

X-ray Diffraction Effects of Atomic Size in Alloys. II

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A modification of the diffraction theory for a disordered substitutional solid solution containing atoms of different sizes gives a more accurate and simpler expression for the size effect diffuse scattering. A comparison of the theory with measurements of the diffuse scattering for Cu_3Au near $hkl = 200$ shows good agreement, even though the specimen contained some short-range order.

1. Introduction

In a recent paper by Borie (1957) (referred to here as part I) the writer developed a theory for the diffraction effects to be observed because of atomic size from a binary substitutional solid solution. The theory is an extension of the ideas of Huang (1947) and Warren, Averbach & Roberts (1951). It was shown that, in general, both the Huang diffuse scattering and the Warren modulations of the diffuse scattering are to be observed, and that the Bragg maxima, though still sharp, are reduced in intensity by a factor similar to the Debye factor for thermal motion. All three effects were expressed in terms of a single parameter, C_A , which is a measure of the degree to which the sizes of the two kinds of atoms differ from the average atomic size as determined by the lattice constants of the alloy.

It was necessary to evaluate the lattice sum associated with the Huang diffuse scattering by means of an integral approximation. The resultant expression for the total diffuse scattering was rather complicated, and certainly very approximate. It is the object of this paper to show that for a solid solution with no order, the diffuse scattering may be expressed in a much simpler and more accurate form, in terms of a single lattice sum which may be readily evaluated numerically.

2. Diffraction theory

It is convenient to begin this modification of the size effect theory with equation (14) of part I which may be written:

$$\begin{aligned}
 I/N = & (m_A f_A + m_B f_B)^2 (1 - 2M') \sum_{n \neq m} \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] \\
 & + (m_A f_A^2 + m_B f_B^2) \\
 & + 2m_A C_A (m_A f_A + m_B f_B) (f_A - f_B) \sum_{n \neq m} \frac{i\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \\
 & \times \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] + (m_A f_A + m_B f_B)^2 \sum_{n \neq m} H_{mn} \\
 & \times \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}]. \quad (1)
 \end{aligned}$$

The notation is that of part I: I/N is the scattered X-ray intensity in electron units per atom; $\mathbf{k} = 2\pi(\mathbf{s} - \mathbf{s}_0)/\lambda$ where \mathbf{s} and \mathbf{s}_0 are unit vectors in the directions of the scattered and incident beams; and \mathbf{r}_{mn} is the vector between atomic sites m and n in the undistorted lattice. The crystal is composed of A and B atoms, a fraction m_A of which are A atoms of atomic scattering factor f_A . Associated with the size difference of the two kinds of atoms are distortion constants C_A and C_B which are related by the expression $m_A C_A + m_B C_B = 0$.

$2M'$ and H_{mn} are both lattice sums:

$$2M' = \frac{m_A}{m_B} C_A^2 \sum_{j \neq m} \frac{(\mathbf{k} \cdot \mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6}. \quad (2)$$

$$H_{mn} = \frac{m_A}{m_B} C_A^2 \sum_{j \neq m, n} \frac{\mathbf{k} \cdot \mathbf{r}_{mj} \mathbf{k} \cdot \mathbf{r}_{nj}}{|\mathbf{r}_{mj}|^3 |\mathbf{r}_{nj}|^3}. \quad (3)$$

To the first term of equation (1) we add $(m_A f_A + m_B f_B)^2 (1 - 2M')$ to complete the sum for $n = m$, and we subtract it from the remaining terms.

$$\begin{aligned}
 I/N = & (m_A f_A + m_B f_B)^2 (1 - 2M') \sum_n \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] \\
 & + m_A m_B (f_A - f_B)^2 \\
 & + 2m_A C_A (m_A f_A + m_B f_B) (f_A - f_B) \sum_{n \neq m} \frac{i\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \\
 & \times \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] + (m_A f_A + m_B f_B)^2 \\
 & \times \{2M' + \sum_{n \neq m} H_{mn} \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}]\}. \quad (4)
 \end{aligned}$$

The first part of (4) corresponds to the sharp crystalline reflections reduced in intensity by a factor $(1 - 2M')$. The remaining terms give the diffuse scattering which, with the aid of (2) and (3), may be written

$$\begin{aligned}
 \frac{I_D}{m_A m_B N} = & (f_A - f_B)^2 + 2(f_A - f_B)(m_A f_A + m_B f_B) \frac{C_A}{m_B} \\
 & \times \sum_{n \neq m} \frac{i\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] \\
 & + (m_A f_A + m_B f_B)^2 \frac{C_A^2}{m_B^2} \left\{ \sum_{j \neq m} \frac{(\mathbf{k} \cdot \mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6} \right. \\
 & \left. + \sum_{n \neq m} \sum_{j \neq m, n} \frac{\mathbf{k} \cdot \mathbf{r}_{mj} \mathbf{k} \cdot \mathbf{r}_{nj}}{|\mathbf{r}_{mj}|^3 |\mathbf{r}_{nj}|^3} \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] \right\}. \quad (5)
 \end{aligned}$$

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Equation (5) is a perfect square if the square of the summation in the second term gives the two lattice sums of the last term. With the notation

$$G(\mathbf{k}, n) = \frac{i\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}]$$

we may write

$$\begin{aligned} |\sum_{n \neq m} G(\mathbf{k}, n)|^2 &= \sum_{n \neq m} \frac{i\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \\ &\times \exp [i\mathbf{k} \cdot \mathbf{r}_{mn}] \sum_{j \neq m} \frac{-i\mathbf{k} \cdot \mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3} \exp [-i\mathbf{k} \cdot \mathbf{r}_{mj}] \\ &= \sum_{j \neq m} \frac{(\mathbf{k} \cdot \mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6} + \sum_{n \neq m} \sum_{j \neq m, n} \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \frac{\mathbf{k} \cdot \mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3} \\ &\times \exp [i\mathbf{k} \cdot (\mathbf{r}_{mn} - \mathbf{r}_{mj})]. \end{aligned} \quad (6)$$

The first summation of (6) is identical with the first sum of the last term of equation (5). Since $\mathbf{r}_{mn} - \mathbf{r}_{mj} = \mathbf{r}_{jn}$, and since for a large crystal the sum over any two of the three indices m, n, j is equivalent to the sum over any other two, the second sum of (6) may be written

$$\sum \sum \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \frac{\mathbf{k} \cdot \mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3} \exp [i\mathbf{k} \cdot \mathbf{r}_{jn}].$$

The double sum is taken over any two of the three indices m, n, j with the restriction that no two of them may equal each other. This is clearly equivalent to the second sum of the last term of (5). Since $G^*(\mathbf{k}, n) = G(\mathbf{k}, -n)$, $\sum G(\mathbf{k}, n)$ is real and equation (5) may be written

$$\frac{I_D}{m_A m_B N} = \{(f_A - f_B) + (m_A f_A + m_B f_B) \frac{C_A}{m_B} \sum_{n \neq m} G(\mathbf{k}, n)\}^2. \quad (7)$$

3. Comparison of the theory with experiment

We specialize the result of equation (7) for a close-packed cubic crystal, and we compare the diffuse scattering distribution thus obtained with that experimentally measured for Cu_3Au . The vector \mathbf{r}_{mn} may be written $\mathbf{r}_{mn} = l_1 \mathbf{a}'_1 + l_2 \mathbf{a}'_2 + l_3 \mathbf{a}'_3$ where $\mathbf{a}'_1, \mathbf{a}'_2,$ and \mathbf{a}'_3 are half the usual cubic cell vectors. For a close-packed cubic cell, $l_1, l_2,$ and l_3 are integers whose sum is even. With $\mathbf{b}'_1, \mathbf{b}'_2, \mathbf{b}'_3$ reciprocal to $\mathbf{a}'_1, \mathbf{a}'_2, \mathbf{a}'_3$, \mathbf{k} may be written $\mathbf{k} = 2\pi(h_1 \mathbf{b}'_1 + h_2 \mathbf{b}'_2 + h_3 \mathbf{b}'_3)$. The continuous variables $h_1, h_2,$ and h_3 are equal to half the Miller indices at a reciprocal lattice point. Since the summation of (7) over the imaginary part of $G(\mathbf{k}, n)$ vanishes, this equation may be written

$$\begin{aligned} \frac{I_D}{m_A m_B N} &= \{(f_A - f_B) - (m_A f_A + m_B f_B) \frac{8C_A}{m_B a_0^3} \\ &\times \sum_{l_1 l_2 l_3} \frac{2\pi(l_1 h_1 + l_2 h_2 + l_3 h_3)}{(l_1^2 + l_2^2 + l_3^2)^{3/2}} \sin 2\pi(l_1 h_1 + l_2 h_2 + l_3 h_3)\}^2, \end{aligned} \quad (8)$$

where a_0 is the cubic unit cell size.

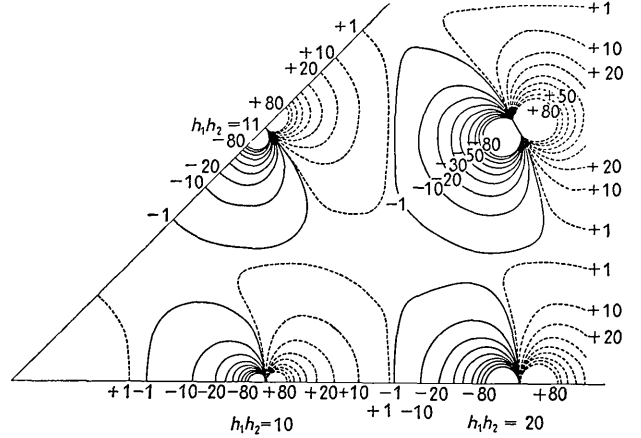


Fig. 1. The close-packed cubic size effect lattice sum,

$$\sum_{l_1 l_2 l_3} \frac{2\pi(l_1 h_1 + l_2 h_2 + l_3 h_3)}{(l_1^2 + l_2^2 + l_3^2)^{3/2}} \sin 2\pi(l_1 h_1 + l_2 h_2 + l_3 h_3)$$

in the $h_1 h_2 0$ plane of reciprocal space. Contours greater than 80 have been omitted.

The size effect lattice sum of equation (8) is readily evaluated numerically. Its distribution in the $h_1 h_2 0$ plane of reciprocal space is shown in Fig. 1. There are singularities at each reciprocal lattice point, and in the vicinity of each point the function is negative on the side of the point nearest the origin, and positive on the far side. In general, the function is large near lattice points and increases in magnitude with distance from the origin.

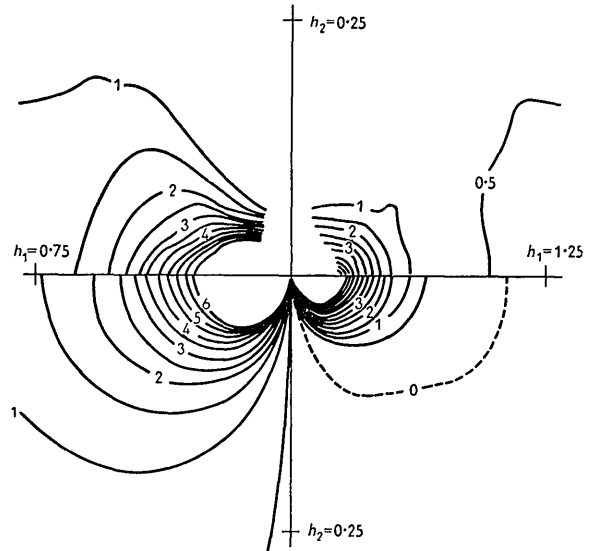


Fig. 2. Comparison of the observed (above) and computed (below) I_D/Nf_A^2 in the vicinity of $h_1 h_2 h_3 = 100$ for Cu_3Au . Contours greater than six have been omitted.

With $C_A = -0.072 \text{ \AA}^3$ for disordered Cu_3Au (copper atoms are called A), as determined in Part I from the decreased integrated intensities of the Bragg maxima,

and with $a_0 = 3.74 \text{ \AA}$, the diffuse scattering in the vicinity of $h_1 h_2 h_3 = 100$ ($hkl = 200$) in the $h_1 h_2 0$ plane was computed by means of equation (8) and the size effect function of Fig. 1. It is compared with the experimentally measured distribution in Fig. 2. The experimental data are those shown in Fig. 4 of Part I.

4. Discussion

By a rearrangement of the expression for the diffuse intensity associated with the atomic size effect, it has been shown that Huang's integral approximation is unnecessary and that the diffuse scattering may be expressed in a very simple form. In spite of the fact that the Cu_3Au specimen used contained a significant degree of short-range order, agreement between ob-

served and calculated intensity distributions in the vicinity of the Bragg maxima is quite good. It is interesting that the Laue monotonic diffuse scattering, the second term of equation (4), here completes a square, while in the case of short-range order with no size effect, it is the leading term of a Fourier series.

Equation (8) has been arranged so that the size effect function of Fig. 1 is quite general and may be used to compute the diffuse scattering for any close-packed cubic solid solution.

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A Note on the Magnetic Intensities of Powder Neutron Diffraction

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General intensity formulae of powder neutron diffraction lines are given for magnetic structures with a single-spin-axis as a function of the spin direction with respect to the crystallographic axes. If we disregard the vector properties of spins and assign a positive or negative scattering amplitude to the magnetic atoms, these scalar scatterers constitute a 'configurational symmetry' of the magnetic structure. When this symmetry is tetragonal, rhombohedral or hexagonal, the powder intensities cannot provide more information than the angle between the spin direction and the unique axis of the structure. The ambiguity of spin directions in $\alpha\text{-Fe}_2\text{O}_3$, NiAs and MnO type structures is discussed.

1. Introduction

Neutron intensities of magnetic origin at a Bragg reflection can be obtained by straightforward calculations based upon the fundamental formula of Halpern & Johnson (1939). If suitable single domain crystals are available for neutron diffraction studies of magnetic compounds, the interpretation of the magnetic intensities gives a unique solution for the spin arrangements. However, if one must depend upon the powder data alone, some ambiguities arise because of the superposition of several non-identical reflections with the same Bragg angle θ .

It has been known that the spin direction cannot be deduced from the powder data of cubic ferromagnetics, such as Fe, because any spin direction with respect to the crystallographic axis gives the same magnetic intensities if the domains are oriented randomly. The ambiguity of spin structures in cubic antiferromagnetics of the MnO-type has been discussed in detail by Li (1955) and by Keffer & O'Sullivan (1957) considering the possibility of multi-spin-axis orientations.

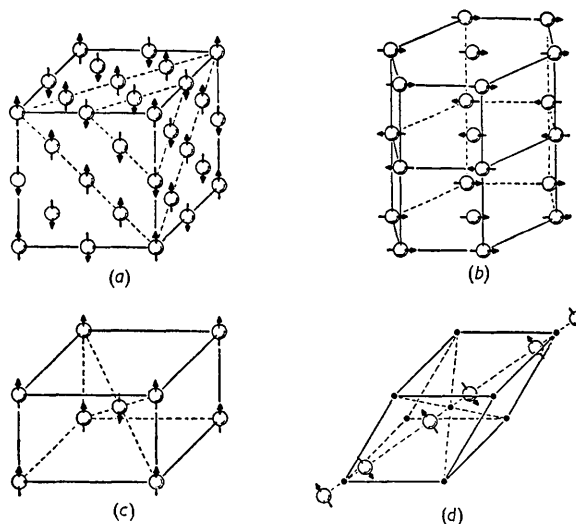


Fig. 1. Examples of antiferromagnetic spin arrangements, (a) MnO type, (b) NiAs type, (c) Rutile type, (d) Fe_2O_3 type—after Shull & Wollan (1956).