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HAL Id: jpa-00217235
https://hal.archives-ouvertes.fr/jpa-00217235
Submitted on 1 Jan 1977

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THE TRANSITION STATE AS AN INTERPRETATION OF DIFFUSE INTENSITY
CONTOURS IN SUBSTITUTIONALLY DISORDERED SYSTEMS (1)

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Résumé. — Si le diagramme de diffraction d’un système désordonné par substitution présente des
intensités diffuses concentrées sur un lieu géométrique dans l’espace réciproque, l’état d’ordre corres-
pondant est défini comme un état de transition. On propose un modèle qui permet la description de l’
ordre en termes de cluster prédominant d’un type de polyédres spécifiés ; les opérateurs d’occu-
pation des sites de ces polyédres obéissent à la même relation linéaire. Ce cluster, tout comme la
relation, peuvent être déduits du développement de Fourier du lieu géométrique. La valeur de telle
relation de cluster particulier peut être estimée à partir des paramètres d’ordre à courte distance
obtenus expérimentalement et la relation relative au cluster prédominant, est la solution d’un pro-
bème de valeurs propres. Le modèle est illustré par quelques systèmes spécifiques.

Abstract. — If the diffraction pattern of a substitutionally disordered system shows diffuse intensity
confined to a geometrical locus in reciprocal space, the corresponding ordering state is defined as the
transition state. A model is proposed which allows the description of the ordering in terms of predomi-
nant clusters of a specific polyhedral type with the common feature that the occupation operators of
their sites obey the same linear relation. The cluster as well as the relation can be derived from the
Fourier expansion of the geometric locus. The goodness of any particular cluster relation can be
estimated from experimentally obtained SRO parameters and the predominant cluster relation can be
obtained as the solution of an eigenvalue problem. Finally the model is illustrated by means of some
specific systems.

1. Introduction. — In a number of binary systems
a state of substitutional order has been identified
showing a degree of order which is intermediate
between that according to the classical concept of
short range order and that of the final long range order
state. This state, termed transition state is charac-
terized by well defined contours of diffuse intensity in
the diffraction patterns.

This intensity distribution is not expected from a
mean field theory, say from the Clapp and Moss
formula [1], if it is assumed that the range of pairwise
interaction is limited to a small number of neigh-
bours. However if long range interactions, due
to singularities in the electronic part of the interaction
energy are involved, it has been shown that the diffuse
intensity distribution may show special features. Diffu-
sity contours observed in the electron diffraction
sive intensity is then expected to appear at the end-
point of reciprocal lattice vectors spanning parallel
flats of the Fermi surface [2, 3, 4]. Application of
this general idea to a number of alloys has proved
to be successful. The splitting of diffuse intensity
maxima in Cu-Au [2, 5], Cu-Pt [6] and Cu-Pd sys-
tems [6] has been explained on this basis.

Castles et al. [7] have interpreted the diffuse inten-
sity contours observed in the electron diffraction
patterns of metallic TiO$_2$ (1.00 < x < 1.25) as direct
images of the Fermi-surface flats. Moss and Walker
also suggested that the diffuse intensity surface
observed in the electron diffraction patterns of
vacancy short range ordered substoichiometric tran-
sition metal carbides and nitrides should be related
to the electronic structure of the compound [4].
However, Sauvage and Parthé have interpreted the
latter observations in terms of the local environment
which reflects the tendency to order [8]. The local
order is described by a small number of predominant
interpenetrating atomic clusters of a specific poly-
hedral type. This ordering model was first introduced
by Brunel et al. [9] to explain the diffuse intensity
distribution associated with short range order of the
lithium and iron ions in LiFeO$_3$ and is based on one of
Pauling’s rules governing the structure of ionic
ordered systems [10].

In this paper we shall give a more general formula-
lation of the ideas of Sauvage and Parthé and show that,
if the diffuse intensity is strictly confined to a geo-
metric locus, the order in the system can be described
by means of a linear relation between the occupation
operators of cluster sites. In the ideal transition state,
the occupation of the cluster sites is such that the
cluster relation is satisfied for each cluster of the
crystal.
Since the cluster relation should also be satisfied in the long range order state, the transition state can be considered as a prefiguration of the state of long range order. Since the cluster relation is derived only from the geometry of the diffuse intensity locus (no intensity measurements have to be performed) this relation cannot give a complete picture of the ordering state; for instance, the frequency distribution of different clusters satisfying the same cluster relation cannot be derived from the geometrical data.

We shall give the basis of the theory and discuss some applications to substitutional vacancy ordering in intercalation compounds and in a complex oxide. Applications to several other systems can be found in references [11, 12, 13, 14, 15].

2. Theoretical basis. — As far as purely geometrical features of the diffuse intensity contours are concerned, the influence of multiple Bragg-scattering is irrelevant and the simple kinematical approach will thus be adequate for the treatment of this problem. Experimental evidence for the validity of this argument is shown in figure 1 for the diffuse intensity contours obtained from a Ti, S, 2 (x \approx 0.2) single crystal. The sharp X-ray intensity hexagon of figure 1a obtained by Moret et al. [16] whose position coincides with the first Brillouin zone boundary can be compared to the corresponding electron diffraction contour in figure 1b, showing identical geometrical features. Since most experimental data are restricted to binary systems, we will limit ourselves here to such compounds, although the theory can easily be generalised to n component systems [15].

![Image](a) and electron diffraction pattern (b) of Ti, S, 2 (x \approx 0.2). Note the strong resemblance between both patterns. The X-ray pattern is taken from [16]. The electron diffraction pattern is from L. Van Goethem.

For a binary system, containing two species of atoms, A and B with respective fractions m, and m, the amplitude of the diffuse intensity in the framework of the kinematical theory is given by the well known expression:

\[ A_p(g) = \left| f_p(g) - f_A(g) \right| \sum_j \sigma_j e^{2\pi i \mathbf{g} \cdot \mathbf{r}_j} \]  

(1)

where \( g \) represents the general position vector in reciprocal space and \( r_j \) the position vectors of the lattice sites (j). \( f_p(g) \) and \( f_A(g) \) are the atomic scattering amplitudes of an A respectively B atom and \( \sigma_j \) is the so-called Flinn operator which takes the values: \( \sigma_j = m_A \) if position \( j \) is occupied by an A atom and \( \sigma_j = -m_B \) if position \( j \) is occupied by a B atom.

From (1) the reduced scattering amplitude takes the form of a Fourier series:

\[ a(g) = \frac{A_p(g)}{f_p(g) - f_A(g)} = \sum_j \sigma_j e^{2\pi i \mathbf{g} \cdot \mathbf{r}_j}. \]  

(2)

It can be shown that \( a(g) = 0 \) at the Bragg positions, the expression for the diffuse intensity can then be written as:

\[ i(g) = \sum_k \sigma_k \sigma_j e^{2\pi i \mathbf{k} \cdot (\mathbf{r}_k - \mathbf{r}_j)}. \]  

(3)

Assuming that the lattice can be based on a primitive unit cell (e.g. fcc, bcc, ...) \( \mathbf{r}_k - \mathbf{r}_j \) is again a lattice vector [a generalisation of the theory to non-primitive lattices is given in [15]], and hence:

\[ i(g) = N m_A m_B \sum_j a_{0j} e^{2\pi i \mathbf{g} \cdot \mathbf{r}_j} \]  

(4)

with \( a_{0j} \) the Warren-Cowley short range order (SRO) parameters defined by:

\[ a_{0j} = \frac{1}{N m_A m_B} \sum_i \sigma_i \sigma_{i+j} = \langle \sigma_i \sigma_{i+j} \rangle / m_A m_B. \]  

(5)

The SRO parameters which are the coefficients of the Fourier series, representing the periodic diffuse intensity, can be obtained from the Fourier inversion of (4):

\[ a_{0j} = \frac{1}{m_A m_B N V^*} \int_{V^*} dg i(g) e^{-2\pi i \mathbf{g} \cdot \mathbf{r}}, \]  

(6)

with \( V^* \) the volume of the reciprocal unit cell.

3. The «transition state». — Consider an ideal transition state, characterised by an infinitely thin locus of diffuse intensity in reciprocal space whose equation is given by:

\[ f(g) = 0. \]

Since the locus shows the translation symmetry of the lattice, \( f(g) \) can be represented by means of a Fourier series:

\[ f(g) \equiv \sum_k \omega_k e^{-2\pi i \mathbf{g} \cdot \mathbf{r}_k} = 0. \]  

(7)
If the diffuse intensity is exactly confined to this locus, one has the identity:

\[ a(g) f(g) = 0 \]  \hspace{1cm} (8)

Using (2) and (7) this expression can be written explicitly as:

\[ \sum_j \sum_k \omega_k \sigma_{j+k} e^{2 \pi i g \cdot r_k} = 0 \]  \hspace{1cm} (9)

which leads to a set of linear homogeneous relations between the occupation operators:

\[ \sum_k \omega_k \sigma_{j+k} = 0 \text{ for all } j . \]  \hspace{1cm} (10)

With each lattice point \( r_j \), a cluster with position vectors \( r_j + r_k \) (\( k = 0, 1; S_0 - 1 \)) can be associated; relation (10) then expresses a condition between the occupation operators of the cluster sites. The cluster type as well as the corresponding coefficients \( \omega_k \) of this so-called cluster relation can be deduced from the geometry of the diffuse intensity locus.

On the other hand, if a relation such as (10) is satisfied for all clusters of a type defined by a polyhedron \{ \( r_k \) \} it can be concluded that the diffuse intensity is located on a geometrical locus \( f(g) \). It is important to note that this particular ordering state is not described in statistical terms. The order in the transition state is described by a cluster relation whereas the disorder results from the degrees of freedom that are still left.

In actual systems, the number of cluster vector \( r_k \) appears to be small and the corresponding cluster type is a simple one.

Whenever \( f(g) \) is a real function as it is the case for a centro-symmetric cluster for which \( \omega_k = \omega_{-k} \) the corresponding locus is in general a surface. If on the other hand \( f(g) \) is a complex function, the equation of the locus can be written as:

\[ f(g) = \varphi(g) + i \psi(g) \]  \hspace{1cm} (11)

representing a curve in reciprocal space; i.e. the intersection of the respective surfaces:

\[ \varphi(g) = 0 \text{ and } \psi(g) = 0 . \]  \hspace{1cm} (12)

A non-centrosymmetrical cluster leads to a complex function:

\[ | \omega_k | \neq | \omega_{-k} | . \]  \hspace{1cm} (13)

In practice, due to topological reasons or compositional requirements, it is not always possible to satisfy a cluster relation such as (10) in each lattice point; a residue value for the cluster relation can then be attributed to each lattice point. This residue is defined by:

\[ r_j = \sum_k \omega_k \sigma_{j+k} \]  \hspace{1cm} (14)

which differs from zero whenever the relation is violated. The goodness of any particular cluster relation can be estimated from the variance \( \langle \varepsilon_j^2 \rangle \) of the distribution of its residue values for which it can be shown [13] that:

\[ \langle \varepsilon_j^2 \rangle = \frac{1}{N} \frac{1}{V^*} \int_{V^*} dg | f(g) |^2 . \]  \hspace{1cm} (15)

From this formula it follows that the more a particular cluster relation is prominent in the ordering system, the more the diffuse intensity is concentrated in the neighbourhood of the locus, where \( | f(g) | \) is small.

Conversely, if a locus is chosen in the vicinity of the diffuse intensity distribution, the variance of its corresponding cluster relation will be small.

A more convenient parameter for the estimation of the importance of an arbitrary cluster relation is the normalised variance \( S^2 \) which compares \( \langle \varepsilon_j^2 \rangle \) to its variance \( \langle \varepsilon_j^2 \rangle_0 \) in the totally disordered state:

\[ i.e. \quad S^2 = \frac{\langle \varepsilon_j^2 \rangle}{\langle \varepsilon_j^2 \rangle_0} . \]  \hspace{1cm} (16)

4. Relation to the SRO parameters. — 4.1 Goodness of an arbitrary cluster relation. — The variance of any arbitrary cluster relation can be related to the SRO parameters by substituting (4) for \( i(g) \) and (7) for \( f(g) \) into expression (15) yielding:

\[ \langle \varepsilon_j^2 \rangle = \frac{1}{NV^*} N m_{x} m_{y} \sum_{j,k} \alpha_j \omega_k \omega_k \int_{V^*} e^{2 \pi i g \cdot (r_j + r_k)} dg \]

\[ = m_{x} m_{y} \sum_k \omega_k \alpha_{-k} \sigma_{-k} \omega_k \]  \hspace{1cm} (17)

which can be written in bracket notation as

\[ \langle \varepsilon_j^2 \rangle = m_{x} m_{y} \langle \omega | \alpha | \omega \rangle \]  \hspace{1cm} (18)

with \( | \omega \rangle \) the so-called cluster vector whose components are the coefficients \( \omega_k \) of the cluster relation under consideration

\[ | \omega \rangle = \begin{pmatrix} \omega_0 \\ \omega_1 \\ \vdots \end{pmatrix} \]  \hspace{1cm} (19)

and \( \langle \omega | \) its corresponding row vector.

The \( \alpha \) matrix is then defined by:

\[ \alpha_{ij} = \alpha_{-i-j} . \]  \hspace{1cm} (20)

In a totally disordered system, \( \alpha \) is the unit matrix so that:

\[ \langle \varepsilon_j^2 \rangle_0 = m_{x} m_{y} \langle \omega | \omega \rangle \]  \hspace{1cm} (21)
and the normalised variance takes the form:

$$S^2 = \frac{\langle \omega | \alpha | \omega \rangle}{\langle \omega | \omega \rangle}.$$  \hspace{1cm} (22)

The goodness of any particular cluster relation in any state of the ordering process can thus be determined from the experimentally obtained SRO parameters by means of the normalised variance (22); $S^2 = 0$ corresponding to a relation being exactly satisfied in each lattice point and $S^2 = 1$ corresponding to the case of complete disorder.

4.2 The predominant cluster relation. — From the foregoing we are able to propose that the predominant clusters describing the transition state, can be defined as the clusters obeying the relation corresponding to the smallest normalised variance. The derivation of this cluster relation can be reduced to finding the minimum for $S^2$ given by (22), a problem which is very similar to the well-known quantum mechanical problem of finding the ground state energy level and the corresponding wave function for a given Hamiltonian. By a variational principle it can be transformed into an eigenvalue/eigenvector equation similar to the stationary Schrödinger equation:

$$a | \omega \rangle = S^2 | \omega \rangle.$$  \hspace{1cm} (23)

Although in principle the dimensions of $a$ and $| \omega \rangle$ may be infinite it can be shown [15] that the study can be restricted to $r$-point clusters by simply replacing $a$ by its leading principal submatrix or order $r$ without changing the eigenvalues and eigenvectors. It can furthermore be shown [15] that all the eigenvalues are non-negative with an average value of 1; this can be used as a consistency test for the measured SRO parameters. A necessary and sufficient condition for a cluster relation to be satisfied in each lattice point is:

$$\det a = 0.$$  \hspace{1cm} (24)

It can be concluded in general that the predominant cluster relation can be obtained as the eigenvector corresponding to the lowest eigenvalue of the matrix consisting of the SRO coefficients. This eigenvalue is the normalised variance $S^2$ of the cluster relation.

4.3 Application to vacancy ordering in VC$_x$ (0.70 $\leq x \leq$ 0.89). — VC$_x$ has a defective sodium chloride structure, one of the FCC sublattices being occupied by metal atoms and the other by carbon atoms and vacancies. For this system Sauvage et al. [17] were able to obtain reliable values for the SRO parameters by careful measurements of kinematical neutron diffraction intensities. These values were used in a 14 site eigenvalue calculation, yielding for the predominant cluster relation [15]:

$$\sum_{\text{octahedron}} \sigma_i - 0.9 \sum_{\text{cube}} \sigma_i = 0$$

in agreement with the electron diffraction results described in [13]. For the corresponding normalised variance we obtained a small value, slightly negative but equal to zero within the experimental error:

$$S^2 = -0.015$$

which emphasizes the predominance of this particular relation in the ordering system.

It should be noted that this technique can be used to deduce the predominant cluster and its corresponding goodness in any state of the ordering process.

5. Interpretation and application of the cluster relation. — We now discuss a number of cluster relations which have a simple physical or structural interpretation and which are applicable to actual systems.

1) If all $\omega_k = 1$ equation (10) reduces to:

$$\sum_k \sigma_j + k = 0 \text{ for all } j.$$  \hspace{1cm} (25)

This relation expresses that all clusters of the considered type have the same composition which is then necessarily the macroscopic one. It is evident that for a given clustertype this relation can only be satisfied for a discrete set of macroscopic compositions. A similar relation has been put forward by Brunel et al. [9] and also by Sauvage and Parthé [8]. The discussion of ordering in the Ni-Mo and Au-V systems discussed by De Ridder, Van Tendeloo and Amelinckx, was also based on this relation [12].

2) If $\omega_k = +1$ for half of the cluster vectors and $\omega_{-k} = -1$ for the other half, relation (10) becomes explicitly:

$$\sum_{k=1}^{51} \sigma_j + k = \sum_{k=1}^{51} \sigma_j - k.$$  \hspace{1cm} (26)

This relation expresses that the composition of the subcluster $\{ \mathbf{r}_j + k \}$ is equal to the composition of the subcluster $\{ \mathbf{r}_j - k \}$. This relation is applied in the discussion of ordering in octahedral sites of intercalated ions in the NbS$_2$ layer structure [14, 18] to be discussed below.

In figure 2a the diffuse intensity is located on the locus:

$$\sin \pi(2h + k) \sin \pi(h + 2k) \sin \pi(h - k) = 0.$$  \hspace{1cm} (27)

Expressing this relation as a sum of exponentials, one finds:

$$e^{2\pi i(2h + k)} + e^{-2\pi i(h + 2k)} + e^{-2\pi i(h - k)} =$$
$$-e^{-2\pi i(2h + k)} + e^{2\pi i(h + 2k)} + e^{2\pi i(h - k)} = 0$$
or:

$$\sum_{i=1}^{6} \omega_i e^\theta_{i} x_{i} = 0.$$
The two-dimensional cluster vectors $r_i$ and corresponding $\omega$ coefficients are:

\[
\begin{align*}
    r_1 &= [21] \quad \omega_{21} = 1 \\
    r_2 &= [12] \quad \omega_{12} = 1 \\
    r_3 &= [\bar{1}1] \quad \omega_{\bar{1}1} = 1 \\
    r_4 &= [2\bar{1}] \quad \omega_{2\bar{1}} = -1 \\
    r_5 &= [12] \quad \omega_{12} = -1 \\
    r_6 &= [1\bar{1}] \quad \omega_{1\bar{1}} = -1
\end{align*}
\]

leading to the composition requirement:

\[
\sigma_{21} + \sigma_{1\bar{2}} + \sigma_{\bar{1}1} = \sigma_{2\bar{1}} + \sigma_{12} + \sigma_{1\bar{1}}.
\] (28)

The prominent clusters are six point clusters which obey the above relation, i.e., the compositions of the triangular subclusters $\{1, 3, 5\}$ and $\{2, 4, 6\}$ have to be the same (figure 2b).

3) In some experimental situations [19] a class of diffuse intensity loci can be observed as a function of composition.

The equation for these loci can be represented in the form:

\[
f_1(\mathbf{g}) + \omega f_2(\mathbf{g}) = 0
\] (29)

where $\omega$ is a parameter depending on composition and on heat treatment. The functions $f_1$ and $f_2$ are of the form:

\[
\begin{align*}
    f_1(\mathbf{g}) &= \sum_{k_1} g^{2\pi i x_{k_1}} \\
    f_2(\mathbf{g}) &= \sum_{k_2} g^{2\pi i x_{k_2}}
\end{align*}
\] (30)

The corresponding cluster relation takes the form:

\[
\sum_{k} \sigma_{j+k_1} + \omega \sum_{k_2} \sigma_{j+k_2} = 0.
\] (31)

We shall now discuss in some detail two applications of this kind of relation. The applications refer to two-

![Diffuse intensity observed in Cu,NbS₂ as a function of the composition.](image)

Fig. 2. - a) Diffuse intensity situated along the Brillouin zone boundaries in Ni₆₃:NbS₂. b) Cluster used for explaining the presence of diffuse intensity along the Brillouin zone.

Fig. 3. - Diffuse intensity of the transition state observed in Cu₆₃:NbS₂ as a function of the composition. a, b) $x = 0.5$; c, d) $x = 0.75$; e, f) $x = 0.9$. The patterns on the left side are taken in the exact hexagonal section and very few diffuse scattering is observed, the patterns on the right are slightly tilted indicating that the maxima are situated out of the basal plane.
dimensional ordering. First we shall discuss the ordering of copper intercalate atoms in CuxNbS2 as a function of composition. Afterwards we shall treat the ordering of niobium oxide strings in the tungsten bronze structure.

5.1 ORDERING OF COPPER IONS IN CuxNbS2 [14, 19]. - The hexagonal section of the diffraction pattern of CuxNbS2 shows remarkably sharp diffuse intensity contours which vary with composition (figure 3). The presence of diffuse scattering is attributed to the ordering of the copper-ions and vacancies between the NbS2 sandwiches.

For CuxNbS2 with 0.2 < x < 0.8 all the geometric loci can be described by an equation of the type:

\[ \cos 2\pi k + \cos 2\pi h + \cos 2\pi(h + k) + \omega = 0 \]  

(32)

where \( \omega \) is a composition dependent parameter. A schematic representation of the curves corresponding to different values of \( \omega \) are shown in figure 4.

Writing (32) in exponential form and identifying with (7) leads to the 7-point cluster of figure 4b.

The corresponding cluster relation is:

\[ 2\omega \sigma_j + \sum_{k=1}^{6} \sigma_{j+k} = 0 \]  

(33)

where \( \sigma_j \) refers to the central site.

For different compositions (i.e. different \( \omega \)-values) the occupation of vacancies or Cu-ions on the 7-point cluster will be different [18].

As shown in [19] this cluster relation can be satisfied for a large fraction of the sites if the copper arrangement consists of small domains of the long range order structure in such a way that also across the domain boundaries the cluster relation is satisfied. The cluster model is thus consistent with a microdomain structure.

5.2 TRANSITION STATE IN OCTAHEDRAL INTERCALATES. — In the octahedral intercalation compounds MxNbS2 (with \( M = Mn, Fe, Ni \) and 0.25 < x < 0.33) the appearance of diffuse scattering along the first Brillouin zone boundaries is prominent. This can be interpreted on the basis of the curves (32) with \( \omega = 1.33 = 4/3 \). Figure 4a indicates that diffuse intensity will be concentrated in triangular areas in the vicinity of the centres of the triangles of basic reflections, as observed experimentally. In the particular case x = 0.33 we have \( \sigma_{1c} = -1/3 \) and \( \sigma_{2c} = 2/3 \) with \( \omega = 4/3 \) the cluster relation gives a residue of \(-2/9\) for the cluster of figure 5a whereas for the cluster of figure 5b the residue is \( 7/9 \) and it becomes larger if there are more copper atoms among nearest neighbours. This clearly means that although the relation is not exactly satisfied the best configuration of nearest neighbours is described by the cluster of figure 5a in which each copper atom is surrounded by six vacancies. The relation can be exactly satisfied for \( \omega = 1.5 \) and x = 0.33. In this particular case the curves of figure 4a reduce to isolated points in the centers of the triangles of basic spots and the superstructure is completely determined as we shall see below.

If the cluster center is a vacancy the residues indicated in figures 5c, d, e are obtained (for \( \omega = 4/3 \) and x = 0.33). The clusters of figures 5f, g, h are clearly incompatible with the first condition and have thus to be discarded. It turns out that the cluster of figure 5c is the best. The cluster relation can again be satisfied
FIG. 5. — Different clusters referred to in the discussion of the transition state in octahedral intercalates.

exactly with this cluster for \( \omega = 1.5 \) and \( x = 0.33 \). The two configurations 5a and 5c completely determine the two dimensional arrangement, i.e. the superstructure of figure 6a. In a disordered system the cluster relation cannot be satisfied at each site since this leads to LRO.

The locus of diffuse intensity also imposes conditions on the configurations of second nearest neighbours through the eq. (27), which is an analytical expression for the lines along which segments of the first Brillouin zone are situated. Rewriting this expression in the form of a Fourier series leads immediately to the cluster condition (28), which expresses that the occupation of the sites 1, 3, 5 has to be the same as that of the sites 2, 4, 6 of the cluster of figure 7a. Note that this relation is also satisfied for the superstructure of figure 6a.

FIG. 6. — Different superstructures of intercalate ions in a hexagonal host crystal: a) \( x = 0.33 \); b) \( x = 0.25 \); c) \( x = 0.25 \).

FIG. 7. — Cluster configuration: a) second nearest neighbours; b) nearest neighbours.

A model for the transition state has therefore to be based on micro-domains of the superstructure of figure 6a; separated by interfaces across which the relation between second nearest neighbours is satisfied. This ensures that both cluster relations are satisfied simultaneously in all sites of the micro-domains and moreover that the number of violations along the boundaries and in particular at boundary triple points is reduced to a minimum. Optical simulation using a grating, constructed on these principles, produces a diffraction pattern which exhibits the same characteristics as the electron diffraction pattern.

For the composition \( x = 0.25 \) reinforcements are observed along the Brillouin zone boundaries in the middles of the segments joining the basic spots. This suggests that the nearest neighbour configuration produces diffuse scattering along parts of the lines \( \omega = 1 \) of figure 4a. The corresponding cluster relation is

\[
2\sigma_0 + \sum_{k=1}^{6} \sigma_k = 0 \quad \text{with} \quad \sigma_0 = -1/4 \quad \text{and} \quad \sigma_M = 3/4.
\]

With a metal atom at the centre this leads to the cluster of figure 5a, i.e. all nearest neighbours should again be
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vacancies. If a vacancy occupies the center two metal atoms have to be present among the nearest neighbours. Taking the first relation into account two clusters are acceptable (figures 5d, e).

The reinforcements are also on the locus

\[ \sin \pi h \sin \pi k \sin \pi(h + k) = 0 \]

consisting of lines through the basic spots. The cluster relation corresponding to this locus is:

\[ \sigma_1 + \sigma_2 + \sigma_3 = \sigma_4 + \sigma_5 + \sigma_6 \]

where the operators refer to the sites represented in figure 7b. This relation suppresses the prominence of the cluster of figure 5d, i.e. we are left with the clusters 5a and 5e; together these two determine completely the LRO structure from which the transition state is derived (figure 6b). Clusters of type 5d although not prominent can still occur and contribute to the diffuse scattering outside the reinforcements.

The second nearest neighbours relation remains the same as for the composition \( x = 0.33 \) because of the prominence of the scattering at the Brillouin zone boundaries (the form of the relation is such that it can be satisfied for a variety of compositions). In the LRO structure just derived this relation is clearly again satisfied. We conclude that for this composition \( x = 0.25 \) the transition state has to be based on a majority of micro-domains of the superstructure represented in figure 6b possibly also of micro-domains of the superstructure represented in figure 6c, which has the same composition, separated by interfaces across which the second nearest neighbours satisfy the relation (28). 5.3 ORDERING OF ATOM STRINGS IN TERNARY W-Nb OXIDES [20]. — The complex oxide 17Nb2O5.48WO3 exhibits a tetragonal tungsten bronze structure. The unit cell (represented in figure 5) contains four pentagonal tunnels in the \[001\] directions. These tunnels are partly vacant, partly filled by niobium-oxygen strings. The occupation of the tunnels can be described as substitutional ordering of two components (niobium oxide strings and vacancies) on a two dimensional lattice.

The electron diffraction pattern of such material exhibits diffuse intensity rings around the Bragg reflections (figure 6) and the corresponding high resolution picture shows a disordered configuration of white dots, related to the tunnel positions in the matrix (figure 7).

The locus of diffuse intensity is well described by an equation of the type:

\[ \cos \pi(h + k) \cos \pi(h - k) + \frac{\omega}{4} = 0 \quad (34) \]

or

\[ e^{2\pi ih} + e^{-2\pi ik} + e^{2\pi hk} + e^{-2\pi ih} + \omega = 0 \]

from which the cluster relation:

\[ \sigma_{10} + \sigma_{10} + \sigma_{01} + \sigma_{01} + \omega \sigma_{00} = 0 \quad (35) \]

is immediately deduced.

By introducing the cluster operator \( \lambda \)

\[ \lambda_{00} = \sigma_{10} + \sigma_{10} + \sigma_{01} + \sigma_{01} \]

the relation can be written as:

\[ \sigma_j^{(k)} = 0 \quad (36) \]

with

\[ \sigma_j^{(k)} = \lambda_j^{(k)} + \omega \sigma_j^{(k)} \quad (37) \]

The operators \( \sigma^{(k)} \) refer to the same sublattice \( (k) \). The cluster characterising the ordering is therefore formed by a site and its four nearest neighbours on the same sublattice. The possible predominant clusters are represented in figure 8. An optical simulation using a

![Diagram](image)

**FIG. 8.** — Projection of the unit cell on the (001) plane of the tungsten bronze structure. The position vectors \( \rho_i \) \((i=1, 2, 3, 4)\) of the niobium oxide strings in the pentagonal tunnels are indicated.

![Diffraction Pattern](image)

**FIG. 9.** — Electron diffraction pattern (after Iijima and Anstis [20]) of 17Nb2O5.48WO3 showing diffuse intensity rings around the basic reflections of the (001) diffraction pattern.
grating constructed with these cluster restrictions produces a diffraction pattern extremely similar to the electron diffraction pattern [21].

6. Conclusion. — A simple method for the interpretation of diffuse intensity contours in the transition state was developed. If an analytical expression for the idealized intensity contours can be obtained, the derivation of the predominant clusters is straightforward. This method which uses the geometry of the intensity locus only, yields the essential features of the transition state; it has not the ambition to give a detailed picture. The cluster description is shown to be consistent with the description of order in terms of SRO parameters; in particular it has been shown how the predominant clusters can be derived from the knowledge of the SRO parameters.

Optical simulation confirms the results in specific cases [14, 19, 21].

References