	No.	$(H_{rx}H_{ry}H_{rz})$	No.	$(H_{rx}H_{ry}H_{rz})$
1	110	8	$\bar{3}30$	15	$5\bar{1}2$	22	$\bar{1}\bar{1}6$
2	200	9	420	16	$5\bar{3}0$	23	532
3	$\bar{1}\bar{1}2$	10	402	17	334	24	514
4	$3\bar{1}0$	11	204	18	600	25	226
5	222	12	$3\bar{3}2$	19	006	26	622
6	312	13	510	20	424	27	316
7	114	14	$3\bar{1}4$	21	442	28	$7\bar{1}0$

where  $\mathbf{H}' = n\mathbf{H}_r + 2\mathbf{H}$  is also the secondary superstructure reciprocal lattice vector. It follows from (65) that the vector  $\mathbf{H}_r$  is determined to within twice an arbitrary reciprocal lattice vector. Without the loss of generality, we may therefore use the substitution  $\mathbf{H}_r - 2\mathbf{H}' \rightarrow \mathbf{H}_r$  in the numerator of (66). This substitution gives

$$\tau = \frac{\mathbf{H}_r}{2(2n - 1)} \quad (67)$$

where  $\mathbf{H}_r$  is one of the vectors determined by (65) and listed in Table I.

In certain cases the vector  $\mathbf{k}_1$  is located outside the first Brillouin zone. It is removed by the distance  $[1/2(2n - 1)] \cdot \mathbf{H}_r$  from the nearest "rutile" point  $1/2\mathbf{H}_r$  which is also located outside the Brillouin zone. The latter follows from Eq. (64) which demonstrates that  $(1/2)\mathbf{H}_r$  differs by the reciprocal lattice vector  $\mathbf{H}$  from  $\mathbf{k}_r = (\frac{1}{2}\bar{1}0)$ .

Taking these facts into account we have

$$\mathbf{k}_1 = \frac{1}{2} \mathbf{H}_r + \tau = \frac{1}{2} \mathbf{H}_r + \frac{1}{2(2n-1)} \mathbf{H}_r \quad (68a)$$

or

$$\mathbf{k}_1 = \frac{n}{2n-1} \mathbf{H}_r. \quad (68b)$$

According to the definition (65),  $H_{rx} - H_{ry}$  is an even number. Hence, the substitution

of (68a) into (48) yields

$$\frac{\cos[\pi/2(2n-1)](H_{rx} - H_{ry})}{|\cos[\pi/2(2n-1)](H_{rx} - H_{ry})|} \cdot e^{-(i\pi/2)(H_{rx}-H_{ry})} = 1. \quad (69)$$

Interest centers on the superstructures with  $s_1 = 3$ , the only superstructures with odd  $s_1$  generated by a single dominant wave and, therefore, with the maximal amplitude for that wave. As  $s_1 = 2n - 1$ , we have  $n = 2$  for  $s_1 = 3$ . Therefore, according to (67),

$$\tau = \frac{1}{8} \mathbf{H}_r. \quad (70)$$

By definition, requirement (70) places  $\tau$  in the first Brillouin zone of the secondary superstructure (36); this, combined with the restriction (69) at  $n = 2$ , enables us to select the suitable  $\mathbf{H}_r$  from Table I. They are (200), ( $\bar{1}\bar{1}2$ ), and (312) only. Since  $\mathbf{k}_1 = (n/2n-1) \cdot \mathbf{H}_r$ , we have at  $n = 2$  the series

$$\mathbf{k}_1 = \frac{2}{3}(200), \frac{2}{3}(\bar{1}\bar{1}2), \frac{2}{3}(312). \quad (71)$$

Substitution of the vectors  $\mathbf{k}_1$  from (71) to (40a) shows that the minimal eigenvalue,  $\bar{\lambda}_{(-)}(\mathbf{k}_1) = -2W_3 - W_2 - W_4$  is realized at  $\mathbf{k}_1 = (\frac{2}{3}\bar{1}\bar{1}2)$ . We then have, according to (40b)

$$v_{(-)}(\rho, \mathbf{k}_1) = \frac{1}{\sqrt{2}} (1, e^{-i4\pi/3}).$$

The total distribution function has the form

$$\begin{aligned}
 n^{(3)}(p, \mathbf{r}) &= \frac{2}{3} - \frac{\sqrt{2}}{3} v_{(-)}(p, \mathbf{k}_1) \cdot \exp(i2\pi\mathbf{k}_1\mathbf{r}) - \frac{\sqrt{2}}{3} v_{(-)}^*(p, \mathbf{k}_1) \exp(-i2\pi\mathbf{k}_1\mathbf{r}) \\
 &= \begin{cases} \frac{2}{3} - \frac{2}{3} \cos 2\pi \frac{2}{3} (\xi_1 - \xi_2 + 2\xi_3) & \text{if } p = 1 \\ \frac{2}{3} - \frac{2}{3} \cos 2\pi \frac{2}{3} (\xi_1 - \xi_2 + 2\xi_3 - 1) & \text{if } p = 2 \end{cases} \quad (72)
 \end{aligned}$$

where  $\mathbf{r} = a \cdot (\xi_1, \xi_2, \xi_3)$  are the coordinates of the bcc lattice sites "permitted" in the primary structure.

Using the same procedure as in going

from (42) to (44), distribution (72) may be rewritten in terms of the sites of the initial bcc lattice  $\{\mathbf{R}\}$ :

$$\begin{aligned}
 n_s(p, \mathbf{R}) &= n_1(p, \mathbf{R})n^{(3)}(p, \mathbf{R}) \\
 &= \begin{cases} \frac{1}{3} + \frac{1}{3} e^{i\pi(x-y)} - \frac{1}{3} \cos \frac{4\pi}{3} (x-y+2z) - \frac{1}{3} \cos \frac{\pi}{3} (x-y-4z) & \text{at } p = 1 \\ \frac{1}{3} + \frac{1}{3} e^{i\pi(x-y)} - \frac{1}{3} \cos \frac{4\pi}{3} (x-y+2z-1) - \frac{1}{3} \cos \frac{\pi}{3} (x-y-4z+2) & \text{at } p = 2. \end{cases} \quad (73)
 \end{aligned}$$

The concentration of occupied positions in  $O_x$  and  $O_z$  sublattices is equal to 1/3, as follows from (73). The oxide phase formula may therefore be written  $M_2O_3$  or  $[M_{2/3} \square_{1/3}]_{1/2} [M_{2/3} \square_{1/3}]_{1/2} O$ . For the Ti-O system, we have  $Ti/O = \frac{2}{3}$ , i.e., the ratio corresponding to the trivalent titanium state. Injecting Ti atoms in  $O_x$  and  $O_y$  sites where the  $n_3(p, \mathbf{R})$  function (73) is equal to unity we obtain the structure shown in Fig. 4. Within small displacements of oxygen atoms this configuration coincides with the corundum structure,  $\alpha\text{-Al}_2\text{O}_3$ , typical for trivalent transition metal oxides formed by elements of the first transition metal series (7). For a more accurate description of the real corundum structure, the oxygen atoms must be displaced from the bcc host lattice sites in alternating  $(1\bar{1}0)_{\text{bcc}}$  planes along the  $[110]_{\text{bcc}}$  direction by  $1/12 [110]$ . In addition, the bcc oxygen host lattice undergoes uniform tetragonal distortion with  $c/a < 1$ . Both distortions may easily be obtained by

static displacements in the bcc host lattice caused by an ordered distribution (73) of interstitial atoms. These displacements result in instability of the bcc host lattice causing its transformation to an hcp lattice. Irrespective of the displacements of oxygen atoms, the general atomic arrangement remains the same and may be described by (73).

Summing up the foregoing, one should note that the concentration wave approach and, particularly, the maximal amplitude principle, combined with the simplest short-range interaction model enables us to predict the atomic structure of oxides for which metal atoms have integer valencies. As applied to the Ti-O system, the theory provides the correct structures for all the observed oxides with fixed stoichiometry: rutile, its  $\alpha\text{-PbO}_2$  polymorph, and corundum. What is more, the theoretical derivation does not predict any "incorrect" structure, i.e., a structure which would not be



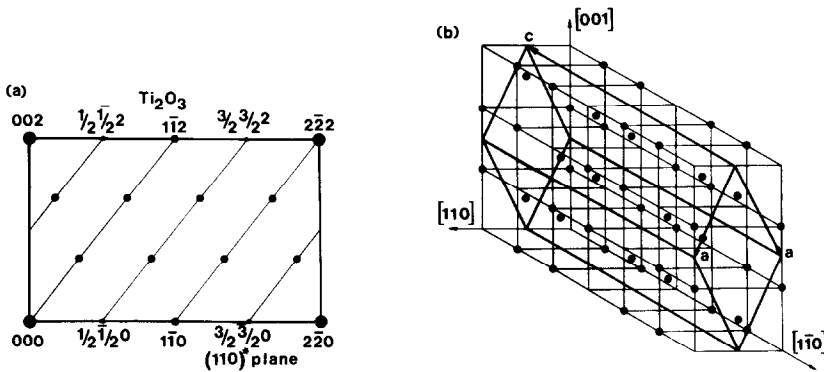


FIG. 4. The  $\text{Ti}_2\text{O}_3$  tertiary superstructure (corundum); (a) Reciprocal lattice pattern in the  $(110)^*$  plane section. Large size circles are fundamental reciprocal lattice points of the bcc host crystal. Size of the reciprocal lattice points is proportional to their intensities in the diffraction pattern. (b) Atomic lattice; thin lines show the bcc host lattice frame. Solid line shows the conventional unit cell of the corundum structure: ●—Ti.

observed experimentally. It has been shown that the predicted phases are the most stable bcc-based interstitial superstructures whose stoichiometry fits the simple valency rule with metal atoms having integer valencies +3 and +4.

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