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Prediction of Diffuse Intensity Surfaces in Short-Range-Ordered Ternary Derivative Structures Based on ZnS, NaCl, CsCl and Other Structures

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The atom arrangement in ternary and quaternary ionic long-range-ordered derivative structures of ZnS, NaCl, CsCl and others is governed by a principle which is known as Pauling's electrostatic valence rule. This valence rule is actually part of a more general ordering principle for derivative structures, which is not restricted to ionic compounds and requires that the smallest building blocks of the structure (centred tetrahedra, octahedra or cubes) have as far as possible a composition identical with the overall composition of the compound. Depending on the type of polyhedron, this rule can be fulfilled only for a limited number of overall compositions. In this case it is possible to produce an analytical formulation of the general ordering principle giving relations amongst the Warren short-range-order parameters. Use of these relations in a structure-factor formula of the binary base structure permits the derivation of the general location (lines, planes or a general surface) of superstructure reflexions or diffuse intensity in reciprocal space for the cases of long-range order or short-range order respectively. With this method it is possible not only to explain the experimentally determined diffuse intensity shapes due to short-range order in NaCl-related structures, but also to predict the diffuse intensity shape for ZnS and CsCl-related structures and others for which no experimental data are yet available.

Introduction

In a recent electron diffraction study of $VC_{0.75}$ with NaCl defect structure, curved diffuse streaks were found by Billingham, Bell & Lewis (1972*b*), which were explained by Sauvage & Parthé (1972) as being caused by a short-range order of carbon atoms and vacancies occupying the corners of the vanadium-centred octahedra. However no explanation was given for the form of the diffuse intensity surface which, according to our experimental results, obeys approximately the equation

$$\cos \pi h_1 + \cos \pi h_2 + \cos \pi h_3 = 0 \ ,$$

where h_1, h_2 and h_3 are continuous variables in reciprocal space. Dr de Bergevin drew our attention to the work of Brunel, de Bergevin & Gondrand (1972) on possible short-range order in ionic $LiFeO_2$ with a NaCl-derivative structure which predicted a diffuse-intensity surface obeying the above equation.

We have generalized the theory of de Bergevin to include not only the defect carbides with NaCl-related structures, but also to predict possible short-range-order diffuse-intensity surfaces in non-ionic crystals built up from other polyhedra.

A general ordering principle for derivative structures

As $LiFeO_2$ is an ionic compound Brunel *et al.* (1972) applied Pauling's electrostatic valence rule (Pauling, 1960). This rule has been shown many times to be successful in explaining the atomic arrangement in ternary and quaternary ionic ordered derivative structures of ZnS, NaCl and other structure types. Brunel *et al.* postulated that the charge of the oxygen ion must also be compensated in the short-range-ordered state, requiring an occupation of the surrounding octahedron by three Fe^{3+} and three Li^+ ions.

Pauling's electrostatic valence rule for ionic compounds may be generalized to give an ordering principle for derivative structures, which requires that the smallest building blocks of the structure have as far as possible a composition identical with the overall composition of the compound. As will be shown in the next section, this statement gives rise to relations amongst short-range-order parameters. As no assumption has been made about the nature of the interatomic forces, this formulation also includes for example defect structures like V_6C_5 where each V atom has five carbon atoms and one vacancy on the corners of a surrounding octahedron. Thus it is not necessary to touch upon the difficult problem of specifying what the actual charge, if any, of V and C in the compound should be.

Equations for short-range-order parameters for derivative structures

Let us consider a compound $(A_{x_A}B_{x_B})Y_y$ which occurs with a derivative structure of XY_y. Atoms A and B are distributed on the corners of polyhedra centred by Y atoms (octahedra, trigonal prisms, tetrahedra or cubes in NaCl, NiAs, ZnS or CsCl-related structures respectively). Short-range interatomic forces are assumed to be strong enough for the ordering principle to be fulfilled. To characterize the state of order several parameters will be used in the calculations which follow:

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α_m: Short-range-order parameter related to the overall probability p_m^{AB} for an A atom to have a B atom as mth-nearest neighbour through the formula:

$$\alpha_m = 1 - \frac{p_m^{AB}}{x_B} \tag{1}$$

N: total number of polyhedra in the crystal

N_m^{AB}: total number of AB pairs, mth-nearest neighbours in the crystal

S: number of corners of a polyhedron

p: number of Y-centred polyhedra which share one corner

e_m: number of Y-centred polyhedra which share one pair of mth-nearest neighbours.
In ZnS-related structures the tetrahedra share corners only, in NaCl and NiAs-related structures the octahedra and trigonal prisms respectively share edges, in CsCl-related structures the cubes share faces and in CaF_2-related structures the Y-centered cubes share edges only. The corresponding values for S, p and e_m are therefore:
ZnS-related structures: $S=4$, $p=4$, $e_1=1$
NaCl-related structures: $S=6$, $p=6$, $e_1=2$, $e_2=1$
NiAs-related structures: $S=6$, $p=6$, $e_1=3$, $e_2=2$, $e_3=1$
CsCl-related structures: $S=8$, $p=8$, $e_1=4$, $e_2=2$, $e_3=1$
CaF_2-related structures: $S=8$, $p=4$, $e_1=2$, $e_2=1$, $e_3=1$.

k_m: number of mth-nearest neighbours of one atom in an isolated polyhedron. The values of k_m are for a
tetrahedron: $k_0=1$, $k_1=3$
octahedron: $k_0=1$, $k_1=4$, $k_2=1$
trigonal prism: $k_0=1$, $k_1=1$, $k_2=2$, $k_3=2$
cube: $k_0=1$, $k_1=3$, $k_2=3$, $k_3=1$.

In the trigonal prisms we define, regardless of the relative prism dimensions, first neighbours as those on the prism axis, second those in the prism base and third those on the prism face diagonal.

We note that

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m = S\,. \tag{2}$$

p_m^{AB} can be expressed in terms of the above quantities:

$$p_m^{AB} = \frac{N_m^{AB}}{(x_A NS/p)\,(k_m p/e_m)} \tag{3}$$

where $x_A NS/p$ is the total number of A atoms in the crystal and $k_m p/e_m$ the maximum number of mth-nearest neighbours per atom within the Y-centred polyhedral framework.

(1) and (3) lead to

$$k_m(1-\alpha_m) = \frac{e_m N_m^{AB}}{x_A x_B NS}\,. \tag{4}$$

Summing over m and using (2) gives:

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m\alpha_m = S - \frac{1}{x_A x_B NS}\cdot \sum_{m=0}^{1\ \text{polyhedron}} e_m \,.\, N_m^{AB}\,. \tag{5}$$

From now on, three different cases may be distinguished:

(1) The structure is built from *one kind of polyhedron only* whose corners are occupied by $x_A S$ and $x_B S$, A and B atoms respectively, in agreement with the bulk ratio of A to B atoms. Since $x_A S$ and $x_B S$ must be whole numbers ($x_A=0$, $1/S$, $2/S, \ldots 1$), depending on the type of polyhedra involved, only a limited number of overall compositions $(A_{x_A}B_{x_B})Y_y$ is possible. Restricting ourselves to the cases where $x_B \ge x_A$ the possible ternary compositions (multiplied to give integral composition parameters) are:

AB_3Y_4, ABY_2 for ZnS-derivative structures
AB_5Y_6, AB_2Y_3, ABY_2 for NaCl and NiAs-derivative structures
AB_7Y_8, AB_3Y_4, $A_3B_5Y_8$, ABY_2 for CsCl-derivative structures
and
AB_7Y_4, AB_3Y_2, $A_3B_5Y_4$, ABY for CaF_2-derivative structures.

The basic polyhedron is characterized by the values n_m^{AB} which are the numbers of A–B bonds between mth-nearest neighbours within this polyhedron. The total number of A–B pairs within one polyhedron is given by

$$\sum_{m=0}^{1\ \text{polyhedron}} n_m^{AB} = x_A S \,.\, x_B S = x_A \,.\, x_B S^2\,. \tag{6}$$

As an example Fig. 1 shows various polyhedra where $x_A = x_B = \frac{1}{2}$, together with the corresponding n_m^{AB} values.

As only one type of polyhedron is considered, the total number of AB pairs mth-nearest neighbours is given by:

$$N_m^{AB} = \frac{n_m^{AB}}{e_m} N\,. \tag{7}$$

Consequently

$$\sum_{m=0}^{1\ \text{polyhedron}} e_m N_m^{AB} = N x_A x_B S^2 \tag{8}$$

and thus (5) takes on a very simple form:

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m \alpha_m = 0 \tag{9}$$

which has the special solutions for a derivative structure with Y-centred

tetrahedra: $\alpha_0 + 3\alpha_1 = 0$ (9.1)

octahedra: $\alpha_0 + 4\alpha_1 + \alpha_2 = 0$ (9.2)

trigonal prisms: $\alpha_0 + \alpha_1 + 2\alpha_2 + 2\alpha_3 = 0$ (9.3)

cubes: $\alpha_0 + 3\alpha_1 + 3\alpha_2 + \alpha_3 = 0$. (9.4)

Brunel, de Bergevin & Gondrand (1972) found the equation $4\alpha_1 + \alpha_2 = -1$ for the particular case of a NaCl-derivative structure with $x_A = x_B = \frac{1}{2}$. This is identical to (9.2), the equation for derivative structures with Y-centred octahedra.

(2) In polyhedra with more than four corners, a unique value of the occupation ratio may correspond to several distributions of A and B among the S corners as shown in Fig. 1. When the structure consists of a *mixture* of polyhedra with the *same A/B ratio* but *different* individual n_{mi}^{AB} values, (7) is no longer valid but must be replaced by a summation over i:

$$N_m^{AB}=\frac{1}{e_m}\sum_{i=1}^{n} N_i n_{mi}^{AB} \qquad (10)$$

where N_i denotes the tòtal number of type-i polyhedra.

Considering that

$$\sum_{i=1}^{n} N_i = N \qquad (11)$$

and that (6) does not depend on i since x_A, x_B and S are the same in all polyhedra, we obtain

$$\sum_{m=0}^{1\text{ polyhedron}} e_m N_m^{AB}=\sum_{i=1}^{n} N_i \sum_{m=0}^{1\text{ polyhedron}} n_{mi}^{AB}=N x_A x_B S^2. \qquad (12)$$

Relation (12) is identical to (8) and thus (9) is also valid in this case.

There are two interesting features of equation (9). One is that it depends neither on the value of S nor on the particular values of x_A and x_B as long as the restrictive condition is fulfilled that $x_A S$ and $x_B S$ are whole numbers. This condition implies that all Y-centred polyhedra have the same A/B occupation ratio (regardless of whether the individual n_m^{AB} are the same or not). Secondly, the particular type of linkage between the polyhedra does not enter in the formula although it affects the individual α_m values. Only the polyhedron itself determines the particular form of (9) which is thus a general mathematical formulation of our ordering principle for derivative structures. The special solutions apply to all derivative structures having Y-centred tetrahedra, octahedra, trigonal prisms and cubes. When α refers only to the occupation of the Y-centred polyhedron corners, which is usually but not always the case, the presence of other atoms outside the polyhedral framework does not affect the validity of (9). Examples for these more complicated derivative structures with composition $A_{x_A}B_{x_B}Y_yZ_z$ might be found with spinels or garnets. If there are different types of polyhedra in the structure, then (9) should be valid for each polyhedron framework separately. The above equations for short-range-order parameters are valid for short-range as well as long-range-ordered

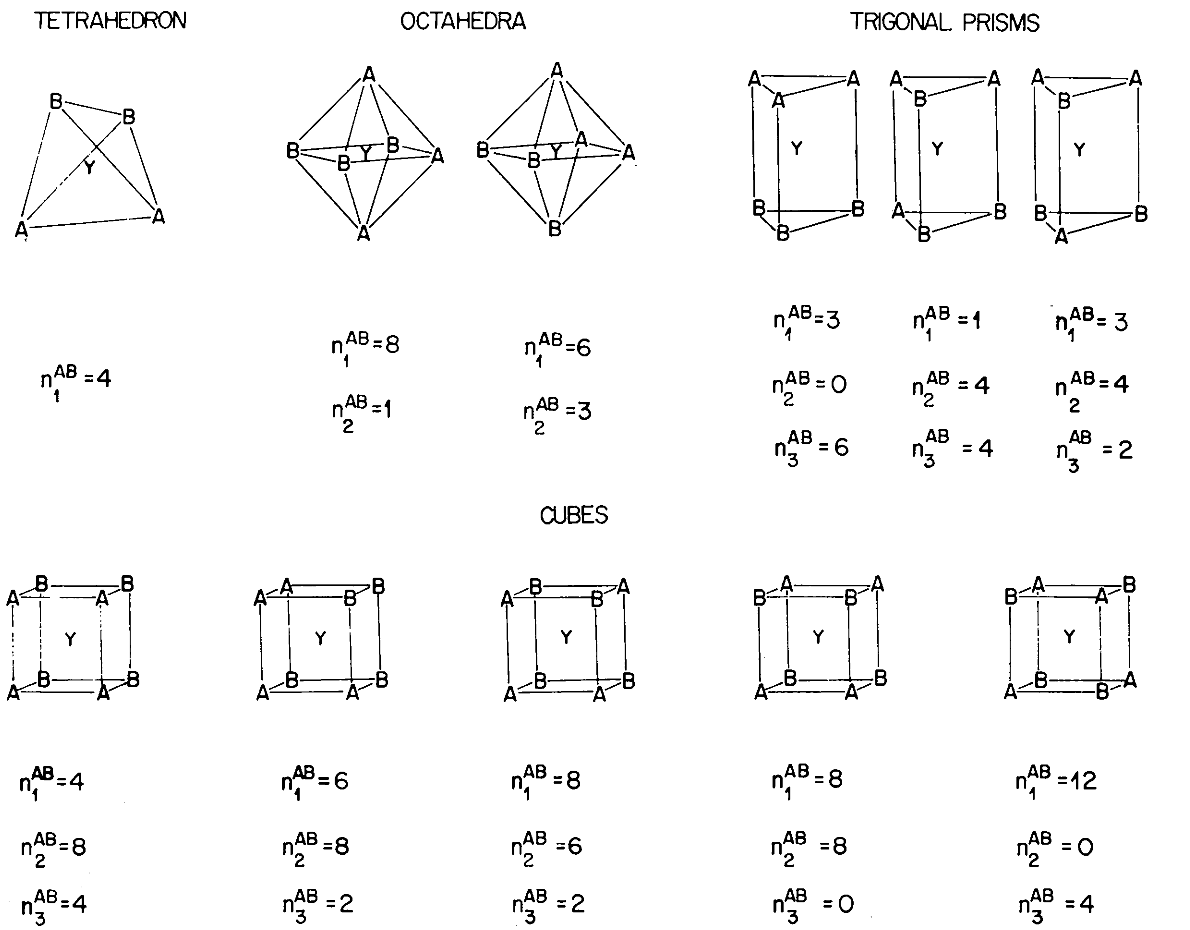


Fig. 1. Polyhedron corner occupation when $x_A=x_B=\frac{1}{2}$.

derivative structures. In the first case, the particular substituted polyhedra are not arranged periodically, while in the second case a periodical distribution of polyhedra leads to a superstructure unit cell.

(3) If the bulk composition is such that it is not possible to build the whole crystal with N identical Y-centred polyhedra, the sample can still be described as an *association* of N polyhedra showing *n different occupation ratios* ($N_1 \ldots N_i \ldots N_n$ polyhedra with $x_{A_1}S \ldots x_{A_i}S \ldots x_{A_n}S$ A atoms and $x_{B_1}S \ldots x_{B_i}S \ldots x_{B_n}S$ B atoms on their S corners).

To ensure that the overall concentration is preserved, the following relations must be fulfilled:

$$\left.\begin{aligned} &\sum_{i=1}^{n} N_i = N \\ &\frac{\sum_{i=1}^{n} N_i x_{A_i}}{\sum_{i=1}^{n} N_i} = \langle x_{A_i} \rangle = x_A \\ &\frac{\sum_{i=1}^{n} N_i x_{B_i}}{\sum_{i=1}^{n} N_i} = \langle x_{B_i} \rangle = x_B \end{aligned}\right\} . \tag{13}$$

N_m^{AB} is still given by (10), but (6) is now different for each type of polyhedron:

$$\sum_{m=0}^{1\ \text{polyhedron}} n_{mi}^{AB} = x_{A_i} x_{B_i} S^2 . \tag{14}$$

As a consequence the summation over i cannot be readily performed and (12) becomes:

$$\sum_{m=0}^{1\ \text{polyhedron}} e_m N_m^{AB} = S^2 \sum_{i=1}^{n} N_i x_{A_i} x_{B_i} . \tag{15}$$

Combining (5) and (15), one obtains:

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m \alpha_m = S \left(1 - \frac{\sum_{i=1}^{n} N_i x_{A_i} x_{B_i}}{x_A x_B N} \right) . \tag{16}$$

Making use of (13), (16) can be written:

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m \alpha_m = S \left(1 - \frac{\langle x_{A_i} x_{B_i} \rangle}{\langle x_{A_i} \rangle \langle x_{B_i} \rangle} \right) \tag{17}$$

where, since x_{A_i} and x_{B_i} are correlated variables ($x_{A_i} + x_{B_i} = 1$), the mean value of their product is different from the product of their mean values.

For a numerical evaluation it is more convenient to express (17) in a different way:

$$\sum_{m=0}^{1\ \text{polyhedron}} k_m \alpha_m = S \frac{\sum_{i=1}^{n} \sum_{j=1}^{n} \frac{N_i}{N} \frac{N_j}{N} (x_{A_i} - x_{A_j})^2}{2 \cdot x_A \cdot x_B} . \tag{18}$$

The numerator of the right-hand side is always greater than zero unless all the x_{A_i} are equal, which corresponds to the case dealt with previously.

In the cases of interest here, two differently substituted polyhedra will usually be sufficient to build the crystal. Thus

$$x_A = \frac{N_1}{N} x_{A_1} + \frac{N_2}{N} x_{A_2} \quad \text{and} \quad x_B = \frac{N_1}{N} x_{B_1} + \frac{N_2}{N} x_{B_2} .$$

Further, the two polyhedra involved show occupation ratios as close as possible to the bulk ratio of A to B atoms. In this case one finds that

$$|x_{A_1} - x_{A_2}| = 1/S \tag{19}$$

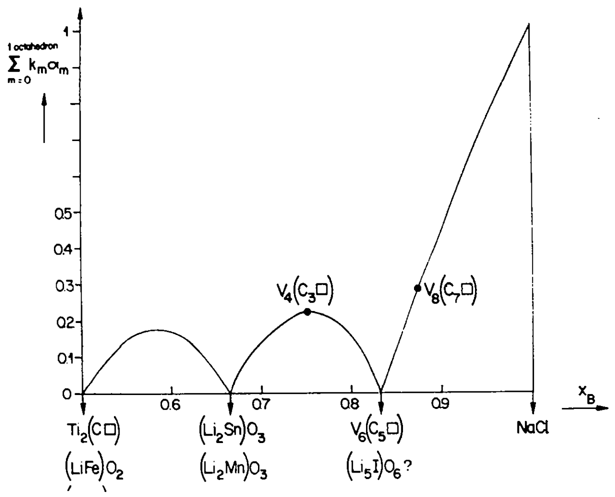


Fig. 2. Variation of $\sum k_m \alpha_m$ with composition for NaCl-derivative structures. $Ti_2C\square$: Bell & Lewis (1971), Goretzki (1967); $V_6C_5\square$: Venables, Kahn & Lye (1968), Billingham, Bell & Lewis (1972*a*), Hiraga (1973); $V_8C_7\square$: Guerin & De Novion (1971); $FeLiO_2$, $NaFeO_2$: Brunel, de Bergevin & Gondrand (1972); Li_2SnO_3: Lang (1954), Lang (1966); Li_2MnO_3: Jansen & Hoppe (1973); Li_5IO_6: Lang (1966).

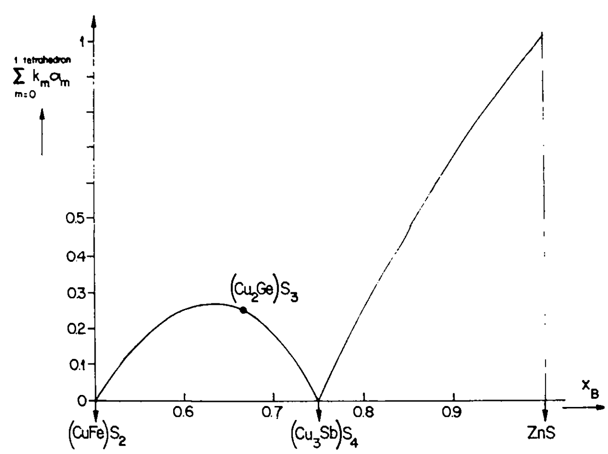


Fig. 3. Variation of $\sum k_m \alpha_m$ with composition for ZnS-derivative structures. $CuFeS_2$: *Strukturbericht* (1928–1932); Cu_2GeS_3: Parthé & Garin (1971); Cu_3SbS_4: *Structure Reports for 1957* (1964).

and (18) takes on the simple form

$$\sum_{m=0}^{1\text{ polyhedron}} k_m\alpha_m = \frac{1}{S} \cdot \frac{\frac{N_1}{N} \cdot \frac{N_2}{N}}{x_A \cdot x_B} \quad . \qquad (20)$$

Fig. 2 shows the variation of the sum

$$\sum_{m=0}^{1\text{ octahedron}} k_m\alpha_m = \alpha_0 + 4\alpha_1 + \alpha_2$$

with composition for NaCl-derivative structures according to equation (20). The values corresponding to the long-range-ordered phases like V_8C_7, V_6C_5, Li_2SnO_3 and $LiFeO_2$ are indicated together with the calculated value for the short-range-ordered phase V_4C_3. It is known from n.m.r. data that this phase consists of equal numbers of V-centred octahedra having either 5C and 1 vacancy (□) or 4C and 2□ which leads to: $\alpha_0 + 4\alpha_1 + \alpha_2 = +0{\cdot}222$. Froidevaux & Rossier (1967) have investigated a composition range of NaCl-related phases from $VC_{0\cdot67}\square_{0\cdot33}$ to $VC_{0\cdot89}\square_{0\cdot11}$. They found a mixture of octahedra having 5C and 1□ with octahedra having 6C and 0□ or 4C and 2□ depending on composition.

Fig. 3 shows the variation of the sum

$$\sum_{m=0}^{1\text{ tetrahedron}} k_m\alpha_m = \alpha_0 + 3\alpha_1$$

with composition for ZnS-derivative structures according to equation (20). It is easy to check that the value $1 + 3\alpha_1 = 0{\cdot}25$ calculated for Cu_2GeS_3 with the assumption that it consists of $\frac{2}{3}$ of *S*-centred tetrahedra with 1Ge and 3Cu and $\frac{1}{3}$ with 2Ge and 2Cu is in perfect agreement with an α_1 value of $-\frac{1}{4}$ determined directly by inspection of the crystal structure (Parthé & Garin, 1971).

The occurrence of polyhedra which are not the closest to the nominal composition results in a value of $\sum k_m\alpha_m$ larger than the one calculated from equation (20).

Relations between short-range-order parameter equations and the intensity scattered in between the reflexions of the base structure

In the following we shall show that a relation exists between the equations for the short-range-order parameters and the intensity scattered in between the reflexions of the base structure. As a result, scattered intensity may occur only on certain surfaces in reciprocal space which may be reduced to planes or even lines depending on the base structure. If we have short-range order only, diffuse intensity should be observed anywhere on these surfaces. If the substituted polyhedra are long-range-ordered, discrete superstructure reflexions occur which must be located somewhere on these same surfaces.

The connexion between short-range-order parameters and the intensity $I(\mathbf{H}')$ scattered in between the reflexions of the base structure is given by:

$$\alpha_m = \frac{1}{V^*} \int_{V^*} I(\mathbf{H}') \exp (2\pi i \mathbf{H}' \cdot \mathbf{r}_m) \mathrm{d}V^* \qquad (21)$$

where $\mathbf{H}'$ is any position vector in reciprocal space

$$\mathbf{H}' = h_1\mathbf{a}_1^* + h_2\mathbf{a}_2^* + h_3\mathbf{a}_3^*\ ,$$

$\mathbf{a}_1^*$, $\mathbf{a}_2^*$ and $\mathbf{a}_3^*$ are the reciprocal vectors of the base structure, h_1, h_2, and h_3 can have any value and are *not* necessarily integers and $\mathbf{r}_m$ is a vector connecting *m*th-nearest neighbours in the direct structure.

The existence of a relation such as (9) between the α parameters implies certain conditions on the function $I(\mathbf{H}')$. This was shown for (9.2) applicable to NaCl-related structures by Brunel, de Bergevin & Gondrand (1972). We shall treat here in detail the calculation for CsCl-related structures.

In CsCl-related structures the atoms involved in the ordering process are distributed on cube corners and therefore each atom has:

6 first-nearest neighbours with $\mathbf{r}_1 = \pm\mathbf{a}\langle 100\rangle$

12 second-nearest neighbours with $\mathbf{r}_2 = \pm\mathbf{a}\langle 110\rangle,\ \pm\mathbf{a}\langle\bar{1}10\rangle$

8 third-nearest neighbours with $\mathbf{r}_3 = \pm\mathbf{a}\langle 111\rangle,\ \pm\mathbf{a}\langle\bar{1}11\rangle$.

The α parameters used for (9) are given by the average of (21) over equivalent $\mathbf{r}_m$ vectors which leads to:

$$\alpha_0 = \frac{1}{V^*}\int_{V^*} I(\mathbf{H}')\mathrm{d}V^* = 1 \qquad (22.0)$$

$$\alpha_1 = \frac{1}{V^*}\int_{V^*} I(\mathbf{H}') \cdot \tfrac{1}{3} (\cos 2\pi h_1 + \cos 2\pi h_2 + \cos 2\pi h_3)\mathrm{d}V^* \qquad (22.1)$$

$$\alpha_2 = \frac{1}{V^*}\int_{V^*} I(\mathbf{H}')\tfrac{1}{3}(\cos 2\pi h_1 \cdot \cos 2\pi h_2 + \cos 2\pi h_2 \cdot \cos 2\pi h_3 + \cos 2\pi h_1 \cdot \cos 2\pi h_3)\mathrm{d}V^* \qquad (22.2)$$

$$\alpha_3 = \frac{1}{V^*}\int_{V^*} I(\mathbf{H}') \cdot \cos 2\pi h_1 \cdot \cos 2\pi h_2 \cdot \cos 2\pi h_3 \mathrm{d}V^*. \qquad (22.3)$$

Putting (22) in (9.4), one obtains:

$$\frac{1}{V^*}\int_{V^*} I(\mathbf{H}') \cdot [(1+\cos 2\pi h_1) \cdot (1+\cos 2\pi h_2) \times (1+\cos 2\pi h_3)]\mathrm{d}V^* = 0\ . \qquad (23)$$

For (23) to be satisfied $I(\mathbf{H}')$ must have non-zero values only on the surface described by the equation:

$$(1+\cos 2\pi h_1) \cdot (1+\cos 2\pi h_2) \cdot (1+\cos 2\pi h_3) = 0 \qquad (24)$$

which corresponds to a set of planes in reciprocal space with

$$h_1=\frac{2m+1}{2}, \quad h_2=\frac{2n+1}{2}, \quad h_3=\frac{2p+1}{2} \qquad (25)$$

where m, n, p represent any integer. This surface is shown in Fig. 4(c).

Following the same procedure one can obtain for NaCl-derivative structures an equation equivalent to (23):

$$\sum k_m\alpha_m=\frac{1}{V^*}\int_{V^*} I(\mathbf{H}')\tfrac{2}{3}\,(\cos \pi h_1+\cos \pi h_2 + \cos \pi h_3)^2 dV^*=0\,. \qquad (26)$$

Thus the diffuse intensity $I(\mathbf{H}')$ has to be on a surface described by

$$\cos \pi h_1+\cos \pi h_2+\cos \pi h_3=0\,. \qquad (27)$$

This triple periodic surface is shown in Fig. 4(b).

Starting with (9.1) and using the same approach one can derive for the general location of intensity in zinc-blende-derivative structures the relation

$$1+\cos \pi h_1\,.\,\cos \pi h_2+\cos \pi h_2\,.\,\cos \pi h_3 + \cos \pi h_3\,.\,\cos \pi h_1=0\,. \qquad (28)$$

The solutions of (27) represent a set of lines

$$\begin{cases} h_1=2m+1 \\ h_2=2n \end{cases} \quad \begin{cases} h_1=2m \\ h_2=2n+1 \end{cases} \quad \begin{cases} h_1=2m+1 \\ h_3=2p \end{cases}$$

$$\begin{cases} h_1=2m \\ h_3=2p+1 \end{cases} \quad \begin{cases} h_2=2n \\ h_3=2p+1 \end{cases} \quad \begin{cases} h_2=2n+1 \\ h_3=2p \end{cases} \qquad (29)$$

which are shown in Fig. 4(a).

Comparison with experimental data

(1) *Short-range-ordered structures*

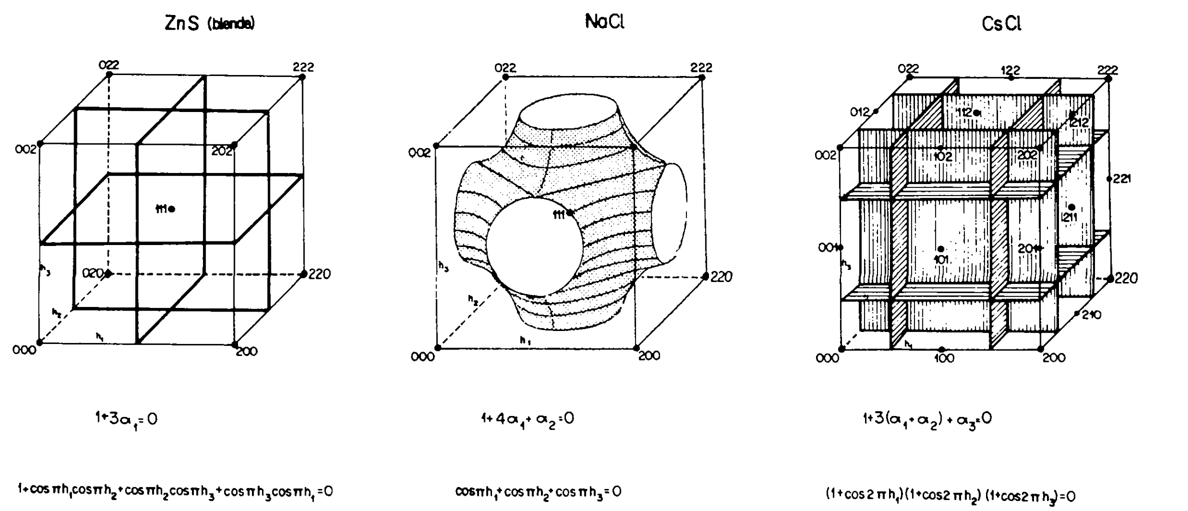
The only available data refer to NaCl-derivative structures. Two main groups are to be distinguished: first the substoichiometric transition-metal carbides and nitrides $T(C,N)_{1-x}$ and second mixed oxides like $LiFeO_2$.

Short-range-ordered compounds with nominal compositions $T_6C_5\square$ exist for T = Nb and T = Ta where broad diffuse bands appear on electron diffraction patterns along a surface obeying (27) (Venables & Meyerhoff, 1972). In V_6C_5 the vacancies are mostly ordered at low temperature. However an electron diffraction pattern by Hiraga (1973) shows narrow diffuse streaks in the correct location.

TiN_{1-x} ($x\simeq 0{\cdot}33$) and TiC_{1-x} ($x\simeq 0{\cdot}5$) have the same type of diffuse scattering as NbC_{1-x} (Billingham, Bell & Lewis, 1972b).

The diffuse intensity distribution in the short-range-ordered compound $V_4(C_3\square)$ is also fairly well described by (27), although the nominal composition implies the existence of two differently substituted octahedra. It was shown that a better matching with the observed intensity distribution was obtained by introducing a correcting term in (27) but this hardly changed the α values (Sauvage & Parthé, 1972). The sum $\alpha_0+4\alpha_1+\alpha_2$ remained close to zero instead of approaching 0·22, a value to be expected from (20). In order to overcome this contradiction a quantitative estimation of diffuse intensity, which was previously assumed to be constant and concentrated on the theoretical surface, has been performed by neutron diffraction. The results of this experiment will be presented in a forthcoming paper.

The second example of short-range-ordered compounds with NaCl-related structures is provided by the double oxides like $LiFeO_2$. De Bergevin & Brunel (1968) had predicted that diffuse intensity should be located on the surface given by (27) but they could not produce direct experimental evidence because they worked on powder samples. The confirmation of their predictions was obtained by Cowley (1973) and Allpress (1971) with electron diffraction techniques.



(a) (b) (c)

Fig. 4. Allowed location for diffuse intensity within one reciprocal unit cell of the base structure for ZnS, NaCl and CsCl-derivative structures.

(2) *Long-range-ordered structures*

Examples of long-range ordered derivative structures of NaCl and ZnS (blende) have already been indicated in Figs. 2 and 3 respectively. Structure types related to the CsCl type are $FeSi_2$, Li_3Bi, Cu_2MnAl, $PtHg_4$ and others. If the structure has a composition and atom ordering such that (9) is fulfilled, all superstructure reflexions must be located on the surface described by (24), (27) or (28) respectively. In order to make a test, the *hkl* values related to the superstructure unit cell have to be transformed into h_1, h_2, h_3 referring to the base-structure unit cell. Superstructure reflexions allowed by the space group but which do *not* satisfy the surface equation must have a *zero* structure factor. This has been verified for the monoclinic and trigonal modifications of V_6C_5 (Sauvage & Parthé, 1973). As another example the two monoclinic NaCl-derivative structure types $LiMnO_3$ and $LiSnO_3$ recently investigated by Jansen & Hoppe (1973) are considered here. In Table 1 are given the monoclinic *hkl* values for the two types, the $h_1h_2h_3$ values, the sum corresponding to (27) and the calculated intensities. Making use of the condition on structure factors it is possible to get information on local atomic arrangement in an unknown superstructure.

Supposing that the composition of the compound is such that (9) cannot be applied and must be replaced by (20) then an equation such as (26) for NaCl-derivative structures takes the form:

$$\sum k_m\alpha_m = \frac{1}{V^*}\int_{V^*} \tfrac{2}{3}I(\mathbf{H}')\,(\cos\pi h_1+\cos\pi h_2 + \cos\pi h_3)^2 \mathrm{d}V^* = \frac{1}{S}\,\frac{N_1N_2}{N^2x_Ax_B} \qquad (30)$$

or written differently:

$$\frac{1}{V^*}\int_{V^*} \tfrac{2}{3}I(\mathbf{H}')\,[(\cos\pi h_1+\cos\pi h_2+\cos\pi h_3)^2 - \mathrm{const.}]\mathrm{d}V^* = 0\,. \qquad (31)$$

The quantity between square brackets may take negative values over the integration range and thus no condition can be derived for the intensity $I(\mathbf{H}')$. For example with V_8C_7 or Cu_2GeS_3 non-zero superstructure reflexions may occur away from the surfaces given by (27) and (28) respectively.

Conclusion

It has been possible to formulate a general ordering principle for derivative structures. This has permitted the explanation of diffuse intensity observed in NaCl-related structures and the prediction of the location

Table 1. *Test of validity of the ordering principle for* Li_2MnO_3 *and* Li_2SnO_3 *structure types*

hkl	h_1	h_2	h_3	$\cos\pi h_1+\cos\pi h_2+\cos\pi h_3$	Intensities† calculated for Li_2MnO_3 with Li_2MnO_3 structure type	Li_2SnO_3 structure type
002	$\frac{1}{2}$	$\frac{1}{2}$	$\frac{1}{2}$	0	19·8	18·0
020	0	$\frac{2}{3}$	$-\frac{2}{3}$	0	2·6	0·9
110	$\frac{3}{4}$	$\frac{1}{12}$	$-\frac{7}{12}$	0	0	5·1
$11\bar{1}$	$\frac{1}{2}$	$-\frac{1}{6}$	$-\frac{5}{6}$	0	5	1·5
021	$\frac{1}{4}$	$\frac{11}{12}$	$-\frac{5}{12}$	0	0	4·2
111	1	$\frac{1}{3}$	$-\frac{1}{3}$	0	3·9	1·1
$11\bar{2}$	$\frac{1}{4}$	$\frac{5}{12}$	$\frac{13}{12}$	0	0	2·7
022	$\frac{1}{2}$	$\frac{7}{6}$	$-\frac{1}{6}$	0	2·8	0·7
112	$\frac{5}{4}$	$\frac{7}{12}$	$-\frac{1}{12}$	0	0	1·7
$11\bar{3}$	0	$-\frac{2}{3}$	$-\frac{4}{3}$	0	2·2	0·4
023	$\frac{3}{4}$	$\frac{17}{12}$	$\frac{1}{12}$	0	0	1·0
130	$\frac{3}{4}$	$\frac{3}{4}$	$-\frac{5}{4}$	$-3\sqrt{2}/2$	0	0
200	$\frac{3}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	0	2·9	2·7
$13\bar{1}$	$\frac{1}{2}$	$\frac{1}{2}$	$-\frac{3}{2}$	0	5·4	5·0
113	$\frac{3}{2}$	$\frac{5}{6}$	$\frac{1}{6}$	0		
004*	1	1	1		1·9	0·5
131*	1	1	−1	−3*	0·9*	0·5*
$20\bar{2}$*	1	−1	−1		0	0·2
$13\bar{2}$	$\frac{1}{4}$	$\frac{1}{4}$	$-\frac{7}{4}$	$3\sqrt{2}/2$	0	0
$11\bar{4}$	$\frac{1}{4}$	$\frac{13}{12}$	$-\frac{19}{12}$	0	0	0·6
040	0	$\frac{4}{3}$	$-\frac{4}{3}$	0	1·0	0
$22\bar{1}$	$\frac{5}{4}$	$-\frac{1}{12}$	$-\frac{17}{12}$	0	0	0·5
220	$\frac{3}{2}$	$-\frac{1}{6}$	$-\frac{5}{6}$	0	1·1	0
132	$\frac{5}{4}$	$\frac{5}{4}$	$-\frac{3}{4}$	$-3\sqrt{2}/2$	0	0
041	$\frac{1}{4}$	$\frac{19}{12}$	$\frac{13}{12}$	0	0	0·4
024	1	$\frac{5}{3}$	$\frac{1}{3}$	0	1·0	0
$22\bar{2}$	1	$-\frac{1}{3}$	$-\frac{5}{3}$	0	0·4	0
202*	2	0	0	3*	8·7*	7·9*
$13\bar{3}$*	0	0	2		17·0*	15·5*

* Fundamental reflexions.

† After Jansen & Hoppe (1973).

of diffuse intensity in short-range-ordered ZnS and CsCl-derivative structures. It is essential that these predictions be verified by experimental studies. We are actively pursuing this problem. Experimental determination of diffuse intensity in TiO by Castles, Cowley & Spargo (1971) has indicated a surface quite different from the ones discussed here. Fermi-surface effects were used to explain the particular shape, but it would be interesting to know if some other explanation based on a simple geometrical ordering principle might not be possible.

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Sur la Modulation des Franges Entourant la Raie 111 Donnée par un Empilement de Couches Minces Au–Cu–Au

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Thin-film specimens having the layered polycrystalline structure Au–Cu–Au have been prepared for study by X-ray diffraction. When there is approximately only one atomic plane of copper between two similar gold films of thicknesses $\simeq 200$ Å, it is found that the upper layers of Cu and Au grow epitaxically on the first gold deposit, all their crystals having a common [111] axis nearly perpendicular to the surface plane. Photographs of the 111 line given by such specimens reveal secondary fringes, the spacing and intensity of which are shown to depend on the spacing δ introduced by the copper layer between the two gold films. A comparison of the two fringe patterns obtained respectively before and after copper diffusion into the gold yields the value: $\delta=(2-0{,}16\pm 0{,}02)d_{111}$(Au) for a copper layer equivalent to one atomic plane grown epitaxically between two (111) gold planes. This result is compared with the theoretical value deduced from a 'hard spheres' model for the structure of the Au–Cu–Au layered system.

Introduction

Croce, Gandais & Marraud (1961) ont montré que l'on pouvait déterminer expérimentalement l'épaisseur de films métalliques minces polycristallins à partir du système de franges qui apparaissent dans certaines conditions autour de la raie 111 du diagramme de diffraction de rayons X obtenu par un montage en réflexion (montage de Brentano).

Rappelons que cette mesure est possible lorsque les grains constituant le film sont monocristallins en épaisseur, avec un plan (111) sensiblement parallèle à la surface du support, et que, d'autre part, leurs dimensions latérales sont suffisamment grandes devant leur