New Procedures for Quantitative Studies of Diffuse X-ray Scattering

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Abstract

Equations are derived for errors due to counting statistics in the determination of local order parameters and interatomic displacements from the diffuse X-ray scattering from solid solutions or nonstoichiometric compounds. The Georgopoulos–Cohen procedure is employed, which permits the determination of displacements for individual \((AA)\) and \((BB)\) pairs. It is shown that certain analysis procedures and a large variation in the ratio of scattering factors through the measured volume in reciprocal space improve the accuracy of the separation of the various contributions to the intensity with this procedure, particularly with respect to the terms due to displacements. Therefore, a short-wavelength radiation (Mo K\(\alpha\), for example) is sometimes desirable. Weighting the measured intensities with respect to the counting errors also improves the separation. The new procedures also facilitate the analysis of high-temperature measurements and data from ternary systems.

Introduction

From absolute measurements of diffuse intensities from solid solutions, non-stoichiometric compounds, etc., it is possible to obtain considerable detail on the short-range order or clustering of the species in solution, or the point defects. In particular, the local atomic arrangements and displacements can be probed. [For recent examples of such studies see Auvray, Georgopoulos & Cohen (1981), who examined GP zones in an Al–Cu alloy, and Georgopoulos & Cohen (1981), who studied the arrangements of point defects in non-stoichiometric NiAl.] Several methods have been proposed for such studies [Borie & Sparks, 1971; Williams, 1972; Georgopoulos & Cohen, 1977 (G–C)]. Errors in the first two procedures have been discussed in the literature (Gragg, Hayakawa & Cohen, 1973; Hayakawa, Bardhan & Cohen, 1975; Morinaga & Cohen, 1979). Both assume that scattering-factor (\(f\)) terms like \(f_j/\Delta f_j\), which appear in the expressions for the diffuse intensity components due to displacements, are independent of position in reciprocal space, not only in separating the various intensity contributions, but also in Fourier transforming these separated components to obtain information about interatomic displacements. Because of this assumption, satisfactory results can be obtained only when the displacements are small, especially when there is clustering. Furthermore, information on displacements is obtained as a complex sum of terms involving \((AA)\) and \((BB)\) pairs. Both of these problems are eliminated in the G–C method, which was first suggested by Tibballs (1975). This method makes use of the variation in scattering factors with \(\sin \theta/\lambda\) to separate the various contributions to the intensity. Results can be judged by several criteria. First, we define the Warren short-range-order parameter as:

\[
x_{mn}^i = 1 - \frac{P_{mn}^{ij}}{C_j},
\]

where \(P_{mn}^{ij}\) is the conditional pair probability that an atom or defect of type \(j\) is at site \(n\), if there is an \(i\) atom (or defect) at \(m\), and \(C_j\) is the atomic or sublattice fraction. The \(x\)'s are obtained by Fourier transforming the intensity due to local order, which has been separated from the intensity contributions due to displacements. Suitable criteria for a satisfactory study are then as follows:

1. \(x_{mn}^i \approx 1\), because \(P_{mn}^{ij} \approx 0\), and experimental values should be within the expected error of this value;
2. \(x_{mn}^i\) values should not differ from their maximum possible negative value, \(1 - 1/C_j\), by more than the expected error;
3. The back-calculated diffuse intensities (from the \(x\)'s and displacements) should not differ appreciably from the measured values;
4. The separated diffuse intensity components should have the proper symmetry for each term;
5. The displacements (obtained by transforming the separated intensity terms due to these displacements) should be physically reasonable.

The G–C procedure has been tested for the effects of various experimental errors via computer simulation (G–C) for a few typical cases, and recent experimental studies with the method appear to satisfy criteria 1–3 and 5 (Auvray et al., 1981; Georgopoulos & Cohen, 1981). Item (4) has not yet been examined. However, no equations for evaluating the errors in a given
experiment have been presented. It is the purpose of this paper to provide such equations for the errors due to counting statistics. Also, improvements in the technique have resulted from our considerations. These improvements facilitate analysis of measurements at high temperatures, and are helpful in considering data from ternary systems, as will be discussed.

Scattering equations

For simplicity we treat here a cubic multicomponent substitutional alloy, with one atom per lattice point. The theory is available for more complex situations (Hayakawa & Cohen, 1975). The intensity of X-ray scattering in electron units at a general position in reciprocal space described by the dimensionless co-
ordinates \( h_1, h_2, h_3 \) is (G-C):

\[
I_p(h_1, h_2, h_3) = N \left( \sum_{i<j} C_i C_j (f_i - f_j)^2 \right) + \sum_{i} C_i \sum_{j} f_j (h_1 Q_{ij}^i + h_2 Q_{ij}^j + h_3 Q_{ij}^z) + 2 \sum_{i<j} C_i C_j f_i f_j (h_1 Q_{ij}^i + h_2 Q_{ij}^j + h_3 Q_{ij}^z) + h_3 Q_{ij}^z + \sum_{i} C_i \sum_{j} f_j (h_1 R_{ij}^i + h_2 R_{ij}^j + h_3 R_{ij}^z) + h_3 R_{ij}^z + \sum_{i} C_i \sum_{j} f_j (h_1 S_{ij}^i + h_2 S_{ij}^j + h_3 S_{ij}^z) + 2 \sum_{i<j} C_i C_j f_i f_j (h_1 h_2 S_{ij}^{i\delta} + h_2 h_3 S_{ij}^{i\gamma} + h_3 h_1 S_{ij}^{i\alpha})
\]

where \( N \) is the total number of atoms in the X-ray beam and the \( i \)th constituent’s scattering factor is denoted by \( f_i \). This expression includes up to quadratic terms in the displacements. For cubic symmetry, the intensity components, \( I_{sko} \), \( Q, R, S \) are defined as follows:

\[
I_{sko}^i = \sum_{l} \sum_{m} \sum_{n} \alpha_{lmn}^i \cos 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

\[
Q_x^i = -2\pi \sum_{l} \sum_{m} \sum_{n} \left( 1 + \sum_{j=1} C_j^i \alpha_{lmn}^j \right) \times \langle X_i^{l^0} X_{lmn}^i \rangle \sin 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

\[
Q_z^i = -2\pi \sum_{l} \sum_{m} \sum_{n} (1 - \alpha_{lmn}^i) \times \langle X_i^{l^0} X_{lmn}^i \rangle \sin 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

and similarly for \( Q_y^i, Q_y^j, Q_y^j \) and \( Q_y^j \).

\[
R_x^i = 4\pi^2 \sum_{l} \sum_{m} \sum_{n} \left( 1 + \sum_{j} C_j^i \alpha_{lmn}^j \right) \times \langle X_i^{l^0} X_{lmn}^i \rangle \cos 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

\[
S_{xy}^i = -8\pi^2 \sum_{l} \sum_{m} \sum_{n} \left( 1 + \sum_{j=1} C_j^i \alpha_{lmn}^j \right) \times \langle X_i^{l^0} X_{lmn}^i \rangle \sin 2\pi h_1 l \sin 2\pi h_2 m \cos 2\pi h_3 n,
\]

\[
S_{yz}^i = -8\pi^2 \sum_{l} \sum_{m} \sum_{n} (1 - \alpha_{lmn}^i) \times \langle X_i^{l^0} X_{lmn}^i \rangle \sin 2\pi h_1 l \sin 2\pi h_2 m \cos 2\pi h_3 n.
\]

The coefficients in the angle brackets \( \langle \rangle \) of (3) are lattice averages of fractional atomic displacements from the ideal lattice sites. That is, \( \langle X_i^{l^0} X_{lmn}^i \rangle \) is the average displacement in the \( X \) direction of an \( i \) atom, located near site \( (lmn) \), when the origin is occupied by a \( j \) atom. The term \( \langle X_i^{l^0} X_{lmn}^i \rangle \) is a measure of the correlation of displacements between sites; it is the average of the product of the displacement of an \( i \) atom at site \( (lmn) \) and that of a \( j \) atom at the origin of the interatomic vector \((l+m+n)a\).

Because there is an average structure:

\[
\sum_{l} \sum_{m} \sum_{n} C_i^j P_{l^0 kn} \langle X_i^{l^0} X_{lmn}^i \rangle = 0.
\]

Therefore, one of the components due to the average static displacements (in the terms for \( \langle X \rangle \), or \( \langle Y \rangle \), or \( \langle Z \rangle \)) can be eliminated in (2). A similar elimination is not possible for the quadratic terms. For a binary alloy, this results in 25 components for the total diffuse intensity (G-C):

\[
I_p(h_1, h_2, h_3) = NC_A C_B (f_A^4 - f_B^4)^2
\]

\[
\times \langle X_A^{l^0} X_{lmn}^A \rangle \cos 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

\[
R_x^{ij} = 4\pi^2 \sum_{l} \sum_{m} \sum_{n} \left( 1 + \sum_{j} C_j^i \alpha_{lmn}^j \right) \times \langle X_i^{l^0} X_{lmn}^i \rangle \cos 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n,
\]

and similarly for \( R_y^{ij}, R_y^{ij} \) and \( R_y^{ij} \).
in which the components due to the displacements are rewritten as:

\[ Q_{AA}^4 = -2\pi \sum \sum \left( \frac{C_A}{C_B} + \alpha_{AB} \right) \sin 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n, \]

\[ R_{AA}^4 = 4\pi^2 \sum \sum \left( \frac{C_A}{C_B} + \alpha_{AB} \right) \cos 2\pi h_1 l \cos 2\pi h_2 m \cos 2\pi h_3 n, \]

etc. Also:

\[ \eta = \frac{f_A}{f_A - f_B}, \quad \xi = \frac{f_B}{f_A - f_B}. \]

By measuring the diffuse intensity at an associated set of more than 25 \( h_1, h_2, h_3 \) values, for which the intensity components each have the same or opposite value, the resultant system of equations can be solved by least squares for the individual intensity terms \( I_{SRO}, Q, R, S \) (at \( h_1, h_2, h_3 \)). Similarly, for the ternary case, there are 54 components (including three short-range-order intensity components, \( I_{SRO}^{ABC}, I_{SRO}^{BC} \) and \( I_{SRO}^{CA} \)) and more associated points are needed for solution. [General equations with this approach for multicomponent systems are given by Hayakawa & Cohen (1975).]

In solving (5) by least squares, the matrix is ill conditioned. It is to be emphasized that this conditioning is due to the coefficients of the \( Q, R, S \) terms in (5) not due to the measured intensities. It is these coefficients that constitute the matrix, and the ill conditioning occurs because the variations in \( \eta, \xi \) in reciprocal space are similar. Nonetheless, quite useful solutions with actual data can be obtained by standard least-squares procedures, provided the following steps are taken:

1. Constraints are added that relate the various components by symmetry. These merely become rows in the matrix such as \( Q_{AA}^4(h_1 h_2 h_3) - Q_{AA}^4(h_2 h_1 h_3) = 0 \).

2. A Householder transformation with iterative optimization and double precision is employed (Golub, 1965). This transformation avoids matrix inversion in obtaining the solution.

With such procedures, good values of \( I_{SRO} \) are obtained, and also for the \( Q \) terms although the error in \( Q \) is high. The individual \( K \) and \( S \) terms are highly correlated and very poor results are obtained for these quantities (see, for example, Auvray et al., 1981; Georgopoulos & Cohen, 1981).

In order to decrease the error estimates and to improve the values of the quantities themselves (such that \( \alpha_{000} \) is close to unity for example), we now do two things. Firstly, we carry out the solutions using 'ridge-regression' techniques (Hoerl, 1959, 1962; Marquardt, 1963; Hoerl & Kennard, 1970a, b). The error matrix can be written (Hoerl & Kennard, 1970a):

\[ M_B = \sigma^2 (X'X + K^2 I)^{-1} \]

\[ -\sigma^2 K^3 [(X'X + K^2 I)^{-1}] [(X'X + K^2 I)^{-1}]' \] 

\[ + K^4 (X'X + K^2 I)^{-1} BB' [(X'X + K^2 I)^{-1}]. \]

(13a)

When \( K = 0 \), the second and third terms are zero, and the resultant errors are the same as in normal least squares. When \( K \) is large, the first term is zero. As the correct solution is not known in advance, (13a) cannot really be used to calculate errors in \( B \) (the intensity

Secondly, we do the best we can to be sure that the expansion to quadratic terms in the atom displacements is adequate to describe the results.

Consider first an equation of the form:

\[ Y = XB + \epsilon, \]

where \( Y \) is the vector of measured quantities (intensities), \( X \) is a known matrix, \( B \) is the vector of desired quantities (\( I_{SRO}, Q_{AA}^4 \), etc.) and \( \epsilon \) is the vector of experimental errors. The usual least-squares solution is

\[ \hat{B} = (X'X)^{-1} X'Y. \]

Ridge regression considers the equation as

\[ (X'X + K^2 I)^{-1} X'Y, \]

with solution

\[ \hat{B} = (X'X + K^2 I)^{-1} X'Y, \]

where \( K \) is an arbitrary small positive parameter and \( I \) is the unit matrix. The diagonal terms of \( X'X \) are augmented. Consider

\[ J = [Y - X\hat{B}][Y - X\hat{B}] + K^2 \hat{B}'\hat{B}. \]

The smaller the value of \( K \), the more important is the residual in the minimization, compared to the solution vector \( \hat{B} \). Conversely, the larger the \( K \) value, the more important is the solution vector. As \( K \) increases the solution vector rapidly decreases in magnitude and then varies slowly. The residual vector, on the other hand, varies slowly in magnitude with \( K \) until large values are used, when it increases dramatically. We generally vary \( K \) until the product of the derivatives (with respect to \( K \)) of the norms of solution vector and residual vector is a minimum. (This value shows a factor of two variation in reciprocal space, being smallest where the total diffuse intensity is largest.) Another procedure is to examine a plot of the norm of the residual vs norm of the solution vector [see Lawson & Hanson (1974) for a discussion of both procedures].

For certain values of \( K \), the errors in this procedure are known to be smaller (by as much as a factor of two) than for normal least squares (Hoerl, 1962; Hoerl & Kennard, 1970a, b). The error matrix can be written (Hoerl & Kennard, 1970a):

\[ M_B = \sigma^2 (X'X + K^2 I)^{-1} \]

\[ -\sigma^2 K^3 [(X'X + K^2 I)^{-1}] [(X'X + K^2 I)^{-1}]' \] 

\[ + K^4 (X'X + K^2 I)^{-1} BB' [(X'X + K^2 I)^{-1}]. \]

(13a)
components) although the solution \( \hat{B} \) can be employed as an estimate. As \( K \) is selected as a compromise between the sizes of the residual and the solution, the error is clearly between the above two limits. If the third term in (13a) is neglected, the estimated error is too small (Hoerl & Kennard, 1970a). Since the second term is negative and the third positive, and since (13a) is a series in powers of \( K \) where \( K < 1 \), neglecting both the second and third terms gives an approximation to the total error. Therefore, we estimate the errors from

\[
M = \sigma^2(X'X + K^2)I^{-1}. \tag{13b}
\]

In fact, in actual cases we find (using the solution \( \hat{B} \) as \( B \)) that the total error, (13a), is generally within 5% or less of (13b), and, in fact, (13b) overestimates the total by this amount. Furthermore, we can judge the bias in ridge regression because after the separation of intensity components at all points in the minimum volume, the transformation of \( f_{\text{ISO}} \) should produce \( \alpha_{000} = 1 \), and \( \alpha_{mn} \) which cannot be negative by more than a certain amount, as mentioned in the introduction. Our results indicate that the biasing is at most a few percent throughout reciprocal space.

This ridge-regression procedure could also be useful in combining data taken with several wavelengths to solve these kinds of problems for ternary or higher alloys, or in neutron scattering, combining data with several isotopes to obtain the partial radial distribution functions. It would be useful in such a case to simulate data, add errors and thereby test the procedures.

We turn now to our second procedure. The expansions to obtain the sums of (5) include up to quadratic terms in displacements of atoms from lattice points. For example, consider displacement term \( \langle (X_{mn}^{AB})^2 \rangle \). This is \( \langle (X_0^A - X_0^{AB})^2 \rangle = \langle (X_0^A)^2 \rangle + \langle (X_0^{AB})^2 \rangle - 2\langle X_0^A X_0^{AB} \rangle \). Clearly, the mean-square values do not converge to zero with increasing \( lmn \), whereas the cross terms do. Also, there are higher-order terms. Our second procedure is to include the mean-square terms as Debye-Waller factors, which also partially corrects for higher-order terms, if the equations are not written to include such terms. [This is discussed by Hayakawa & Cohen (1975)]. They chose one approach to do this, but a better one is present here. We first examine their approach. The total scattered intensity in electron units can be written in terms of the pair probabilities, \( P \), and total displacements from the average lattice, \( V \):

\[
I_T = \sum_m \sum_n (C_A f_A^2 P_{mn}^{AA} \langle \exp[ik.V_{mn}^{AA}] \rangle + C_A f_A f_B P_{mn}^{AB} \langle \exp[ik.V_{mn}^{AB}] \rangle + C_B f_A f_B P_{mn}^{BB} \langle \exp[ik.V_{mn}^{BB}] \rangle + C_B f_B P_{mn}^{B} \langle \exp[ik.V_{mn}^{B}] \rangle) \exp[ik.R_{mn}] \tag{14}\]

Here, the angle-brackets imply an average for all \( AA \) pairs at a given interatomic vector, \( n-m \). Following Hayakawa, Bardhan & Cohen (1975), these averages can be rewritten as

\[
\langle \exp[ik.V_{mn}^{ij}] \rangle \approx \exp[-\frac{1}{2} \langle (k.V_{mn}^{ij})^2 \rangle]
\]

and, including up to quadratic terms in the displacements, as for (2) (higher-order terms are subtracted in a calculation of higher-order TDS):

\[
\approx e^{-\frac{1}{2} \langle (k.V_{mn}^{ij})^2 \rangle} \times (1 + i\langle k.V_{mn}^{ij} \rangle).
\tag{15a}\]

This procedure ensures convergence of the Fourier series for the total intensity [because as \( (m-n) \) increases, the correlated terms in the exponent in (14b) go to zero]. However, for \( m = n \):

\[
\langle \exp ik.V_{mn}^{ij} \rangle = 1 - e^{-2M_{ij}} \{ 1 + \langle k.V_{mn}^{ij} \rangle \}. \tag{16}\]

A more satisfactory formulation can be obtained by separating the displacements into components, \( \delta \), due to static (size) effects and those \( (U) \) due to thermal vibrations, and assuming that the thermal components are independent of the species at the end of the vector \( (n-m) \). Then (14) can be rewritten:

\[
I_T = \sum_m \sum_n (C_A f_A^2 P_{mn}^{AA} \langle \exp[ik.A^{AA}] \rangle + C_A f_A f_B P_{mn}^{AB} \langle \exp[ik.A^{AB}] \rangle + C_B f_A f_B P_{mn}^{BB} \langle \exp[ik.A^{BB}] \rangle + C_B f_B P_{mn}^{B} \langle \exp[ik.A^{B}] \rangle \times \exp[ik.R_{mn}] \langle \exp[ik.U_{mn}] \rangle). \tag{17}\]

The static displacements are generally small compared to the interatomic distance (5–10%), and expanding the exponents involving \( \delta \) to include up to quadratic terms, and following G–C:

\[
\langle I_T \rangle = (C_A f_A + C_B f_B)^2 \sum_m \sum_n \exp[ik.R_{mn}] \langle \exp[ik.U_{mn}] \rangle 
+ C_A f_A f_B \sum_m \sum_n \{ z_{mn} + i\langle k.A^{AA} \rangle \times (C_A/C_B + z_{mn}) f_A/(f_A - f_B) + i\langle k.A^{AB} \rangle f_B/(f_B - f_A) 
+ (C_A/C_B + z_{mn}) \langle \exp[ik.A^{AA}] \rangle f_A/(f_A - f_B)^2 
+ 2(1 - z_{mn}) \langle \exp[ik.A^{AB}] \rangle f_A f_B/(f_A - f_B)^2 
+ (C_A/C_B + z_{mn}) \langle \exp[ik.A^{BB}] \rangle f_B/(f_B - f_B)^2 \times \exp[ik.R_{mn}] \langle \exp[ik.U_{mn}] \rangle. \tag{18a}\]

The first summation on the right-hand side of (18a) is nothing more than the Bragg peaks plus TDS (including higher-order TDS) from the average
structure. Consider the second sum, which is of interest here. For \( m = n \), i.e. \( a_{mn} = 0 \), \( b_{000} = 1 \), as indicated earlier, and \( U_{mn} = U_m - U_n = 0 = \delta_{mn} \). Therefore, the second sum for a binary alloy is \( NC_A C_B (f_A - f_B)^2 \). However, for \( m \neq n \):

\[
\langle \exp i k \cdot U_{mn} \rangle \approx e^{-2M \left[ 1 + \langle \langle k \cdot U_{mn} \rangle \rangle \right]}
\]

\[
eq e^{-2M \left[ 1 + \langle \langle k \cdot U_{mn} \rangle \rangle \langle k \cdot U_{mn} \rangle \rangle \right]}
\]

where \( \langle \langle k \cdot U_{mn} \rangle \rangle = 0 \) for the thermal vibrations.

Thus, all terms beyond the first in \((18a)\) can be written (for a binary cubic alloy with one atom per lattice point) as

\[
NC_A C_B (f_A - f_B)^2 (1 - \exp -2M)
++ \exp -2M [\text{equation (2)}] \quad \quad (19)
\]

The first term must be subtracted from the total intensity (as well as higher-order TDS, if it is appreciable) prior to the separation of (2) into its components by least squares. For dilute alloys, the term to be subtracted is small, as it depends on \( C_A C_B \) and, therefore it can be neglected. Also, when the remaining intensity is converted to Laue units, the divisor is \( NC_A C_B (f_A - f_B)^2 \exp -2M \).

Error equations

Only the error due to counting statistics is considered here. (For other errors, see G-C.) From the Fourier inversion of the separated short-range-order intensity \( \hat{I}_{\text{SRO}} \), the Warren short-range-order parameters can be estimated, for example, for a binary alloy:

\[
\hat{a}_{lmn} = \frac{1}{N} \Delta h_1 \Delta h_2 \Delta h_3
\times \sum_{h_1} \sum_{h_2} \sum_{h_3} \hat{I}_{\text{SRO}}(h_1) \cos 2\pi h_1 \cos 2\pi m h_2 \cos 2\pi n h_3,
\]

where \( \Delta h_1 \) is the experimental increment of the (dimensionless) variable in reciprocal space, and the sum extends over one unit cell in reciprocal space. Now the variance \( \sigma^2 \) is

\[
\sigma^2(a_{lmn}) = E \langle (a_{lmn} - \hat{a}_{lmn})^2 \rangle,
\]

where \( a_{lmn} \) is the true short-range-order parameter and \( E \) denotes the expectation value of the quantity within the brackets. Employing (21):

\[
\sigma^2(a_{lmn}) = \left( \frac{1}{6} \Delta h_1 \Delta h_2 \Delta h_3 \right)^2
\times \sum_{h_1} \sum_{h_2} \sum_{h_3} \sigma^2[I_{\text{SRO}}(h_1 h_2 h_3)] M(h_1 h_2 h_3)
\times \cos 2\pi h_1 \cos 2\pi m h_2 \cos 2\pi n h_3
\times \cos 2\pi h_1 \cos 2\pi m h_2 \cos 2\pi n h_3
+ \cos 2\pi h_1 \cos 2\pi m h_2 \cos 2\pi n h_3
+ \cos 2\pi h_2 \cos 2\pi m h_1 \cos 2\pi n h_3
+ \cos 2\pi h_4 \cos 2\pi m h_1 \cos 2\pi n h_3
+ \cos 2\pi h_3 \cos 2\pi m h_1 \cos 2\pi n h_3,
\]

where \( M(h_1 h_2 h_3) \) is the multiplicity (due to symmetry) of the point \((h_1 h_2 h_3)\) \((M = 1, 2, 4, \text{or} 8 \text{if} 3, 2, 1, \text{or} 0 \text{reciprocal-lattice coordinates are} 0)\). The variance \( I_{\text{SRO}} \) can be obtained from the moment matrix of the particular least-squares solution (ridge regression for example, as described earlier). Similar expressions can be obtained for the other coefficients in (6) and (7) and are given in Table 1.

If intensity errors can be estimated for any procedure for separating the components of diffuse inten-
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Table 1. Variances of SRO and displacement coefficients: cubic systems

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Variance</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_{imn}$</td>
<td>(1/64)$\sum \sum \sum \sigma^2[I_{SRO}(l, l, h)] M(l, h, h) \cos 2\pi l h \cos 2\pi m h \cos 2\pi n h$</td>
</tr>
</tbody>
</table>

In order to examine the influence of error in a typical situation, diffuse intensities were simulated in a volume of reciprocal space using reasonable parameters for one binary system, Al–1.7 at.% Cu. The $a_{imn}$ and displacements were taken from Auvray et al. (1981). The intensities due to Compton scattering, background, etc. were included and random counting errors were then introduced, to resemble a real experiment. Two sets of data were simulated in this manner: one with Cu Kα radiation and the other with Mo Kα radiation. About 30 associated points for each point along an [h00] direction were selected so that they were uniformly distributed in the measured reciprocal space. The intensity for points near the Bragg peaks was typically around 7000 counts and, for points away from the peaks, around 1000 counts.

As ternary systems, intensities from Cu$_2$PtPd (at the Pt L edge, for Ag Kα, and at the Cu K edge) and Zn$_2$AgAu (at the Au L edge) were synthesized. The $a_{imn}$ were at most 0.05, and chosen following the known long-range ordering in these systems. The displacement terms were chosen so that ISRO was 30–70% of the total, and a typical count was 3000. [As mentioned earlier, intensity expressions for multicomponent systems in the format used in these simulations can be found in Hayakawa & Cohen (1975). These are 54 terms for a ternary alloy.]

All computations were carried out on CDC 6600 or CDC Cyber 730 computers.

(a) The effect of the weighting factor

In least-squares analysis, there are two alternative solutions: one from minimizing the squared residuals, and the other from minimizing the weighted squared residuals. Statistically, the latter provides a better result if the expected error of each measurement can be estimated. For the simulated Al–Cu data, the weighting factors were evaluated from the counting statistics, and a slightly better separation was indeed found, although we have observed that the change in separated intensity components can be small (a few percent). However, after Fourier inversion of $I_{SRO}$ it was clear that the weighting scheme was superior. As it is known from the definition of the parameter that $a_{imn}$ and $a_{imn}^B$, the value of $a_{imn}^B$ differed by only 0.5% from unity, but the difference was 5% for...
the unweighted result. Also, there were about three times fewer parameters which exceeded the theoretical limit, -0.018, for the weighted result than for the unweighted result.

(b) The effect of scattering-factor variation

When measurements are made with X-rays, the scattering factors vary across the sampled volume of reciprocal space. In fact the procedure for separating the intensity components [in (5)] from the total diffuse intensity requires that there be a variation in the scattering-factor ratio \( \text{a [A]} / \Delta \text{f} \). It can easily be seen that if the scattering-factor ratio remains constant, as required in the Borie & Sparks (1971) method, the individual components, \( Q_{AA} \) and \( Q_{BB} \), can never be separated by the G–C procedure from the combined term, \( \eta Q_{AA} + \zeta Q_{BB} \). A separation can best be achieved with a large variation of the ratio. By using a short wavelength, a set of associated points for a least-squares solution at each \( h, l, h_3 \) can be obtained with a large variation of the scattering-factor ratio. The results for the simulations of an Al–Cu alloy with two different wavelengths are shown in Figs. 1 and 2. The improvement for Mo K\( \alpha \) is quite significant, especially for the displacement intensity. A typical result from this simulation for all terms of the separation at one point in reciprocal space is given in Table 2.

The results for the ternary systems are interesting. For Cu\(_2\)PtPd, with simulated data for all three wavelengths, the various terms were well separated. If the data was simulated only at the Pt L edge, the separation was good for Cu–Pd and Pt–Cu terms, and poor for Pd–Pt. The same results occurred for combined (simulated) data with the wavelength at the Cu K edge, and at the Pt L edge. For Zn\(_2\)AgAu, at the Au L edge, information on Zn–Ag and Zn–Au was satisfactorily obtained, but not for Ag–Au pairs. (It is also worth mentioning that ridge regression was especially useful in separating these simulated data for ternary systems.)

### Table 2. Comparison of separated intensity terms with Cu K\( \alpha \) and Mo K\( \alpha \) radiations at (0, 3, 0) simulated data

Terms in parentheses are standard deviations.

<table>
<thead>
<tr>
<th></th>
<th>Assumed value</th>
<th>With Cu K( \alpha )</th>
<th>With Mo K( \alpha )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( I_{SRO} )</td>
<td>10.59</td>
<td>11.12 (0.63)</td>
<td>10.57 (0.29)</td>
</tr>
<tr>
<td>( Q_{AA} )</td>
<td>19.18</td>
<td>17.30 (3.74)</td>
<td>19.89 (0.58)</td>
</tr>
<tr>
<td>( Q_{BB} )</td>
<td>24.44</td>
<td>28.99 (9.15)</td>
<td>22.47 (1.64)</td>
</tr>
<tr>
<td>( R_{AA} )</td>
<td>0.25</td>
<td>88.81 (61.56)</td>
<td>2.35 (1.33)</td>
</tr>
<tr>
<td>( R_{BB} )</td>
<td>0.05</td>
<td>-44.0 (301.96)</td>
<td>-12.09 (7.70)</td>
</tr>
<tr>
<td>( R_{AA} )</td>
<td>0.27</td>
<td>54.69 (370.24)</td>
<td>17.79 (11.06)</td>
</tr>
<tr>
<td>( R_{BB} )</td>
<td>0.31</td>
<td>-75.75 (42.42)</td>
<td>0.20 (0.36)</td>
</tr>
<tr>
<td>( R_{AA} )</td>
<td>0.07</td>
<td>37.14 (206.63)</td>
<td>0.70 (2.08)</td>
</tr>
<tr>
<td>( R_{BB} )</td>
<td>0.30</td>
<td>-45.28 (251.68)</td>
<td>-0.37 (2.92)</td>
</tr>
<tr>
<td>( R_{AA} )</td>
<td>0.31</td>
<td>-75.75 (42.42)</td>
<td>0.20 (0.36)</td>
</tr>
<tr>
<td>( R_{BB} )</td>
<td>0.07</td>
<td>37.14 (206.63)</td>
<td>0.71 (2.08)</td>
</tr>
</tbody>
</table>

[Fig. 1. The separated \( I_{SRO} \), using simulated data for the total diffuse intensity (equation 5) for Al-1.7 at.% Cu and a weighted solution. Data separated for: \( \triangle \) Cu K\( \alpha \); \( \square \) Mo K\( \alpha \). Line is actual intensity.]

[Fig. 2. The separated \( Q_{AA} \) in equation (5), using simulated data for the total diffuse intensity from Al-1.7 at.% Cu, and a weighted solution. Data separated for: \( \triangle \) Cu K\( \alpha \); \( \square \) Mo K\( \alpha \). Line is actual intensity.]
Discussion

The G–C procedure for quantitative analysis of diffuse X-ray scattering has several useful features. It has already been shown theoretically and experimentally that it is applicable for the separation of effects due to displacement and local order, whether there is short-range order or clustering, in the presence of large scattering due to displacements (G–C; Auvray et al., 1981) and for separating the individual atom-pair displacements. These are not possible with any other procedure at the moment. As shown in this paper, it is also amenable to estimating errors in the separated intensity terms, the resulting short-range-order parameters and displacements, and in estimating counting times to achieve the desired precision. Computer-simulated data is particularly useful to examine the efficacy of various experimental procedures. For example, it has been shown here that there is considerable improvement in the precision of the information on displacements if Mo Kα rather than Cu Kα or Co Kα is employed. However, a word of caution is of value here. The resolution volume in reciprocal space for a given angular divergence from a monochromator-slit system is inversely proportional to the (wavelength)³. Thus it is particularly difficult with a short wavelength to avoid the contaminating effects of Bragg peaks and still maintain an adequate intensity, except at a storage-ring source, where the high flux and natural collimation will allow a more restricted measuring volume with adequate intensity. In fact, preliminary experiments we have conducted at CHESS (Cornell University’s storage-ring source) indicate that a complete set of data for this kind of analysis can be taken with an order of magnitude improvement in resolution, in 24–36 h (with $I_0$ $3 \times 10^{10}$ counts s⁻¹, employing a singly bent Si monochromator and a float glass mirror to eliminate harmonics).

Currently there is considerable interest in extending this kind of quantitative analysis of diffuse X-ray scattering to ternary and quaternary systems because many interests metallic alloys and ceramic systems involve more than two elements. In fact, measurements have already been reported for one such system (Georgopoulos & Cohen, 1981), but the third element was restricted to one sublattice. While this successful result indicates that the method can be extended to many ternary ceramic materials with a measurement at a single wavelength, this is not clear for the general ternary system for which any atomic species can occupy any equipoint. Accordingly we have presented here some results of simulations for such systems. The separation is satisfactory for three wavelengths. But we have also found that quite interesting results can be obtained even with a single wavelength close to the absorption edge of one element. It is possible that two wavelengths will be as good as three if properly chosen to make large changes in $f/\Delta f$ for elements in the same column of the periodic table. For example, for Cu₂PtPd, wavelengths near Pt and Pd edges would be best, whereas for Zn₂AgAu, the desired wavelengths would be close to Ag and Au edges.

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References