

## The Interpretation of Intensity Distributions From Disordered Binary Alloys\*

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(Received 24 April 1970)

X-ray diffuse scattering from disordered alloys is the primary direct source of information concerning the Warren parameters which describe the existing state of order. However, the short range order diffuse intensity is obscured by other contributions to the diffraction pattern resulting from static atomic displacements from the average lattice, and from effects related to thermal motion. Described here is a method to separate the diffraction pattern into its various components so that each may be interpreted independently. No assumptions are made about the nature of the atomic displacements  $\delta$ , except that they are sufficiently small, and that the diffraction vector  $\mathbf{k}/2\pi$  is sufficiently small, that terms beyond the term quadratic in  $\mathbf{k} \cdot \delta$  may be neglected in the series expansion of  $\exp[i\mathbf{k} \cdot \delta]$ .

### Introduction

Since the early experiments of Wilchinsky (1944) and Cowley (1950), the problem of measuring and interpreting the diffraction patterns of binary substitutional alloys in various states of order has attracted the attention of metallurgical crystallographers. The first approach to the interpretation of these intensity distributions was to assume that the two kinds of atoms are distributed on the atomic sites of a periodic structure. In this case one can show that the diffraction pattern may be divided into two parts:  $I_1$  which is independent of the state of order and which gives rise to the sharp fundamental Bragg reflections, and  $I_2$ , which depends on how the atoms are arranged on the atomic sites.  $I_1$  is the pattern one would have obtained if all the atoms were identical, with atomic scattering factor  $\langle f \rangle$  given by the weighted average of those of the two kinds of atoms present.  $I_2$  depends on the difference in the atomic scattering factors,  $\Delta f$ , and may be written as a Fourier series, as first shown by Cowley, the lead term of which is the Laue monotonic diffuse scattering. If  $I_2$  includes sharp superstructure reflections, then the state of order is said to be long range. However, if the Fourier series converges, then  $I_2$  contains no sharp features, and a Fourier inversion of the resultant diffuse scattering yields the Warren order parameters which describe the state of short range order existing in the crystal.

However, extra modulations, increasing in amplitude with distance from the origin in reciprocal space, were observed and shown by Warren, Averbach & Roberts (1951) to result from static displacements of the atoms from the sites of the undistorted lattice. By allowing the actual interatomic vector  $\mathbf{r}_p - \mathbf{r}_q$  between sites  $p$  and  $q$  to deviate slightly from  $\mathbf{R}_p - \mathbf{R}_q$ , the average value for the lattice, one may write  $\mathbf{r}_p - \mathbf{r}_q = \mathbf{R}_p - \mathbf{R}_q + \delta_p - \delta_q$ . If  $\delta_p$  and  $\delta_q$  are sufficiently small

that  $\exp[i\mathbf{k} \cdot (\delta_p - \delta_q)]$  may be approximated by  $1 + i\mathbf{k} \cdot (\delta_p - \delta_q)$ , the intensity expression includes a third term containing  $i\mathbf{k} \cdot (\delta_p - \delta_q)$ . This third term,  $I_3$ , gives rise to the size effect modulations (Warren *et al.*, 1951). It was shown by Borie (1961) that  $I_1$  and  $I_2$  could be separated from  $I_3$  in two dimensions so that they could be treated separately. A similar treatment in three dimensions was given by Sparks & Borie (1965).

However, it is known that these three terms are not wholly adequate to provide a reasonable complete representation of the diffraction pattern, because no account is taken of either the thermal motion or mean square static distortions as discussed first by Huang (1947). If one allows  $\delta_p - \delta_q$  to include not only static displacements resulting from disorder, but dynamic displacements as well, then the quadratic term  $\langle [\mathbf{k} \cdot (\delta_p - \delta_q)]^2 \rangle$  in the series expansion of  $\exp[i\mathbf{k} \cdot (\delta_p - \delta_q)]$  will account for both the Huang scattering and first order temperature diffuse scattering. The traditional approach to the interpretation of the diffuse intensity is to treat the short range order scattering as the component of interest, and to attempt to remove the others by various sorts of corrections. It is common to attempt to remove the temperature diffuse scattering by making measurements at two temperatures, assuming that the thermal intensity varies linearly with the temperature, and extrapolating to absolute zero. This is at best a fairly crude approximation, even for perfectly periodic crystals. Our theoretical understanding of thermal motion in aperiodic media such as disordered alloys is sufficiently primitive that the quality of the approximation in that case is unknown.

Huang diffuse scattering is usually ignored. One simply hopes that most of it will be concentrated near the fundamental Bragg maxima, and chooses an alloy for study where  $I_2$  is small near the fundamental reflections. The measurements in that region are then discarded and the diffuse intensity is extrapolated smoothly to zero at the reciprocal lattice point. For a simple elastic model for a crystal with no short range

\* Research sponsored by the U.S. Atomic Energy Commission under contract with the Union Carbide Corporation.

order, Huang was able to show that most of the scattering is indeed confined to that region, and Borie (1957, 1959) found that for  $\text{Cu}_3\text{Au}$ , Huang's model agreed reasonably well with experiment, even though the sample contained a high degree of short range order. But Borie & Sparks (1964) found that the model did not fit an alloy of Cu-16 at. % Al. There is no reason to suppose that Huang's simple model is generally applicable.

There is thus a serious discrepancy between our ability to make a set of diffuse scattering measurements, and our ability to unravel them. Measurements obtained with modern experimental techniques exhibit clearly all of the above components of the intensity in accurate and quantitative form. Their interpretation is dependent on a variety of primitive, oversimplified, and questionable models.

We propose here to include the quadratic term which accounts for Huang and first order thermal contributions to the diffuse intensity and to provide a method for the separation of the diffuse intensity into its various components. No models or assumptions about the character of the atomic displacements, either static or dynamic, are necessary, except that  $\mathbf{k} \cdot (\delta_p - \delta_q)$  is sufficiently small that terms beyond the quadratic one in the series expansion of  $\exp[i\mathbf{k} \cdot (\delta_p - \delta_q)]$  may be neglected. The method depends only on the way the components of the diffuse scattering must vary as a function of position in reciprocal space, which follows directly from kinematic diffraction theory.

### Diffraction theory

We begin with the usual expression from kinematic theory for the intensity in electron units scattered by atoms of atomic scattering factor  $f_p$  and positions  $\mathbf{r}_p$ :

$$I = \sum_p \sum_q f_p f_q \exp[i\mathbf{k} \cdot (\mathbf{r}_p - \mathbf{r}_q)].$$

Suppose the atomic positions correspond nearly but not exactly to the sites  $\mathbf{R}_p$  of a periodic structure. Then  $\mathbf{r}_p = \mathbf{R}_p + \delta_p$  where  $\delta_p$  is very small, and

$$I = \sum_p \sum_q f_p f_q \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \exp[i\mathbf{k} \cdot (\delta_p - \delta_q)].$$

Let  $\mathbf{k} \cdot (\delta_p - \delta_q)$  be sufficiently small that the second exponential in the above equation may be adequately approximated by

$$\exp[i\mathbf{k} \cdot (\delta_p - \delta_q)] \simeq 1 + i\mathbf{k} \cdot (\delta_p - \delta_q) - \frac{1}{2}[\mathbf{k} \cdot (\delta_p - \delta_q)]^2.$$

The intensity may then be written

$$\begin{aligned} I = & \sum_p \sum_q f_p f_q \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ & + i \sum_p \sum_q f_p f_q \mathbf{k} \cdot (\delta_p - \delta_q) \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ & - \frac{1}{2} \sum_p \sum_q f_p f_q [\mathbf{k} \cdot (\delta_p - \delta_q)]^2 \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)]. \quad (1) \end{aligned}$$

The first double sum is simply the intensity one would have observed if there were no displacements from the ideal atomic sites. Cowley shows that it may be written

$$\begin{aligned} (I_1 + I_2)/Nf_A^2 = & A(\mathbf{k}) \\ = & (m_A + m_B\eta)^2/N \sum_p \sum_q \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ & + m_A m_B (1 - \eta)^2 \sum_q \alpha_{pq} \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)]. \quad (2) \end{aligned}$$

In the above, the two kinds of atoms are identified by subscripts  $A$  and  $B$ .  $m_A$  is the fraction of the total number of atoms  $N$  which are  $A$ , and similarly for  $m_B$ . The ratio  $f_B/f_A$  is  $\eta$ , which may be a slowly varying quantity in reciprocal space since  $f_A$  and  $f_B$  may not have exactly the same dependence on  $\sin \theta/\lambda$ . In all that follows, this will be ignored and  $\eta$  treated as a constant. The Warren order parameter  $\alpha_{pq}$  may be defined in terms of the probability  $P_{pq}^{AB}$  of finding a  $B$  atom at site  $q$  after having found an  $A$  atom at site  $p$ :

$$\alpha_{pq} = 1 - P_{pq}^{AB}/m_B. \quad (3)$$

As is apparent from equation (2), the function  $A(\mathbf{k})$  is periodic in reciprocal space. It is usual and convenient to choose a set of reciprocal vectors  $\mathbf{b}_1$ ,  $\mathbf{b}_2$ , and  $\mathbf{b}_3$  (not necessarily reciprocal to the usual unit-cell vectors) such that, if we write  $\mathbf{k} = 2\pi(h_1\mathbf{b}_1 + h_2\mathbf{b}_2 + h_3\mathbf{b}_3)$ , then the repeat interval of  $A(\mathbf{k})$  [or  $A(h_1h_2h_3)$ ] corresponds to unit change in the pure numbers  $h_1$ ,  $h_2$ , and  $h_3$ .

The second double sum of equation (1),  $I_3$ , gives rise to the atomic displacement modulations discovered and first treated by Warren *et al.* (1951). It is apparent from their treatment, or the somewhat more general discussions of Borie & Sparks (1964) that  $I_3$  may be written

$$I_3/Nf_A^2 = h_1B(h_1h_2h_3) + h_2B(h_2h_3h_1) + h_3B(h_3h_1h_2). \quad (4)$$

The Fourier coefficients of the periodic function  $B(h_1h_2h_3)$  [which has a three dimensional repeat interval identical with  $A(h_1h_2h_3)$ ] may be related directly to the average components of the relative displacement vector  $\delta_p - \delta_q$ .

We discuss in some detail the final double sum of equation (1) which we call  $I_4$ . It may be written

$$\begin{aligned} I_4 = & -\frac{1}{2} \sum_p \sum_q f_p f_q (\mathbf{k} \cdot \delta_p)^2 \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ & -\frac{1}{2} \sum_p \sum_q f_p f_q (\mathbf{k} \cdot \delta_q)^2 \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ & + \sum_p \sum_q f_p f_q (\mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q) \exp[i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)]. \end{aligned}$$

The first two sums are identical and may be combined. For a large crystal, we may approximate the double sum by  $N$  times a single sum over the average of the summand for  $pq$  pairs of constant  $\mathbf{R}_p - \mathbf{R}_q$ :

$$I_4 = N \sum'_q \langle f_p f_q(\mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q) \rangle_{pq} \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ - N \sum'_q \langle f_p f_q(\mathbf{k} \cdot \delta_q)^2 \rangle_{pq} \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)]. \quad (5)$$

The primes on the sums of equation (5) indicate that the terms for which  $p=q$  are to be omitted, for it is apparent that in that case the contributions to the two sums cancel. If the indicated averages are taken to be not only spatial but averages over time as well, equation (5) includes the contributions of both static displacements and thermal motion.

Consider the contribution to equation (5) for all atomic pairs such that, say, an  $A$  atom is at both sites  $p$  and  $q$ . Since the number of such pairs for a particular  $\mathbf{R}_p - \mathbf{R}_q$  is  $Nm_A(1 - P_{pq}^{AB})$  or, with the aid of equation (3),  $Nm_A(m_A + m_B\alpha_{pq})$ , the contribution is

$$Q^{AA} = Nf_A^2 m_A \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] (m_A + m_B\alpha_{pq}) \\ \times \{ \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle_{pq}^{AA} - \langle (\mathbf{k} \cdot \delta_q)^2 \rangle_{pq}^{AA} \}. \quad (6)$$

With the aid of the fact that  $m_A P_{pq}^{AB} = m_B P_{pq}^{BA}$ , we may write similar expressions for the other three possible atomic combinations:

$$Q^{AB} + Q^{BA} = Nf_A^2 \eta m_A m_B \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times (1 - \alpha_{pq}) \{ 2 \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle_{pq}^{AB} \\ - \langle (\mathbf{k} \cdot \delta_q)^2 \rangle_{pq}^{AB} - \langle (\mathbf{k} \cdot \delta_p)^2 \rangle_{pq}^{BA} \}. \quad (7)$$

$$Q^{BB} = Nf_B^2 \eta^2 m_B \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times (m_B + m_A\alpha_{pq}) \{ \langle \mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q \rangle_{pq}^{BB} \\ - \langle (\mathbf{k} \cdot \delta_q)^2 \rangle_{pq}^{BB} \}. \quad (8)$$

Hence,

$$I_4 = Q^{AA} + Q^{AB} + Q^{BA} + Q^{BB}. \quad (9)$$

Consider the simplification of, say, equation (6) for  $Q^{AA}$ . We may write

$$\delta_q = x_q \mathbf{a}_1 + y_q \mathbf{a}_2 + z_q \mathbf{a}_3 \quad (10)$$

where  $x_q$ ,  $y_q$ , and  $z_q$  are small pure numbers. Since  $\mathbf{k} = 2\pi(h_1 \mathbf{b}_1 + h_2 \mathbf{b}_2 + h_3 \mathbf{b}_3)$ , the  $\mathbf{b}_n$ 's being reciprocal to the  $\mathbf{a}_n$ 's of equation (10), there results

$$\mathbf{k} \cdot \delta_q = 2\pi(h_1 x_q + h_2 y_q + h_3 z_q)$$

and

$$\mathbf{k} \cdot \delta_p \mathbf{k} \cdot \delta_q = 4\pi^2 [h_1^2 x_p x_q + h_2^2 y_p y_q + h_3^2 z_p z_q \\ + h_1 h_2 (x_p y_q + y_p x_q) \\ + h_2 h_3 (y_p z_q + z_p y_q) + h_3 h_1 (z_p x_q + x_p z_q)]. \quad (11)$$

Equation (11) may now be substituted into equation (6). For statistically cubic alloys and with the aid of relations such as  $\langle x_p y_q \rangle_{pq}^{AA} = \langle y_p x_q \rangle_{pq}^{AA}$ , there results

$$\frac{Q^{AA}}{Nf_A^2} = h_1^2 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 4\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle x_p x_q \rangle_{pq}^{AA} - \langle x_q^2 \rangle_{pq}^{AA}) \} \\ + h_2^2 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 4\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle y_p y_q \rangle_{pq}^{AA} - \langle y_q^2 \rangle_{pq}^{AA}) \} \\ + h_3^2 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 4\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle z_p z_q \rangle_{pq}^{AA} - \langle z_q^2 \rangle_{pq}^{AA}) \} \\ + h_1 h_2 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 8\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle x_p y_q \rangle_{pq}^{AA} - \langle x_q y_q \rangle_{pq}^{AA}) \} \\ + h_2 h_3 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 8\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle y_p z_q \rangle_{pq}^{AA} - \langle y_q z_q \rangle_{pq}^{AA}) \} \\ + h_3 h_1 \sum'_q \exp [i\mathbf{k} \cdot (\mathbf{R}_p - \mathbf{R}_q)] \\ \times \{ 8\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle z_p x_q \rangle_{pq}^{AA} - \langle z_q x_q \rangle_{pq}^{AA}) \}. \quad (12)$$

We now define a periodic function  $C^{AA}(h_1 h_2 h_3)$  to have Fourier coefficients given by the first sum of equation (12),  $\{4\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle x_p x_q \rangle_{pq}^{AA} - \langle x_q^2 \rangle_{pq}^{AA})\}$ , and another such function,  $D^{AA}(h_1 h_2 h_3)$  whose Fourier coefficients are those of the fourth sum of equation (12),  $\{8\pi^2 m_A (m_A + m_B \alpha_{pq}) (\langle x_p y_q \rangle_{pq}^{AA} - \langle x_p y_q \rangle_{pq}^{AA})\}$ . For statistically cubic crystals, equation (12) may be written in terms of these two functions:

$$\frac{Q^{AA}}{Nf_A^2} = h_1^2 C^{AA}(h_1 h_2 h_3) + h_2^2 C^{AA}(h_2 h_3 h_1) + h_3^2 C^{AA}(h_3 h_1 h_2) \\ + h_1 h_2 D^{AA}(h_1 h_2 h_3) + h_2 h_3 D^{AA}(h_2 h_3 h_1) \\ + h_3 h_1 D^{AA}(h_3 h_1 h_2). \quad (13)$$

We may now develop expressions similar to (12) and (13) by substitution of equation (11) into equations (7) and (8), obtaining relations among the other three  $Q$ 's and functions  $C^{AB}$ ,  $C^{BA}$ ,  $C^{BB}$ ,  $D^{AB}$ ,  $D^{BA}$ , and  $D^{BB}$ . With the periodic function  $C$  defined by  $C = C^{AA} + C^{AB} + C^{BA} + C^{BB}$  and  $D$  given by  $D = D^{AA} + D^{AB} + D^{BA} + D^{BB}$ , and with the aid of equation (9), we may write  $I_4$  in terms of these functions:

$$I_4 / Nf_A^2 = h_1^2 C(h_1 h_2 h_3) + h_2^2 C(h_2 h_3 h_1) + h_3^2 C(h_3 h_1 h_2) \\ + h_1 h_2 D(h_1 h_2 h_3) + h_2 h_3 D(h_2 h_3 h_1) + h_3 h_1 D(h_3 h_1 h_2). \quad (14)$$

We note in passing that the functions  $C$  and  $D$  must have some special properties. Since their Fourier coefficients for which  $p=q$  are zero, it follows that  $\int C d\mathbf{v}_b = \int D d\mathbf{v}_b = 0$ , the integrals being performed over the cubic repeat interval in reciprocal space. Further the function  $C$  must include sharp negative peaks at the fundamental Bragg maxima in reciprocal space, since parts of its Fourier coefficients such as  $-\langle x_q^2 \rangle_{pq}^{AA}$  [see the first sum of equation (12)] do not approach zero as  $\mathbf{R}_p - \mathbf{R}_q$

becomes large. This simply accounts for the diminution of the fundamental Bragg maxima due to thermal motion and the static atomic displacements predicted by Debye (1913) and Huang (1947). Since  $\int C dv_b$  over the repeat interval must vanish, it follows that the integral excluding the Bragg peak must be positive and just equal to the decrease in the integrated intensity of the fundamental maxima, divided by  $Nf_A^2(h^2+k^2+l^2)$ , due to the Debye-Waller factor and the Huang effect. It is in this sense that there is a kind of conservation law for the weakened Bragg maxima and the temperature diffuse scattering. However, note that it is contained within the function  $C$  and *not*  $I_4/Nf_A^2$ . So far as the writers know, there is no requirement that the integral of that quantity over the repeat interval vanish, because of the quadratic factors in  $h_n$  appearing in equation (14).

It should be emphasized that the above development is valid only within the quadratic approximation as given by equation (1). Hence the application of the separation technique subsequently to be described must be confined to regions in reciprocal space sufficiently near the origin that that approximation is likely to be a reasonable representation of the diffraction pattern.

We may now combine equations (2), (4), and (14) to obtain an expression for the total intensity in terms of  $A$ ,  $B$ ,  $C$ , and  $D$ :

$$\begin{aligned} I/Nf_A^2 = & A(h_1h_2h_3) + h_1B(h_1h_2h_3) + h_2B(h_2h_3h_1) \\ & + h_3B(h_3h_1h_2) + h_1^2C(h_1h_2h_3) + h_2^2C(h_2h_3h_1) \\ & + h_3^2C(h_3h_1h_2) + h_1h_2D(h_1h_2h_3) + h_2h_3D(h_2h_3h_1) \\ & + h_3h_1D(h_3h_1h_2). \end{aligned} \quad (15)$$

Our object is to separate the measured intensity distribution into its various parts, and to recover each of the four periodic functions. The Fourier coefficients of these functions each give an insight into a different aspect of the disordered alloy.

Define an operator  $A_1$  such that

$$A_1I(h_1h_2h_3)/Nf_A^2 = I(h_1h_2h_3)/Nf_A^2 - I(h_1-1, h_2, h_3)/Nf_A^2.$$

Analogous operators with subscripts 2 or 3 concern the same manipulation of the data with respect to  $h_2$  or  $h_3$ . Then because of the periodic character of the functions of equation (15),

$$\begin{aligned} A_1I(h_1h_2h_3)/Nf_A^2 = & B(h_1h_2h_3) + (2h_1-1)C(h_1h_2h_3) \\ & + h_2D(h_1h_2h_3) + h_3D(h_3h_1h_2), \end{aligned} \quad (16)$$

and

$$A_1^2I(h_1h_2h_3)/Nf_A^2 = 2C(h_1h_2h_3), \quad (17)$$

and

$$A_2A_1I(h_1h_2h_3)/Nf_A^2 = D(h_1h_2h_3). \quad (18)$$

Equations (17) and (18) yield directly the functions  $C$  and  $D$  which may be substituted into equation (16)

to recover  $B$ . The three may then be used with the aid of equation (15) to recover  $A$ .

### Discussion

A method for treating diffuse X-ray scattering data from disordered alloys, allowing its various components to be analyzed separately, is described. Measurements at only one temperature suffice, though certain parts of the temperature diffuse scattering and the Huang diffuse scattering remain combined. Presumably if one wished to separate these, measurements at two temperatures would be required. It should be noted that the procedure described here obviates the need for corrections for the effect of thermal motion on the Warren order parameters such as that proposed by Walker & Keating (1963).

The result of the technique is the recovery of four periodic functions in reciprocal space,  $A$ ,  $B$ ,  $C$ , and  $D$ , each of which is related to a different aspect of the short range structure of a cubic alloy.  $A$  is the only one of the four with complete cubic symmetry. Since it would constitute the total diffraction pattern if there were no static or thermal displacements of the atoms from their sites in the average structure, it must be everywhere positive. The part of  $A$  related to the state of order in the alloy must vanish at the fundamental Bragg maxima, in order to conserve the composition of the alloy.

Like  $C$  and  $D$ , the function  $B$  has a zero average, since its Fourier component for  $p=q$  is zero. It must also vanish at all reciprocal lattice points, both superstructure and fundamental nodes of the reciprocal lattice.  $B(h_1h_2h_3)$  is antisymmetric in  $h_1$  and symmetric in  $h_2$  and  $h_3$ . Unlike  $C$  and  $D$ , it includes no contribution from thermal motion.

The functions  $C$  and  $D$  are determined by both the static displacements and thermal motion.  $C$  is symmetric in all the variables.  $D(h_1h_2h_3)$  is antisymmetric in  $h_1$  and  $h_2$ , and symmetric in  $h_3$ . Like  $B$ ,  $D$  must vanish at all of the nodes of the reciprocal lattice.

Subsequent companion papers will illustrate the technique by its use in determining actual short range structures in specific alloys.

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