

Equations for Diffuse Scattering from Materials with Multiple Sublattices

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General equations are presented for the diffuse scattering due to local ionic arrangements and displacements in systems with more than one ion per lattice point. Up to fourth-order terms are included. These are placed in a form easy to evaluate in specific cases; examples are given of a solid-solution oxide, and an oxide with vacant sites. Methods for employing these equations for the separation of the various contributions are discussed.

Introduction

Most quantitative studies of diffuse X-ray or neutron scattering to reveal local atomic arrangements, such as clustering or local order, have been carried out on metallic alloys. The techniques are still evolving; see Sparks & Borie (1966), Borie & Sparks (1971), Gragg & Cohen (1971), Gragg, Hayakawa & Cohen (1973), Williams (1974), Hayakawa, Bardhan & Cohen (1975), Tibballs (1975) for the latest procedures, techniques and error analyses. Currently, there is considerable interest in such diffuse scattering from other materials, such as oxides and carbides, where diffuse scattering can provide information about clustering or local order of the high density of point defects or of ions in solid solution in such materials; examples are the recent studies by Brunel & Bergevin (1969), Chudinova, Kuz'kina & Shvurin (1970, 1971), Billingham, Bell & Lewis (1972), Andersson, Gjønnnes & Taftø (1974). In metallic alloys there is one atom per lattice point, but in these compounds there can be several. General equations for compounds have not yet been presented and as a result investigators have resorted to various approximations. It is now well known for metallic alloys that the diffuse scattering contains features due to local atomic arrays (clustering or local order) and features due to static and dynamic displacements from lattice sites, and that both effects can extend out to many shells around any given atom. All previous studies on oxides and carbides have neglected the scattering due to mean-square displacements. As this intensity occurs near and under Bragg peaks, in the same location as the intensity due to chemical clustering and is of the same magnitude, the results of such studies are doubtful; studies of short-range order, for which the strongest parts of the two kinds of diffuse scattering are separated in reciprocal space, may be more correct. These prior studies have, however, included the effect of average static displacements, but assumed that these were radial and did not extend beyond the first-neighbor shell.

In this paper the general equations for diffused scattering from a structure with multiple sublattices

out to fourth-order terms are derived and placed in simple form for use with any material. Specific examples for two structures, Fe_xO and NaCl-type materials, are presented. The required measurements to separate the various contributions are given. Actual measurements with the methods are appearing concurrently (Hayakawa, Morinaga & Cohen, 1974; Krawitz & Cohen, 1975).

1. General theory

The intensity will be written in terms of moments of the general kinematic expression following the procedures of Borie & Sparks (1971) for binary alloys. The total intensity in electron units (I_{tot}) can then be written as:

$$I_{\text{tot}} = \sum_m^N \sum_{\mu}^M f_{m\mu} \exp [i\mathbf{k} \cdot (\mathbf{r}_m + \mathbf{r}_{\mu} + \Delta_{m\mu})] \\ \times \sum_n^N \sum_{\nu}^M f_{n\nu} \exp [-i\mathbf{k} \cdot (\mathbf{r}_n + \mathbf{r}_{\nu} + \Delta_{n\nu})], \quad (1)$$

where:

m, n = lattice indices; m (or n) imply m_1, m_2, m_3 , the triplet required to specify a coordinate in the lattice.

μ, ν = sublattice indices,

$f_{m\mu}, f_{n\nu}$ = atomic scattering factors of atoms on the μ th sublattice of the m th lattice point and the ν th sublattice of the n th lattice point respectively,

$\mathbf{r}_m, \mathbf{r}_n$ = the positional vectors of the m th and n th lattice point with respect to an arbitrary origin,

$\mathbf{r}_{\mu}, \mathbf{r}_{\nu}$ = sublattice vectors of the μ th and ν th sublattice with respect to the lattice points,

$\Delta_{m\mu}, \Delta_{n\nu}$ = small displacement vectors of the atoms from their lattice points $\mathbf{r}_m + \mathbf{r}_{\mu}$ and $\mathbf{r}_n + \mathbf{r}_{\nu}$,

N = total number of lattice points,

M = number of sublattices,

\mathbf{k} = the diffraction vector.

Let $\exp [i\mathbf{k} \cdot (\mathbf{r}_m - \mathbf{r}_n)] = A_{mn}$, $\exp [i\mathbf{k} \cdot (\mathbf{r}_{\mu} - \mathbf{r}_{\nu})] = S_{\mu\nu}$, $\exp [i\mathbf{k} \cdot (\Delta_{m\mu} - \Delta_{n\nu})] = \exp (i\mathbf{k} \cdot \Delta_{mn}^{\mu\nu})$. Furthermore, let

x_μ^i be the sublattice fraction of element i on sublattice μ and let $p_{\mu\nu}^{ij}$ be the conditional probability of finding a j -type atom (or ion) on the ν th sublattice of the n th lattice point if there is an i th type on the μ th sublattice of the m th lattice point. Then (1) may be written as:

$$I_{\text{tot}} = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i f_i f_j \times \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle P_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (2a)$$

The average of the displacement term is taken for each set of interatomic vectors associated with i and j species whose total probability is $x_\mu^i P_{\mu\nu}^{ij}$.

Separating the terms in the sum involving the same atoms:

$$I_{\text{tot}} = N \sum_m \sum_i x_\mu^i f_i^2 + \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle S_{\mu\nu} A_{mn} + \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle \times \left(\frac{P_{\mu\nu}^{ij}}{x_\nu^j} - 1 \right) S_{\mu\nu} A_{mn}. \quad (2b)$$

By adding and subtracting the term $m\mu = n\nu$ to the second and third sums the intensity may be written in terms of a component due to the average structure, I_{AVE} , and one related to the local order, $I_{\text{L.O.}}$:

$$I_{\text{tot}} = I_{\text{AVE}} + I_{\text{L.O.}}, \quad (3a)$$

$$I_{\text{AVE}} = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle S_{\mu\nu} A_{mn}, \quad (3b)$$

$$I_{\text{L.O.}} = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle \left(\frac{P_{\mu\nu}^{ij}}{x_\nu^j} - 1 \right) S_{\mu\nu} A_{mn}. \quad (3c)$$

The inner sum of (3c), over i and j , can be simplified by separating the term for $i=j$ and employing the relationships:

$$P_{\mu\nu}^{ii} = 1 - \sum_{k(\neq i)} P_{\mu\nu}^{ik}, \quad (4a)$$

$$x_\nu^i = 1 - \sum_{k(\neq i)} x_\nu^k. \quad (4b)$$

Then equation (3c) can be rearranged to yield:

$$I_{\text{L.O.}} = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i (f_i \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ii}) \rangle - f_j \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle) \left(1 - \frac{P_{\mu\nu}^{ij}}{x_\nu^j} \right) S_{\mu\nu} A_{mn}. \quad (5)$$

It will now be assumed that the displacements of atoms (ions) are small, and that the averages of odd powers of displacements vanish for large interatomic vectors. Under these conditions, the exponential terms in these displacements (Δ 's) can be approximated by a series expansion:

$$\begin{aligned} \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle &= \langle 1 + i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij} - \frac{1}{2}(\mathbf{k} \cdot \Delta_{\mu\nu}^{ij})^2 \\ &\quad - \frac{i}{3!}(\mathbf{k} \cdot \Delta_{\mu\nu}^{ij})^3 + \frac{1}{4!}(\mathbf{k} \cdot \Delta_{\mu\nu}^{ij})^4 + \dots, \\ &\simeq \exp(-\frac{1}{2}\langle(\mathbf{k} \cdot \Delta_{\mu\nu}^{ij})^2\rangle) \\ &\quad \times [1 + i\langle\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}\rangle], \\ &= \exp[-\frac{1}{2}\langle(\mathbf{k} \cdot \Delta_\mu^i)^2\rangle] \\ &\quad \times \exp(-\frac{1}{2}\langle(\mathbf{k} \cdot \Delta_\nu^j)^2\rangle) \\ &\quad \times \exp(\langle\mathbf{k} \cdot \Delta_\mu^i \mathbf{k} \cdot \Delta_\nu^j\rangle) \\ &\quad \times [1 + i\langle\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}\rangle], \end{aligned} \quad (6a)$$

or

$$\begin{aligned} \langle \exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}) \rangle &\simeq \exp(-M_i) \exp(-M_j) \\ &\quad \times \exp(\langle\mathbf{k} \cdot \Delta_\mu^i \mathbf{k} \cdot \Delta_\nu^j\rangle) \\ &\quad \times (1 + i\langle\mathbf{k} \cdot \Delta_{\mu\nu}^{ij}\rangle). \end{aligned} \quad (6b)$$

A comparison of the expansion of (6b) and the expansion of $\exp(i\mathbf{k} \cdot \Delta_{\mu\nu}^{ij})$ will show that the two are identical out to quadratic terms. Beyond these terms, the expansions each include several plus and minus terms which tend to cancel especially if displacements are uncorrelated. Remaining higher-order terms are similar except for weighting factors which differ by two or three. Without this approximation either the effect of all higher-order terms must be neglected, that is, there is no term $\exp(-M_j)$, or the term M_i must vary with interatomic vector (Walker & Keating, 1961). The third exponential in (6b) is now expanded and substituted into (3b) and (3c) and $(1 - P_{\mu\nu}^{ij}/x_\nu^j)$ is set equal to $\alpha_{\mu\nu}^{ij}$. The intensity may then be written in terms of moments of the expansion, with superscripts indicating the order of the moment and f_i implying $f_i \exp(-M_i)$.

$$I_{\text{AVE}}^0 = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j S_{\mu\nu} A_{mn}, \quad (7a)$$

$$I_{\text{AVE}}^1 = i \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle S_{\mu\nu} A_{mn}, \quad (7b)$$

$$I_{\text{AVE}}^2 = \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \mathbf{k} \cdot \Delta_\mu^i \mathbf{k} \cdot \Delta_\nu^j \rangle S_{\mu\nu} A_{mn}, \quad (7c)$$

$$I_{\text{AVE}}^3 = i \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \mathbf{k} \cdot \Delta_\mu^i \mathbf{k} \cdot \Delta_\nu^j \rangle \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle S_{\mu\nu} A_{mn}, \quad (7d)$$

$$I_{\text{AVE}}^4 = \frac{1}{2} \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j x_\mu^i x_\nu^j f_i f_j \times \langle \mathbf{k} \cdot \Delta_\mu^i \mathbf{k} \cdot \Delta_\nu^j \rangle^2 S_{\mu\nu} A_{mn}, \quad (7e)$$

etc.

$$I_{\text{L.O.}}^0 = \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i \neq j} x_\mu^i x_\nu^j f_i' (f_i' - f_j') \times \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}, \quad (8a)$$

$$I_{\text{L.O.}}^1 = i \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i \neq j} x_\mu^i x_\nu^j f_i' (f_i' \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle - f_j' \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}, \quad (8b)$$

$$I_{\text{L.O.}}^2 = i \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i \neq j} x_\mu^i x_\nu^j f_i' (f_i' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle - f_j' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}, \quad (8c)$$

$$I_{\text{L.O.}}^3 = i \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i \neq j} x_\mu^i x_\nu^j f_i' \times (f_i' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle - f_j' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}, \quad (8d)$$

$$I_{\text{L.O.}}^4 = \frac{1}{2} \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i \neq j} x_\mu^i x_\nu^j f_i' \times (f_i' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle^2 - f_j' \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle^2) \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}, \quad (8e)$$

etc.

Equation (7a) represents Bragg peaks as may be readily seen by rearrangement:

$$\begin{aligned} I_{\text{AVE}}^0 &= \sum_m \sum_n \left(\sum_\mu \sum_i x_\mu^i f_i' S_\mu \right) \left(\sum_\nu \sum_j x_\nu^j f_j' S_{-\nu} \right) A_{mn} \\ &= \sum_m \sum_n \left(\sum_\mu f_\mu' S_\mu \right) \left(\sum_\nu f_\nu' S_{-\nu} \right) A_{mn}, \\ &= \sum_m \sum_n FF^* A_{mn}. \end{aligned} \quad (9)$$

Equation (8a) represents the intensity due to local order (clustering or short-range order) of atoms or ions, I_{SRO} , and it can be written as:

$$I_{\text{SRO}} = \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i > j} x_\mu^i x_\nu^j (f_i' - f_j')^2 \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (10)$$

The $m\mu = n\nu$ term gives the 'Laue monotonic', i.e.

$$I_{\text{L.M.}} = N \sum_\mu \sum_{i > j} x_\mu^i x_\mu^j (f_i' - f_j')^2. \quad (11)$$

By dividing and multiplying (10) by this Laue monotonic scattering,

$$I_{\text{SRO}} = \frac{I_{\text{L.M.}}}{N} \sum_m \sum_n \sum_\mu \sum_\nu \sum_{i > j} \frac{x_\mu^i x_\nu^j (f_i' - f_j')^2}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2} \alpha_{\mu\nu}^{ij} S_{\mu\nu} A_{mn}. \quad (12)$$

The α coefficients vanish at large interatomic distances. Therefore, the sum over m, n, μ, ν can be replaced by N times a single sum over interatomic vectors $l\mathbf{a}_1 + m\mathbf{a}_2 + n\mathbf{a}_3$:

$$I_{\text{SRO}} = I_{\text{L.M.}} \sum_l \sum_m \sum_n \times \left[\sum_{i' > j'} \frac{x_{\mu'}^{i'} x_{\nu'}^{j'} (f_{i'}' - f_{j'}')^2 \alpha_{\mu\nu}^{i'j'}(lmn)}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2} \right]_{\mu\nu} A_{lmn}. \quad (13)$$

The brackets $[\]_{\mu\nu}$ imply the summation over all possible combinations of sublattices with a given l, m, n .

The first moments from both local order and the average lattice (7b and 8b) involve average displacements, and are thus due to static, not dynamic displacements. They can be combined to give a term similar to the well known 'modulation' from binary alloys [see Sparks & Borie (1966) for a discussion of this term for alloys]:

$$\begin{aligned} I^1 &= I_{\text{AVE}}^1 + I_{\text{L.O.}}^1, \\ &= i \sum_m \sum_n \sum_\mu \sum_\nu \sum_i [x_\mu^i x_\nu^j f_i'^2 \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle \\ &\quad + \sum_{j(\neq i)} x_\mu^i x_\nu^j f_i' f_j' \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle + \sum_{j(\neq i)} x_\mu^i x_\nu^j f_i'^2 \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle \alpha_{\mu\nu}^{ij} \\ &\quad - \sum_{j(\neq i)} x_\mu^i x_\nu^j f_i' f_j' \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle \alpha_{\mu\nu}^{ij}] S_{\mu\nu} A_{mn}, \\ &= i \frac{I_{\text{L.M.}}}{N} \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \\ &\quad \times \left[\frac{x_\mu^i f_i'^2 (x_\nu^j + \sum_{j(\neq i)} x_\nu^j \alpha_{\mu\nu}^{ij})}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2} \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle \right. \\ &\quad \left. + \sum_{j(\neq i)} \frac{x_\mu^i x_\nu^j f_i' f_j' (1 - \alpha_{\mu\nu}^{ij})}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2} \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle \right] S_{\mu\nu} A_{mn}. \end{aligned} \quad (14)$$

Defining:

$$F_{\mu\nu}^{ii} = \frac{x_\mu^i f_i'^2 (x_\nu^j + \sum_{j(\neq i)} x_\nu^j \alpha_{\mu\nu}^{ij})}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2}, \quad (15a)$$

and

$$F_{\mu\nu}^{ij} = \frac{x_\mu^i x_\nu^j f_i' f_j' (1 - \alpha_{\mu\nu}^{ij})}{\sum_{\mu'} \sum_{i' > j'} x_{\mu'}^{i'} x_{\mu'}^{j'} (f_{i'}' - f_{j'}')^2}, \quad (15b)$$

equation (14) becomes:

$$\begin{aligned} I^1 &= i \frac{I_{\text{L.M.}}}{N} \sum_m \sum_n \sum_\mu \sum_\nu \sum_i \sum_j F_{\mu\nu}^{ij} \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle S_{\mu\nu} A_{mn}, \\ &= i I_{\text{L.M.}} \sum_l \sum_m \sum_n \left[\sum_i \sum_j F_{\mu\nu}^{ij} \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle_{lmn} \right]_{\mu\nu} A_{lmn}. \end{aligned} \quad (16)$$

With identical manipulations, the second moments can be combined. These represent thermal diffuse scattering (TDS) in the harmonic approximation and the analog to Huang intensity in binary alloys, due to mean-square static displacements of ions from their average positions in the structure:

$$I^2 = I_{\text{L.M.}} \sum_l \sum_m \sum_n \left[\sum_i \sum_j F_{\mu\nu}^{ij} \langle \mathbf{k} \cdot \Delta_{\mu\mathbf{k}}^i \cdot \Delta_{\nu}^j \rangle_{lmn} \right]_{\mu\nu} A_{lmn}. \quad (17)$$

Similarly the third and fourth moments can be combined, the latter corresponding to second-order TDS:

$$I^3 = iL_{L.M.} \sum_l \sum_m \sum_n \left[\sum_i \sum_j F_{\mu\nu}^{ij} \times \langle \mathbf{k} \cdot \Delta_{\mu}^i \mathbf{k} \cdot \Delta_{\nu}^j \rangle \langle \mathbf{k} \cdot \Delta_{\mu\nu}^{ij} \rangle_{lmn} \right]_{\mu\nu} A_{lmn}, \quad (18)$$

$$I^4 = \frac{1}{2} L_{L.M.} \sum_l \sum_m \sum_n \left[\sum_i \sum_j F_{\mu\nu}^{ij} \times \langle \mathbf{k} \cdot \Delta_{\mu}^i \mathbf{k} \cdot \Delta_{\nu}^j \rangle_{lmn}^2 \right]_{\mu\nu} A_{lmn}. \quad (19)$$

The third and fourth-order terms will be discussed in § 4. We consider now only terms to the second moment. The vector products are simplified by substituting the following equations:

$$\mathbf{k} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3), \quad (20a)$$

$$\Delta_{\mu}^i = \Delta_{\mu}^{1i}\mathbf{a}_1 + \Delta_{\mu}^{2i}\mathbf{a}_2 + \Delta_{\mu}^{3i}\mathbf{a}_3. \quad (20b)$$

The expression for the total diffuse intensity can then be written as follows, with p representing a component of the coordinate system in reciprocal space:

$$\frac{I_D}{I_{L.M.}} = I'_{\text{SRO}} + \sum_p Q^p h_p + \sum_p R^p h_p^2 + \sum_p S^{p,p+1} h_p h_{p+1}, \quad (21)$$

$$I'_{\text{SRO}} = \sum_l \sum_m \sum_n \bar{\alpha}_{lmn} A_{lmn}, \quad (22a)$$

$$Q^p = i \sum_l \sum_m \sum_n \bar{\gamma}_{lmn}^p A_{lmn}, \quad (22b)$$

$$R^p = \sum_l \sum_m \sum_n \bar{\delta}_{lmn}^p A_{lmn}, \quad (22c)$$

$$S^{p,p+1} = \sum_l \sum_m \sum_n \bar{\epsilon}_{lmn}^{p,p+1} A_{lmn}, \quad (22d)$$

$$\bar{\alpha}_{lmn} = \sum_{i>j} \sum_j \left[\frac{x_{\mu}^i x_{\nu}^j (f_i - f_j)^2}{\sum_{\mu'} \sum_{i>j} x_{\mu'}^i x_{\nu'}^j (f_i - f_j)^2} \alpha_{\mu\nu}^{ij}(lmn) \right]_{\mu\nu}, \quad (23a)$$

$$\bar{\gamma}_{lmn}^p = 2\pi \left[\sum_i \sum_j F_{\mu\nu}^{ij} \langle \Delta_{\mu\nu}^{pij} \rangle_{lmn} \right]_{\mu\nu}, \quad (23b)$$

$$\bar{\delta}_{lmn}^p = 4\pi^2 \left[\sum_i \sum_j F_{\mu\nu}^{ij} \langle \Delta_{\mu}^{pi} \Delta_{\nu}^{pj} \rangle_{lmn} \right]_{\mu\nu}, \quad (23c)$$

$$\bar{\epsilon}_{lmn}^p = 8\pi^2 \left[\sum_i \sum_j F_{\mu\nu}^{ij} \langle \Delta_{\mu}^{pi} \Delta_{\nu}^{p+1,j} \rangle_{lmn} \right]_{\mu\nu}. \quad (23d)$$

Table 1. Sublattice fractions and sublattice vectors for the Fe_xO system

Type of sublattice	Sublattice vector	Oxygen	Sublattice fractions*	
			Iron	Vacancy
F.c.c.	0,0,0	$x_F^O = 1$	$x_F^{\text{Fe}} = 0$	$x_V^{\text{Fe}} = 0$
Octahedral	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$x_O^O = 0$	$x_O^{\text{Fe}} = x - 2x_F^{\text{Fe}}$	$x_V^O = 1 - (x - 2x_F^{\text{Fe}})$
Tetrahedral 1	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	$x_{T_1}^O = 0$	$x_{T_1}^{\text{Fe}} = x_F^{\text{Fe}}$	$x_{T_1}^V = 1 - x_F^{\text{Fe}}$
Tetrahedral 2	$\frac{3}{4}, \frac{3}{4}, \frac{3}{4}$	$x_{T_2}^O = 0$	$x_{T_2}^{\text{Fe}} = x_F^{\text{Fe}}$	$x_{T_2}^V = 1 - x_F^{\text{Fe}}$

* x is the ratio of total number of iron to total number of oxygen ions (as in Fe_xO). Superscripts denote the kind of iron, subscripts the site.

It was first pointed out for binary alloys by Sparks & Borie (1966) and Borie & Sparks (1971) that the terms in (21) can be separated because of their different symmetries in reciprocal space. This will be considered for these more complex materials in § 3. But first in § 2 some examples will be given of the direct manner by which these equations can be simplified for specific systems. For simplicity, the primes on the scattering factors will no longer be employed.

2. Applications to specific systems

A. Fe_xO

In wüstite (Fe_xO) the oxygen ions form a complete f.c.c. structure. However, the octahedral cation sites are partially filled by iron ions, the rest of the sites being vacant (Jette & Foote, 1933). In addition, there are iron ions in tetrahedral sites (Koch & Cohen, 1969); in what follows the two sets of tetrahedral sites are referred to as 'Tet 1' and 'Tet 2'. At low temperatures, there is a clustering of vacancies and tetrahedral ions and the clusters exhibit a long-range order with space group $Pm\bar{3}m$ or $P4\bar{3}m$. At high temperature, the structure is that of NaCl, space group $Fm\bar{3}m$, with only local atomic order. Pertinent information concerning these arrangements is summarized in Table 1. Substituting the values in this table into (11) yields:

$$I_{L.M.} = N(x_O^{\text{Fe}} x_O^V + 2x_{T_1}^{\text{Fe}} x_{T_2}^V) f_{\text{Fe}}^2. \quad (24)$$

The term N is the total number of lattice points (not sublattices).

Table 2. The three types of interatomic vectors and the corresponding sublattice pairs, Fe_xO

Type of lmn *	Possible sublattice pairs
1. l, m, n all $[2p]/4$ $l+m+n=[4q]/4$	F.c.c.-F.c.c., Oct-Oct, Tet1-Tet1, Tet2-Tet2
2. l, m, n all $[2p]/4$ $l+m+n=[4q+2]/4$	F.c.c.-Oct, Oct-F.c.c., Tet1-Tet2, Tet2-Tet1
3. l, m, n all $[2p+1]/4$	F.c.c.-Tet1, F.c.c.-Tet2, Oct-Tet1, Oct-Tet2, Tet1-F.c.c., Tet2-F.c.c., Tet1-Oct, Tet2-Oct

* p and q are integers.

The sublattice vectors are given in Table 2. Direct substitution into (23a) for type 1 vectors yields:

$$\bar{\alpha}_{lmn} = \frac{x_O^{\text{Fe}} x_O^{\text{V}} \alpha_{OO}^{\text{FeV}} + 2x_T^{\text{Fe}} x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})}; \quad (25a)$$

for type 2 vectors:

$$\bar{\alpha}_{lmn} = \frac{2x_T^{\text{Fe}} x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})}; \quad (25b)$$

for type 3 vectors:

$$\bar{\alpha}_{lmn} = \frac{2(x_O^{\text{Fe}} x_T^{\text{V}} \alpha_{OT}^{\text{FeV}} + x_T^{\text{Fe}} x_O^{\text{V}} \alpha_{TO}^{\text{FeV}})}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})}. \quad (25c)$$

When the intensity is separated into its component terms (see § 3) and I_{SRO} is Fourier transformed, it is the $\bar{\alpha}$'s that are obtained, but not the $\alpha_{\mu\nu}^{ij}$. If enough information is obtained from (25b) to plot α_{TT}^{FeV} vs. interatomic distance, values can be extrapolated to Type I interatomic vectors and subtracted to obtain α_{OO}^{FeV} . Furthermore, for wüstite, typically $x_O^{\text{Fe}} = 0.9$, $x_O^{\text{V}} = 0.1$, $x_T^{\text{Fe}} = 0.015$ and $x_T^{\text{V}} = 0.985$. Then $0.0 > x_T^{\text{Fe}} x_O^{\text{V}} \alpha_{OT}^{\text{FeV}} > -0.001$ whereas $0.887 > x_O^{\text{Fe}} x_T^{\text{V}} \alpha_{TO}^{\text{FeV}} > -0.013$. Thus the last term in (25c) can be ignored to a first approximation.

Proceeding in the same manner, the coefficients of the size-effect modulation, the γ 's, (23b) can be evaluated.

(i) Type 1 vectors:

$$\begin{aligned} \bar{\gamma}_{lmn} &= \gamma_{FF}^x + \gamma_{OO}^x + \gamma_{T1T1}^x + \gamma_{T2T2}^x \\ &= 2\pi[F_{FF}^{\text{OO}} \langle x_{FF}^{\text{OO}} \rangle + F_{OO}^{\text{FeFe}} \langle x_{OO}^{\text{FeFe}} \rangle + F_{OO}^{\text{FeV}} \langle x_{OO}^{\text{FeV}} \rangle \\ &\quad + F_{OO}^{\text{VFe}} \langle x_{OO}^{\text{VFe}} \rangle + F_{OO}^{\text{VV}} \langle x_{OO}^{\text{VV}} \rangle + 2(F_{TT}^{\text{FeFe}} \langle x_{TT}^{\text{FeFe}} \rangle \\ &\quad + F_{TT}^{\text{FeV}} \langle x_{TT}^{\text{FeV}} \rangle + F_{TT}^{\text{VFe}} \langle x_{TT}^{\text{VFe}} \rangle + F_{TT}^{\text{VV}} \langle x_{TT}^{\text{VV}} \rangle)]. \end{aligned} \quad (26b)$$

Since the average displacements for any inter- or intrasublattice must be zero, the following relation must hold:

$$\sum_i \sum_j x_{\mu}^i p_{\mu\nu}^{ij} \langle x_{\mu\nu}^{ij} \rangle = 0, \quad (27)$$

for any set of μ and ν . This yields the following relations for type 1 vectors.

$$\langle x_{FF}^{\text{OO}} \rangle = 0, \quad (28a)$$

$$\begin{aligned} x_O^{\text{Fe}} P_{OO}^{\text{FeFe}} \langle x_{OO}^{\text{FeFe}} \rangle + x_O^{\text{Fe}} P_{OO}^{\text{FeV}} \langle x_{OO}^{\text{FeV}} \rangle \\ + x_O^{\text{V}} P_{OO}^{\text{VFe}} \langle x_{OO}^{\text{VFe}} \rangle + x_O^{\text{V}} P_{OO}^{\text{VV}} \langle x_{OO}^{\text{VV}} \rangle = 0, \end{aligned} \quad (28b)$$

$$\begin{aligned} x_T^{\text{Fe}} P_{TT}^{\text{FeFe}} \langle x_{TT}^{\text{FeFe}} \rangle + x_T^{\text{Fe}} P_{TT}^{\text{FeV}} \langle x_{TT}^{\text{FeV}} \rangle + x_T^{\text{V}} P_{TT}^{\text{VFe}} \langle x_{TT}^{\text{VFe}} \rangle \\ + x_T^{\text{V}} P_{TT}^{\text{VV}} \langle x_{TT}^{\text{VV}} \rangle = 0. \end{aligned} \quad (28c)$$

Equation (28b) is written in terms of α_{OO}^{FeV} :

$$\begin{aligned} x_O^{\text{V}} x_O^{\text{Fe}} (1 - \alpha_{OO}^{\text{FeV}}) (\langle x_{OO}^{\text{FeV}} \rangle + \langle x_{OO}^{\text{VFe}} \rangle) \\ = -(x_O^{\text{Fe}2} + x_O^{\text{Fe}} x_O^{\text{V}} \alpha_{OO}^{\text{FeV}}) \langle x_{OO}^{\text{FeFe}} \rangle \\ - (x_O^{\text{V}2} + x_O^{\text{Fe}} x_O^{\text{V}} \alpha_{OO}^{\text{FeV}}) \langle x_{OO}^{\text{VV}} \rangle. \end{aligned} \quad (29a)$$

Similarly the third equation becomes:

$$\begin{aligned} x_T^{\text{V}} x_T^{\text{Fe}} (1 - \alpha_{TT}^{\text{FeV}}) (\langle x_{TT}^{\text{FeV}} \rangle + \langle x_{TT}^{\text{VFe}} \rangle) \\ = -(x_T^{\text{Fe}2} + x_T^{\text{Fe}} x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}) \langle x_{TT}^{\text{FeFe}} \rangle \\ - (x_T^{\text{V}2} + x_T^{\text{Fe}} x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}) \langle x_{TT}^{\text{VV}} \rangle. \end{aligned} \quad (29b)$$

By substituting these relationships into $\bar{\gamma}_{lmn}^x$ for type 1 vectors with $f_{\text{v}} = 0$, and employing equations (15):

$$\begin{aligned} \bar{\gamma}_{lmn}^x &= \frac{2\pi}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})} [x_O^{\text{Fe}} (x_O^{\text{Fe}} + x_O^{\text{V}} \alpha_{OO}^{\text{FeV}}) \langle x_{OO}^{\text{FeFe}} \rangle \\ &\quad + 2x_T^{\text{Fe}} (x_T^{\text{Fe}} + x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}) \langle x_{TT}^{\text{FeFe}} \rangle]. \end{aligned} \quad (30)$$

(ii) Proceeding in the same way for type 2 vectors:

$$\bar{\gamma}_{lmn}^x = \gamma_{FO}^x + \gamma_{OF}^x + \gamma_{T1T2}^x + \gamma_{T2T1}^x, \quad (31a)$$

$$\bar{\gamma}_{lmn}^x = \frac{4\pi}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})} x_T^{\text{Fe}} (x_T^{\text{Fe}} + x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}) \langle x_{TT}^{\text{FeFe}} \rangle. \quad (31b)$$

(iii) Type 3 vectors:

$$\begin{aligned} \bar{\gamma}_{lmn}^x &= \gamma_{FT1}^x + \gamma_{FT2}^x + \gamma_{OT1}^x + \gamma_{OT2}^x \\ &\quad + \gamma_{T1F}^x + \gamma_{T1O}^x + \gamma_{T2F}^x + \gamma_{T2O}^x, \end{aligned} \quad (32)$$

$$\begin{aligned} \bar{\gamma}_{lmn}^x &= \frac{2\pi}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}})} 2[x_O^{\text{Fe}} (x_T^{\text{Fe}} + x_T^{\text{V}} \alpha_{OT}^{\text{FeV}}) \langle x_{OT}^{\text{FeFe}} \rangle \\ &\quad + x_T^{\text{Fe}} (x_O^{\text{Fe}} + x_O^{\text{V}} \alpha_{TO}^{\text{FeV}}) \langle x_{TO}^{\text{FeFe}} \rangle]. \end{aligned} \quad (33)$$

From extrapolations of displacements for type 2 vectors x_{TT}^{FeFe} may be estimated for type 1 vectors and hence the term x_{OO}^{FeFe} is obtained. As the two displacements for type 3 vectors are essentially identical, all displacements can be obtained. This is more detailed information than is obtainable for metallic alloys, where individual displacements cannot be isolated. For metallic alloys ratios of scattering factors appear in the γ 's and it has been generally assumed in the separation procedure that these do not vary over the volume in reciprocal space where measurements are made to obtain the modulation term involving the γ 's. There are no scattering factor ratios in the γ 's for Fe_xO so they are true Fourier coefficients and should be obtainable with higher precision than for metallic systems. This result will always occur when vacancies are involved.

We now proceed to the other coefficients, the terms δ and ϵ which involve mean-square displacements and cross products of displacements. There are no simplifying relationships for these terms. Hence for δ , (23c) with (15):

$$\begin{aligned} \bar{\delta}_{lmn}^x &= \delta_{FF}^x + \delta_{OO}^x + \delta_{T1T1}^x + \delta_{T2T2}^x, \end{aligned} \quad (34a)$$

$$\begin{aligned} &= \frac{4\pi^2}{(x_O^{\text{Fe}} x_O^{\text{V}} + 2x_T^{\text{Fe}} x_T^{\text{V}}) f_{\text{Fe}}^2} [f_{\text{O}}^2 \langle x_{\text{F}}^{\text{O}} x_{\text{F}}^{\text{O}} \rangle + x_O^{\text{Fe}} f_{\text{Fe}}^2 \\ &\quad \times (x_O^{\text{Fe}} + x_O^{\text{V}} \alpha_{OO}^{\text{FeV}}) \langle x_{\text{O}}^{\text{Fe}} x_{\text{O}}^{\text{Fe}} \rangle \\ &\quad + 2x_T^{\text{Fe}} f_{\text{Fe}}^2 (x_T^{\text{Fe}} + x_T^{\text{V}} \alpha_{TT}^{\text{FeV}}) \langle x_{\text{T}}^{\text{Fe}} x_{\text{T}}^{\text{Fe}} \rangle]. \end{aligned} \quad (34b)$$

(ii) Type 2 vectors:

$$\bar{\delta}_{lmn}^x = \delta_{FO}^x + \delta_{OF}^x + \delta_{T1T2}^x + \delta_{T2T1}^x, \quad (35a)$$

$$= \frac{4\pi^2}{(x_O^{Fe} x_O^V + 2x_T^{Fe} x_T^V) f_{Fe}^2} [x_O^{Fe} f_O f_{Fe} \langle x_F^O x_O^{Fe} \rangle$$

$$+ x_O^{Fe} f_{Fe} f_O \langle x_O^{Fe} x_F^O \rangle$$

$$+ 2x_T^{Fe} f_{Fe}^2 (x_T^{Fe} + x_T^V \alpha_{TT}^{FeV}) \langle x_T^{Fe} x_T^{Fe} \rangle]. \quad (35b)$$

(iii) Type 3 vectors:

$$\bar{\delta}_{lmn}^x = \delta_{FT1}^x + \delta_{FT2}^x + \delta_{OT1}^x$$

$$+ \delta_{OT2}^x + \delta_{T1F}^x + \delta_{T1O}^x + \delta_{T2F}^x + \delta_{T2O}^x, \quad (36a)$$

$$= \frac{4\pi^2}{(x_O^{Fe} x_O^V + 2x_T^{Fe} x_T^V) f_{Fe}^2} 2[x_T^{Fe} f_O f_{Fe} \langle x_F^O x_T^{Fe} \rangle$$

$$+ x_T^{Fe} f_{Fe} f_O \langle x_T^{Fe} x_O^V \rangle + \langle x_O^{Fe} f_{Fe}^2$$

$$\times (x_T^{Fe} + x_T^V \alpha_{OT}^{FeV}) \langle x_O^{Fe} x_T^{Fe} \rangle$$

$$+ x_T^{Fe} f_{Fe}^2 (x_O^{Fe} + x_O^V \alpha_{TO}^{FeV}) \langle x_T^{Fe} x_O^{Fe} \rangle]. \quad (36b)$$

For the ϵ 's in (23d):

(i) Type 1 vectors:

$$\bar{\epsilon}_{lmn}^{xy} = \epsilon_{FF}^{xy} + \epsilon_{OO}^{xy} + \epsilon_{T1T1}^{xy} + \epsilon_{T2T2}^{xy}, \quad (37a)$$

$$= \frac{8\pi^2}{(x_O^{Fe} x_O^V + 2x_T^{Fe} x_T^V) f_{Fe}^2} [f_O^2 \langle x_F^O y_F^O \rangle + x_O^{Fe} f_{Fe}^2$$

$$\times (x_O^{Fe} + x_O^V \alpha_{OO}^{FeV}) \langle x_O^{Fe} y_O^{Fe} \rangle$$

$$+ 2x_T^{Fe} f_{Fe}^2 (x_T^{Fe} + x_T^V \alpha_{TT}^{FeV}) \langle x_T^{Fe} y_T^{Fe} \rangle]. \quad (37b)$$

(ii) Type 2 vectors:

$$\bar{\epsilon}_{lmn}^{xy} = \epsilon_{FO}^{xy} + \epsilon_{OF}^{xy} + \epsilon_{T1T2}^{xy} + \epsilon_{T2T1}^{xy}, \quad (38a)$$

$$= \frac{8\pi^2}{(x_O^{Fe} x_O^V + 2x_T^{Fe} x_T^V) f_{Fe}^2} [x_O^{Fe} f_O f_{Fe} \langle x_F^O y_O^{Fe} \rangle$$

$$- x_O^{Fe} f_{Fe} f_O \langle x_O^{Fe} y_F^O \rangle$$

$$+ 2x_T^{Fe} f_{Fe}^2 (x_T^{Fe} + x_T^V \alpha_{TT}^{FeV}) \langle x_T^{Fe} y_T^{Fe} \rangle]. \quad (38b)$$

(iii) Type 3 vectors:

$$\bar{\epsilon}_{lmn}^{xy} = \epsilon_{FT1}^{xy} + \epsilon_{FT2}^{xy} + \epsilon_{OT1}^{xy}$$

$$+ \epsilon_{OT2}^{xy} + \epsilon_{T1F}^{xy} + \epsilon_{T1O}^{xy} + \epsilon_{T2F}^{xy} + \epsilon_{T2O}^{xy}, \quad (39a)$$

$$= \frac{8\pi^2}{(x_O^{Fe} x_O^V + 2x_T^{Fe} x_T^V) f_{Fe}^2} 2[x_T^{Fe} f_O f_{Fe} \langle x_F^O x_T^{Fe} \rangle$$

$$+ x_T^{Fe} f_{Fe} f_O \langle x_T^{Fe} y_F^O \rangle$$

$$+ x_O^{Fe} f_{Fe}^2 (x_T^{Fe} + x_T^V \alpha_{OT}^{FeV}) \langle x_O^{Fe} y_T^{Fe} \rangle$$

$$+ x_T^{Fe} f_{Fe}^2 (x_O^{Fe} + x_O^V \alpha_{TO}^{FeV}) \langle x_T^{Fe} y_O^{Fe} \rangle]. \quad (39b)$$

B. (Fe, Mg)O

Another useful example is a solid solution of oxides, exemplified by the rocksalt structure of (Fe, Mg)O. Depending on the partial pressure of oxygen, there is some trivalent iron present and hence there are some cation vacancies for charge neutrality, but their concentration is too small to detect by diffuse scattering. There is no tetrahedral occupation. Accordingly, we will assume that both sublattices in the NaCl structure are full. The pertinent sublattice concentrations are

given in Table 3 and the types of sublattices in Table 4. With these tables, and with A and C representing anion and cation sublattices respectively:

$$I_{L.M.} = N x_C^{Mg} x_C^{Fe} (f_{Mg} - f_{Fe})^2. \quad (40)$$

Table 3. Sublattice fractions and sublattice vectors for the (Mg, Fe)O system

Type of sublattice	Sublattice vectors	Oxygen	Magnesium	Iron
Anion	0, 0, 0	$x_A^O = 1$	$x_A^{Mg} = 0$	$x_A^{Fe} = 0$
Cation	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$	$x_C^O = 0$	x_C^{Mg}	$x_C^{Fe} = 1 - x_C^{Mg}$

* $x_C^{Mg} = 2x_{Mg}$, $x_C^{Fe} = 2x_{Fe}$, $x_A^O = 2x_O$, $x_{Mg} + x_{Fe} = 0.5$ and $x_O = 0.5$.

Table 4. The two types of interatomic vectors and the corresponding sublattice pairs, (Fe, Mg)O

Type of lmn *	Possible sublattice pairs
1 $l + m + n = [2p]/2$	Anion-Anion, Cation-Cation
2 $l + m + n = [2p + 1]/2$	Anion-Cation, Cation-Anion

* p is an integer.

For type 1 vectors, $\bar{\alpha}_{lmn} = \alpha_{AA} + \alpha_{CC} = \alpha_{CC}^{MgFe}(lmn)$ and for Type 2, $\bar{\alpha}_{lmn} = \alpha_{AC} + \alpha_{CA} = 0$. That this is so can be readily seen; the anion sublattice is completely filled by oxygen ions. Hence from the definition of $\alpha_{\mu\nu}^{ij} = 1 - P_{\mu\nu}^{ij}/x_\nu^j$, both $P_{\mu\nu}^{ij}$ and x_ν^j are unity for α_{CA} and for α_{AC}^{OFe} or α_{AC}^{OMg} both are the sublattice fraction.

For the modulation and other terms the equations can be obtained in the same way and are given in Krawitz & Cohen (1975). For example for type 1 vectors:

$$\bar{\gamma}_{lmn}^x = \gamma_{AA}^x + \gamma_{CC}^x, \quad (41a)$$

and from (15), (23b) and (26):

$$\bar{\gamma}_{lmn}^x = 2\pi [F_{AA}^{OO} \langle x_{AA}^{OO} \rangle + F_{CC}^{MgMg} \langle x_{CC}^{MgMg} \rangle$$

$$+ F_{CC}^{MgFe} \langle x_{CC}^{MgFe} \rangle + F_{CC}^{FeMg} \langle x_{CC}^{FeMg} \rangle$$

$$+ F_{CC}^{FeFe} \langle x_{CC}^{FeFe} \rangle]. \quad (41b)$$

$$\bar{\gamma}_{lmn}^x = \frac{2\pi}{x_C^{Mg} x_C^{Fe} (f_{Fe} - f_{Mg})^2} [\{(x_C^{Mg})^2 f_{Mg} (f_{Mg} - f_{Fe})$$

$$+ x_C^{Mg} x_C^{Fe} \alpha_{CC}^{MgFe} f_{Mg} (f_{Mg} - f_{Fe})\} \langle x_C^{Mg} x_C^{Mg} \rangle$$

$$+ \{(x_C^{Fe})^2 f_{Fe} (f_{Fe} - f_{Mg})$$

$$+ x_C^{Fe} x_C^{Mg} \alpha_{CC}^{MgFe} f_{Fe} (f_{Fe} - f_{Mg})\} \langle x_{CC}^{FeFe} \rangle]. \quad (41c)$$

It is interesting to note that in this system, local order involves terms in the cation sublattice only, but the displacements involve this sublattice and interaction between the cations and anions.

Any other system can be readily developed using the general equations presented here, after Tables like 1 to 4 are prepared. In the next section, we will consider the separation of the components of the diffuse intensity up to second moments, and the minimum regions required in reciprocal space for this separation. The method presupposes that single crystals are available.

While the equations could be averaged for use with powders, the difficulty in obtaining satisfactory data and analysis in this case even with metallic alloys does not seem to warrant the effort. Accurate quantitative data in this kind of study require single crystals. Following the next section on the separation, higher-order moments will be discussed.

3. Separating the contribution to diffuse scattering

For simplicity the examples of cubic systems, Fe_xO and $(\text{Mg}, \text{Fe})\text{O}$, discussed above will be employed. Ignoring third and fourth-order terms for the moment, (21) is identical to the form developed for binary alloys [see Borie & Sparks (1971), Gragg & Cohen (1971)]. Only the coefficients of the series are different, as shown in § 2. For cubic systems, the total diffuse intensity, I_D , has $m3m$ Laue symmetry in reciprocal space, that is, the intensity is symmetric across planes $h_i=0$, across planes $h_i=h_j$ and, owing to the threefold axes, $I_D(h_1, h_2, h_3) = I_D(h_2, h_3, h_1) = I_D(h_3, h_1, h_2)$. If the total intensity across these symmetry elements is written and corresponding terms equated, numerous symmetry relationships can be readily obtained and these are summarized in Table 5. It is immediately apparent that terms like $Q_y(h_1, h_2, h_3)$ and $Q_z(h_1, h_2, h_3)$ can be replaced by $Q_x(h_2, h_3, h_1)$ and $Q_x(h_3, h_1, h_2)$ respectively, and similarly for R_y, R_z, S_{yz}, S_{xz} . Thus I_D may be written:

$$\begin{aligned} I_D(h_1, h_2, h_3) = & I_{\text{SRO}}(h_1, h_2, h_3) \\ & + h_1 Q_x(h_1, h_2, h_3) + h_2 Q_x(h_2, h_3, h_1) \\ & + h_3 Q_x(h_3, h_1, h_2) + h_1^2 R_x(h_1, h_2, h_3) \\ & + h_2^2 R_x(h_2, h_3, h_1) + h_3^2 R_x(h_3, h_1, h_2) \\ & + h_1 h_2 S_{xy}(h_1, h_2, h_3) + h_2 h_3 S_{xy}(h_2, h_3, h_1) \\ & + h_3 h_1 S_{xy}(h_3, h_1, h_2). \end{aligned} \quad (42)$$

Table 5. Symmetries of the components of diffuse intensity for a cubic system

$$\begin{aligned} I_{\text{SRO}}(h_1, h_2, h_3) &= I_{\text{SRO}}(-h_1, h_2, h_3) \\ &= I_{\text{SRO}}(h_1, -h_2, h_3) = I_{\text{SRO}}(h_1, h_2, -h_3) \\ Q_x(h_1, h_2, h_3) &= -Q_x(-h_1, h_2, h_3) \\ &= Q_x(h_1, -h_2, h_3) = Q_x(h_1, h_2, -h_3) \\ R_x(h_1, h_2, h_3) &= R_x(-h_1, h_2, h_3) \\ &= R_x(h_1, -h_2, h_3) = R_x(h_1, h_2, -h_3) \\ S_{xy}(h_1, h_2, h_3) &= -S_{xy}(-h_1, h_2, h_3) \\ &= -S_{xy}(h_1, -h_2, h_3) = S_{xy}(h_1, h_2, -h_3) \\ I_{\text{SRO}}(h_1, h_2, h_3) &= I_{\text{SRO}}(h_2, h_3, h_1) = I_{\text{SRO}}(h_3, h_1, h_2) \\ Q_x(h_1, h_2, h_3) &= Q_y(h_2, h_3, h_1) = Q_z(h_3, h_1, h_2) \\ R_x(h_1, h_2, h_3) &= R_y(h_2, h_3, h_1) = R_z(h_3, h_1, h_2) \\ S_{xy}(h_1, h_2, h_3) &= S_{yz}(h_2, h_3, h_1) = S_{zx}(h_3, h_1, h_2) \\ I_{\text{SRO}}(h_1, h_2, h_3) &= I_{\text{SRO}}(h_1, h_3, h_2) \\ &= I_{\text{SRO}}(h_3, h_2, h_1) = I_{\text{SRO}}(h_2, h_1, h_3) \\ Q_x(h_1, h_2, h_3) &= Q_y(h_2, h_1, h_3) = Q_z(h_3, h_2, h_1) = Q_x(h_1, h_3, h_2) \\ R_x(h_1, h_2, h_3) &= R_y(h_2, h_1, h_3) = R_z(h_3, h_2, h_1) = R_x(h_1, h_3, h_2) \\ S_{xy}(h_1, h_2, h_3) &= S_{yz}(h_3, h_2, h_1) = S_{xy}(h_1, h_3, h_2) = S_{xy}(h_2, h_1, h_3) \end{aligned}$$

A. Separation in a volume

Fe_xO

Because of the phase factor $A_{lmn} = \exp[2\pi i(h_1 l + h_2 m + h_3 n)]$, and since l, m, n are of the form $M/4$ for this material (where M is an integer) all components, I_{SRO}, Q_x, R_x and S_{xy} have a periodicity of 4 along h_i . Accordingly, the various terms can be separated as follows:

$$\begin{aligned} R_x(h_1, h_2, h_3) = & [I_D(h_1 + 4, h_2, h_3) \\ & - 2I_D(h_1, h_2, h_3) \\ & + I_D(h_1 - 4, h_2, h_3)]/32, \end{aligned} \quad (43a)$$

$$\begin{aligned} S_{xy}(h_1, h_2, h_3) = & [I_D(h_1, h_2, h_3) - I_D(h_1 - 4, h_2, h_3) \\ & - I_D(h_1, h_2 - 4, h_3) \\ & + I_D(h_1 - 4, h_2 - 4, h_3)]/16, \end{aligned} \quad (43b)$$

$$\begin{aligned} Q_x(h_1, h_2, h_3) = & [I_D(h_1, h_2, h_3) - I_D(h_1 - 4, h_2, h_3) \\ & - (8h_1 - 16)R_x(h_1, h_2, h_3) \\ & - 4h_2 S_{xy}(h_1, h_2, h_3) \\ & - 4h_3 S_{xy}(h_3, h_1, h_2)]/4. \end{aligned} \quad (43c)$$

Once these terms are known I_{SRO} can be obtained from (42); for each value of I_{SRO} at h_1, h_2, h_3 the intensity must be known at this point and four other points as well.

From the periodicities and symmetries or antisymmetries across $h_i=0$ in Table 5, $I_{\text{SRO}}(h_1, h_2, h_3) = I_{\text{SRO}}(4 - h_1, h_2, h_3) = I_{\text{SRO}}(h_1, 4 - h_2, h_3) = I_{\text{SRO}}(h_1, h_2, 4 - h_3)$, $Q_x(h_1, h_2, h_3) = -Q_x(4 - h_1, h_2, h_3) = Q_x(h_1, 4 - h_2, h_3)$ etc. Thus only one octant of the $4 \times 4 \times 4$ unit cell in reciprocal space is required. Also from these symmetry relationships, by equating the intensities it can be readily shown that the phase factors A_{lmn} simplify considerably. Thus:

$$\begin{aligned} I_{\text{SRO}}(h_1, h_2, h_3) = & \sum_l \sum_m \sum_n \bar{\alpha}_{lmn} \cos 2\pi h_1 l \\ & \times \cos 2\pi h_2 m \cos 2\pi h_3 n. \end{aligned} \quad (44a)$$

Similarly,

$$\begin{aligned} Q_x(h_1, h_2, h_3) = & - \sum_l \sum_m \sum_n \bar{\gamma}_{lmn} \sin 2\pi h_1 l \\ & \times \cos 2\pi h_2 m \cos 2\pi h_3 n, \end{aligned} \quad (44b)$$

$$\begin{aligned} R_x(h_1, h_2, h_3) = & \sum_l \sum_m \sum_n \bar{\delta}_{lmn} \cos 2\pi h_1 l \\ & \times \cos 2\pi h_2 m \cos 2\pi h_3 n, \end{aligned} \quad (44c)$$

$$\begin{aligned} S_{xy}(h_1, h_2, h_3) = & \sum_l \sum_m \sum_n \bar{\epsilon}_{lmn}^{\text{xy}} \sin 2\pi h_1 l \\ & \times \sin 2\pi h_2 m \cos 2\pi h_3 n. \end{aligned} \quad (44d)$$

From the symmetries across $h_i=h_j$ in Table 5 [see equations (44)], the minimum volumes can be further reduced. Note particularly that Q_x and R_x are symmetric across $h_2=h_3$, but that S_{xy} is symmetric across $h_1=h_2$. Furthermore, it is easy to show that for any component:

$$\begin{aligned}
 A(h_1, h_2, h_3) &= A(h_1, h_2 + 2, h_3 + 2) \\
 &= A(h_1 + 2, h_2, h_3 + 2) \\
 &= A(h_1 + 2, h_2 + 2, h_3) . \quad (45a)
 \end{aligned}$$

This result stems from the fact that $2(l+m)$ in the phase factor is always an integer for this system and $4l$, $4m$, $4n$ are even. Combining these relationships with symmetries across $h_i=0$ and $h_i=h_j$ results in

$$\begin{aligned}
 I_{\text{SRO}}(h_1, h_2, h_3) &= I_{\text{SRO}}(h_1, h_2 + 2, h_3 + 2) \\
 &= I_{\text{SRO}}(h_1, 2 - h_2, 2 - h_3) \quad (45b)
 \end{aligned}$$

$$= I_{\text{SRO}}(h_1, 2 - h_3, 2 - h_2) , \quad (45c)$$

$$Q_x(h_1, h_2, h_3) = Q_x(h_1, 2 - h_3, 2 - h_2) , \quad (45d)$$

$$R_x(h_1, h_2, h_3) = R_x(h_1, 2 - h_3, 2 - h_2) , \quad (45e)$$

$$S_{xy}(h_1, h_2, h_3) = S_{xy}(2 - h_2, 2 - h_1, h_3) . \quad (45f)$$

Similarly,

$$I_{\text{SRO}}(h_1, h_2, h_3) = I_{\text{SRO}}(2 - h_1, h_2, 2 - h_3) , \quad (45g)$$

$$Q_x(h_1, h_2, h_3) = -Q_x(2 - h_1, h_2, 2 - h_3) , \quad (45h)$$

$$R_x(h_1, h_2, h_3) = R_x(2 - h_1, h_2, 2 - h_3) , \quad (45i)$$

$$S_{xy}(h_1, h_2, h_3) = -S_{xy}(2 - h_1, h_2, 2 - h_3) . \quad (45j)$$

The final minimum volumes for each component are shown in Fig. 1. The five required regions are brought together in Fig. 2. The volumes *a* and *b* in Fig. 2 are required in (43) for Q_x , *a*, *b*, *c* for R_x and *a*, *b*, *d*, *e* for S_{xy} . These regions have been placed close to the origin so that the size terms (which are multiplied by powers of h_i) are not too large, and yet far enough along the axes to avoid the origin. Also regions like $(h-4)$ have been replaced by $(4-h)$. These regions make up a volume $17/192$ that of the original unit cell, and can be further reduced to $15/192$ of the original volume by applying the symmetries $h_i=h_j$ to Fig. 2, resulting in the region in Fig. 3. If sampled at equal intervals of $\Delta h=0.1$, about 5000 data points are required, three times the number for a binary f.c.c. alloy. With modern high-intensity X-ray generators it is estimated that a typical measurement under computer control would take only about a week.

(Mg, Fe)O

The procedure is identical to that presented for Fe_xO and is therefore presented in abbreviated form. Components of the interatomic vectors are of the form $M/2$ so that the periodicity is two. As a result the difference equations become:

$$\begin{aligned}
 R_x(h_1, h_2, h_3) &= [I_D(h_1 + 2, h_2, h_3) - 2I_D(h_1, h_2, h_3) \\
 &\quad + I_D(h_1 - 2, h_2, h_3)]/8 , \quad (46a)
 \end{aligned}$$

$$\begin{aligned}
 S_{xy}(h_1, h_2, h_3) &= [I_D(h_1, h_2, h_3) - I_D(h_1 - 2, h_2, h_3) \\
 &\quad - I_D(h_1, h_2 - 2, h_3) \\
 &\quad + I_D(h_1 - 2, h_2 - 2, h_3)]/4 , \quad (46b)
 \end{aligned}$$

$$\begin{aligned}
 Q_x(h_1, h_2, h_3) &= I_D(h_1, h_2, h_3) - I_D(h_1, h_2 - 2, h_3) \\
 &\quad - (4h_1 - 4)R_x(h_1, h_2, h_3) \\
 &\quad - 2h_2S_{xy}(h_1, h_2, h_3) \\
 &\quad - 2h_3S_{xy}(h_3, h_1, h_2)]/2 . \quad (47)
 \end{aligned}$$

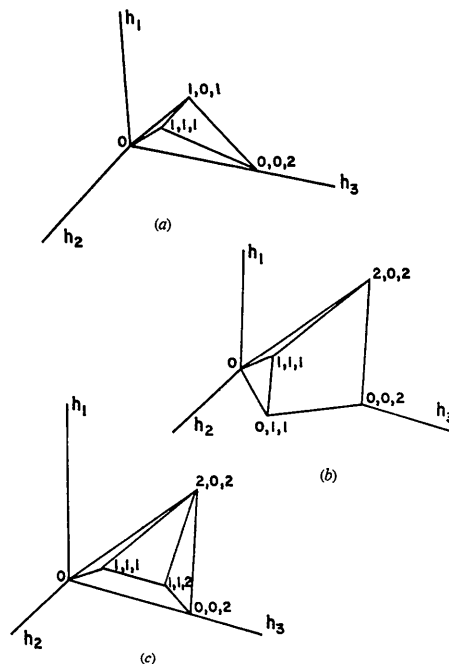


Fig. 1. Minimum repeat volume in reciprocal space (a) for I_{SRO} , (b) for Q_x and R_x , (c) for S_{xy} . For Fe_xO .

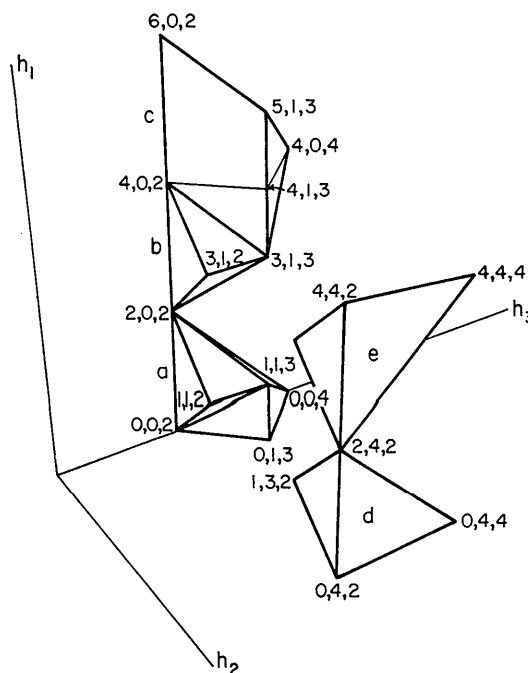


Fig. 2. The composite volume formed by the distribution of the common minimum repeat volumes. Fe_xO .

Furthermore, $I_{\text{SRO}}(h_1, h_2, h_3) = I_{\text{SRO}}(2-h_1, h_2, h_3)$ etc. $Q_x(h_1, h_2, h_3) = -Q_x(2-h_1, h_2, h_3) = Q_x(h_1, 2-h_2, h_3)$ etc. Again, only one octant is required and the last four expressions in Table 5 are employed. The five minimum volumes are shown in Fig. 4, labelled a-e in the same manner as for Fe_xO . This volume is 68/192 of the unit cell in reciprocal space and it can be reduced to 40/192 by applying the symmetry $h_i = h_j$ to yield the region in Fig. 5. This volume is $\frac{1}{3}$ that for Fe_xO .

B. Separation along lines

It has been demonstrated for binary alloys that it is sometimes possible to obtain the local-order coeffi-

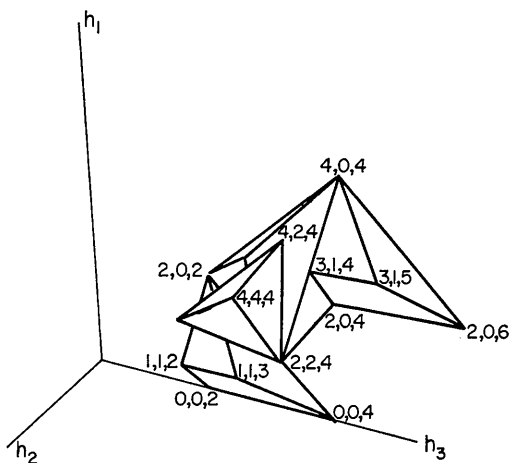


Fig. 3. The minimum volume of measurement in reciprocal space for Fe_xO .

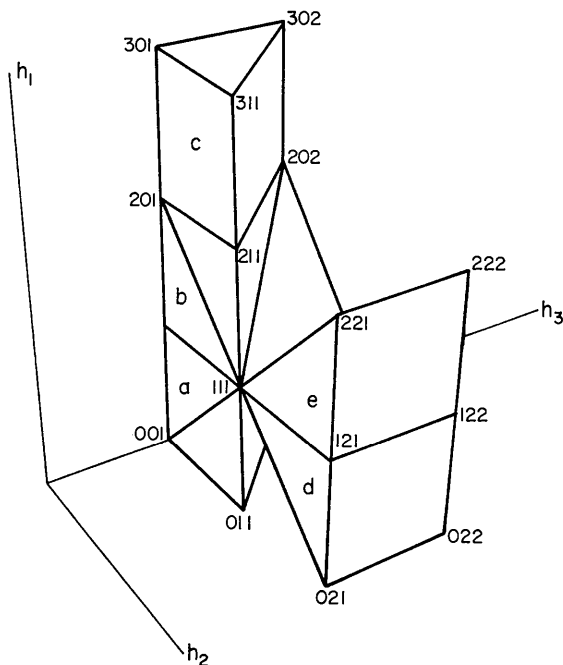


Fig. 4. The volume formed by the distribution of the common minimum repeat volumes in reciprocal space for $(\text{Fe}, \text{Mg})\text{O}$.

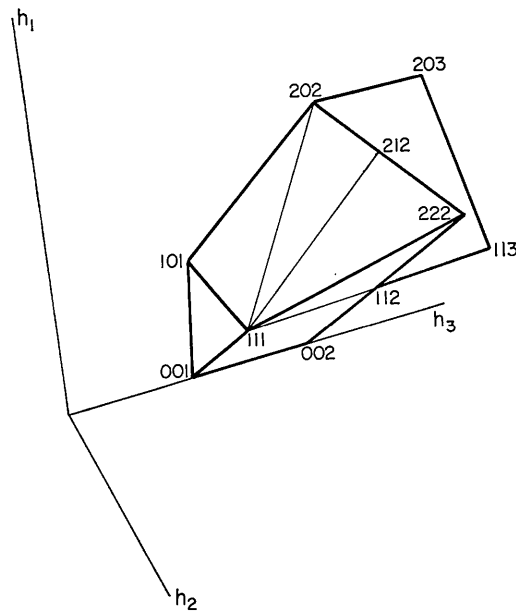


Fig. 5. The minimum separation volume in reciprocal space for the $(\text{Fe}, \text{Mg})\text{O}$ structure.

icients – but not displacements – from data only along lines in reciprocal space [Ericsson, Linde & Cohen (1971) for b.c.c. systems and Berg & Cohen (1973) for f.c.c. systems]. That is, data can be collected along selected line segments in the volumes and separated with the result that I_{SRO} is obtained along the lines, but not enough information is available to invert Q_x or other terms. If the diffuse intensity is weak and broad so that the $\bar{\alpha}$'s differ from zero only for a few neighbor shells, then I_{SRO} along the three lines $[h00]$, $[hh0]$ and $[hhh]$ can be written in terms of a few one-dimensional Fourier coefficients A_n^{hkl} . These coefficients can then be obtained by inversion and solved simultaneously for the $\bar{\alpha}$'s. The procedures for choosing the lines in the minimum volumes are amply documented in the above references. It is only worth pointing out here that for Fe_xO the resulting equations are exactly the same as for a b.c.c. alloy and for $(\text{Fe}, \text{Mg})\text{O}$ these are the same as for an f.c.c. alloy; it is only necessary to halve the coordinates lmn in each of the references, to obtain the formulae for these oxides.

4. The higher-order terms

(a) In a volume in reciprocal space

We return now to an evaluation of the third and fourth moments, equations (18) and (19). Borie (1970) has shown that for thermal diffuse scattering (TDS) higher moments can be expressed as convolutions of lower-order terms. While this procedure could be developed precisely for a pure element, Hayakawa, Bardhan & Cohen (1975) have shown that it could also be done approximately for the combined static and dynamic terms for a binary alloy. This can also be

done for the more complex situations described in this paper. In (23b-d), it will be assumed that, for a given interatomic vector lmn , all displacements are equal, regardless of the species involved.* This assumption is approximately true for even terms when dynamic displacements are dominant. For binary systems, elastic theory can be employed for the odd terms (Hayakawa, Bardhan & Cohen (1975)). Then in coordinates, p ($p=1-3$):

$$I^1 = i2\pi I_{L.M.} \sum_p \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle \Delta^p \rangle_{lmn} A_{lmn} h_p \quad (48a)$$

$$I^2 = 4\pi^2 I_{L.M.} \sum_p \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle (\Delta^p)^2 \rangle_{lmn} h_p^2 A_{lmn} + 8\pi^2 \sum_p \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle \Delta^p \Delta^{p+1} \rangle_{lmn} A_{lmn} h_p h_{p+1} \quad (48b)$$

$$I^3 = 8\pi^3 i I_{L.M.} \sum_p \sum_q \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle \Delta^p \Delta^q \rangle_{lmn} \langle \Delta^q \rangle_{lmn} A_{lmn} h_p^2 h_q + 16\pi^3 i I_{L.M.} \sum_p \sum_q \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle \Delta^p \Delta^{p+1} \rangle_{lmn} \langle \Delta^q \rangle_{lmn} A_{lmn} h_p h_{p+1} h_q \quad (48c)$$

$$I^4 = I_{L.M.} \{ 8\pi^4 \sum_p \sum_q \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle (\Delta^p)^2 \rangle_{lmn} \langle (\Delta^q)^2 \rangle_{lmn} A_{lmn} h_p^2 h_q^2 + 32\pi^4 \sum_p \sum_q \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle (\Delta^p)^2 \rangle_{lmn} \langle \Delta^q \Delta^{q+1} \rangle_{lmn} A_{lmn} h_p^2 h_q h_{q+1} + 32\pi^4 \sum_p \sum_q \sum_l \sum_m \sum_n [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \times \langle \Delta^p \Delta^{p+1} \rangle_{lmn} \langle \Delta^q \Delta^{q+1} \rangle_{lmn} A_{lmn} h_p h_{p+1} h_q h_{q+1} \}. \quad (48d)$$

Defining, from (48a):

$$\bar{\gamma}_{lmn}^p = 2\pi [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \langle \Delta^p \rangle_{lmn}, \quad (49a)$$

from (48)

$$\bar{\delta}_{lmn}^p = 4\pi^2 [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \langle (\Delta^p)^2 \rangle_{lmn}, \quad (49b)$$

and

$$\bar{\epsilon}_{lmn}^{p,p+1} = 8\pi^2 [\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} \langle \Delta^p \Delta^{p+1} \rangle_{lmn}, \quad (49c)$$

and

$$[\sum_i \sum_j F_{\mu\nu}^{ij}]_{\mu\nu} = B_{\mu\nu}. \quad (49d)$$

Then:

$$\frac{I^3}{I_{L.M.}} = i \sum_p \sum_q \sum_l \sum_m \sum_n \left\{ \frac{\bar{\delta}_{lmn}^p \bar{\gamma}_{lmn}^q}{B_{\mu\nu}} A_{lmn} h_p^2 h_q + \bar{\epsilon}_{lmn}^{p,p+1} \frac{\bar{\gamma}_{lmn}^q}{B_{\mu\nu}} A_{lmn} h_p h_{p+1} h_q \right\}, \quad (50a)$$

$$\frac{I^4}{I_{L.M.}} = \frac{1}{2} \sum_p \sum_q \sum_l \sum_m \sum_n \left\{ \frac{\bar{\delta}_{lmn}^p \bar{\delta}_{lmn}^q}{B_{\mu\nu}} (A_{lmn} h_p^2 h_q^2 + \bar{\delta}_{lmn}^p \bar{\epsilon}_{lmn}^{q,q+1} / B_{\mu\nu}) A_{lmn} h_p^2 h_q h_{q+1} + \frac{1}{2} (\bar{\epsilon}_{lmn}^{p,p+1} \bar{\epsilon}_{lmn}^{q,q+1} / B_{\mu\nu}) A_{lmn} h_p h_{p+1} h_q h_{q+1} \right\}. \quad (50b)$$

The α 's, δ 's and ϵ 's are obtained by ignoring I^3 and I^4 , with the separation described in § 3, and then these higher-order terms can be calculated. Only if these are small, can this procedure be trusted to be adequate as a correction. It is important to note that a sufficient number of Fourier coefficients are needed to properly represent the intensities. If the data is taken at intervals in h of 0.1, coefficients of lmn up to 10, 10, 10 are required to calculate I^3 and I^4 .

(b) Along lines in reciprocal space

A direct procedure for including higher-order TDS terms has been developed for linear analysis with binary alloys (Hayakawa, Bardhan & Cohen, 1975). It was shown above that the form of the general equations for I_D stays the same for the more complex materials considered in this paper, as for a binary alloy; only the coefficients of the various contributions change; therefore, the same linear procedure for higher-order terms may be applied as for a binary alloy. The total intensity along lines can be written:

$$I_D(h) = I_{SRO}(h) + hQ(h) + R(h) \{ \exp [b(h)h^2] - 1 \}. \quad (51)$$

It was shown in the given reference that $b(h)$ is a symmetric function of h . Separation equations are also given in the above reference; an additional half-period must be measured in the examples described in this paper.

5. Errors

The principal sources of error in this kind of analysis are the higher-order terms if measurement is made at high temperatures, and the assumption that the scattering-factor ratios in the size terms [the F terms, equations (15)] are independent of position in reciprocal space; this assumption is required for the separation, and for the inversion to obtain size coefficients. This is adequate for neutrons, but may not be so for X-rays. Detailed discussions of such errors for binary alloys have already been given (Gragg, Hayakawa & Cohen, 1973; Hayakawa, Bardhan & Cohen, 1975). Higher-order terms can be estimated from the equations presented here, and if they are small can be subtracted from the data in a reiteration

* More precisely, it is only necessary to assume that the $\langle \mathbf{k} \cdot \Delta \rangle$ in the first and third terms are equal and that the $\langle \mathbf{k} \cdot \Delta \mathbf{k} \cdot \Delta \rangle$ in the second, third and fourth terms are the same.

procedure. The complex but compact volume for measurement is chosen to minimize the variation in the scattering-factor ratios. Nonetheless, errors do result, and because of the complex volume it is difficult to write expressions for the errors, or to generalize from other results. The recommended procedure to estimate errors is to synthesize data in a computer with information obtained by a preliminary analysis and then to analyze this by the procedures described here. It may result that neutron techniques are required for accuracy. Alternatively, Tibballs (1975) has suggested an extension of this procedure which essentially involves measurement of the intensity in a larger volume than described here, at points where the scattering factor is different but the rest of any term is the same. The volume is already large for these systems with multiple sublattices, so the feasibility of this new procedure is as yet unknown; it is currently being tested.

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Molecular Rearrangements in Organic Crystals.

I. Potential Energy Calculations for Some Cases of Reorientational Disorder

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The pairwise potential method was applied to the study of molecular reorientations in organic crystals. Several benzene and naphthalene derivatives were considered, along with some simple heterocycles and a few more complex compounds. The results of the calculations have been matched, where possible, with the results of X-ray analysis and other experimental data. The good performance of the method is considered encouraging in view of its application to the study of more complex solid-state processes.

The most interesting feature of molecular motions and rearrangements that occur in the solid state is that crystal packing can control the process to a very high degree. A theoretical study of such phenomena requires therefore a good insight into packing forces; and, *vice versa*, a knowledge of experimental facts can throw light on crystal force fields.

The most successful theoretical approach to the problem of crystal forces for organic molecules involves the pairwise evaluation of non-bonded interactions between atoms by some kind of empirical potential (Kitaigorodskii, 1961; Kitaigorodskii & Mirskaya, 1962; for a recent review, see Kitaigorodskii, 1970); early calculations of this kind met considerable success