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X-Ray Diffraction Effects of Atomic Size in Alloys*

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To treat the effect of the difference in size of the atoms in a disordered binary alloy, the elastic model of Huang is modified to treat the two kinds of atoms as two different kinds of distortion centers in an average lattice. Four effects are predicted: a reduction in the intensity of the fundamental reflections by a factor $\exp[-2M']$; a broadening of the short-range-order peaks at higher $(\sin\theta)/\lambda$; a Huang diffuse scattering concentrated near the fundamentals and extended radially in reciprocal space; and a size-effect modulation in the diffuse scattering. The four effects are expressed in terms of a single distortion constant. Measurements have been made on a single crystal of Cu_3Au quenched from 600° C., and all four of the effects have been observed. Within experimental error, the magnitudes of all four effects are represented by the same value of the distortion constant.

1. Introduction

In an AB substitutional solid solution in which the two kinds of atoms are arranged with less than perfect order on a set of atomic sites, small local distortions in the crystalline lattice must exist because of the fact that the atoms are of different sizes. For the same coordination shell, it is apparent that AA, AB and BB pairs will have different average interatomic distances, and that the effect should be most pronounced for the first several shells. This effect has been shown by Warren, Averbach & Roberts (1951) to give rise to modulations in the diffuse X-ray scattering, increasing in amplitude in reciprocal space linearly with the distance from the origin. Such modulations were first observed by Roberts (1954).

Huang (1947) has shown that there is another consequence of this atomic-size effect, and that it should manifest itself in the diffraction pattern. If we could measure the interatomic distance for, say, every AA nearest-neighbor pair to be found in the crystal, we would find that they are not all the same. The reason for this is that each pair may be located in a different distribution of large and small atoms on the sites in the vicinity of the pair. Of course, such variations in interatomic distances will also exist for all other coordination shells as well. Huang's theory shows that these variations in interatomic distances give rise to a reduction of the integrated intensities of the Bragg maxima by a factor

$$\exp[-2M'] = \exp[-2B'(\sin^2\theta)/\lambda^2],$$

and to a diffuse scattering.

It is the object of this paper to extend the work of Huang and that of Warren *et al.* to show that both effects predicted by them should be observed, and that they are quantitatively related. The model for a metallic substitutional solid solution used here is a modification of that used by Huang.

2. Diffraction theory for an alloy with no order

To make clear the general features of the theory, it is applied first to the simpler case of a solid solution in which two types of atoms are randomly distributed on a set of atomic sites. Consider an alloy for which there is one atom per unit cell. Let the atomic positions be given by vectors $\mathbf{R}_n$ which differ slightly from vectors $\mathbf{a}_n = n_1\mathbf{a}_1+n_2\mathbf{a}_2+n_3\mathbf{a}_3$, n_1, n_2, and n_3 being integers and $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ vectors along the edges of the *average* primitive unit cell of the alloy. Then $\mathbf{R}_n = \mathbf{a}_n+\boldsymbol{\delta}_n$, where $\boldsymbol{\delta}_n$ is a small displacement. The unmodified component of the scattered X-ray intensity is given by

$$I = \sum_m \sum_n f_m f_n \exp[i\mathbf{k}\cdot(\mathbf{R}_m-\mathbf{R}_n)], \quad (1)$$

where f_m and f_n are the atomic scattering factors of the atoms which occupy sites m and n, and $\mathbf{k} = 2\pi(\mathbf{s}-\mathbf{s}_0)/\lambda$, $\mathbf{s}$ and $\mathbf{s}_0$ being unit vectors in the directions of the scattered and incident beams.

With the two types of atoms designated as A and B, we compute the contribution to the intensity of all atom pairs such that one atom is an A atom and the other B, and such that $\mathbf{a}_m-\mathbf{a}_n = \mathbf{r}_{mn}$ is a constant:

$$I^{mn}_{AB} = \sum f_A f_B \exp[i\mathbf{k}\cdot\mathbf{r}_{mn}+i\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)]. \quad (2)$$

The summation is taken over all such pairs which may be formed in the crystal. If the crystal is large, the number of terms in the summation of equation (2) is very nearly given by $2m_Am_BN$, where N is the total number of atoms in the crystal, m_A is the fraction of them which are A atoms, and m_B the fraction which

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are B. Since only $\boldsymbol{\delta}_m$ and $\boldsymbol{\delta}_n$ may be different for each term in the summation, we may write

$$I_{AB}^{mn} = 2m_A m_B N f_A f_B \exp\,[i\mathbf{k}\cdot\mathbf{r}_{mn}] \times\langle \exp\,[i\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)]\rangle_{AB}^{mn}\,.$$

The average indicated is taken over all pairs which contribute to the summation of equation (2). If $\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)$ is sufficiently small, the exponential may be well approximated by the first three terms of its series expansion, and I_{AB}^{mn} may be written

$$I_{AB}^{mn} = 2m_A m_B N f_A f_B \exp\,[i\mathbf{k}\cdot\mathbf{r}_{mn}]\{1+i\langle\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)\rangle_{AB}^{mn} -\tfrac{1}{2}\langle(\mathbf{k}\cdot\boldsymbol{\delta}_m)^2\rangle_{AB}^{mn}-\tfrac{1}{2}\langle(\mathbf{k}\cdot\boldsymbol{\delta}_n)^2\rangle_{AB}^{mn}+\langle(\mathbf{k}\cdot\boldsymbol{\delta}_m)(\mathbf{k}\cdot\boldsymbol{\delta}_n)\rangle_{AB}^{mn}\}\,. \tag{3}$$

At this point it is necessary to introduce a model for the solid solution which will allow the evaluation of the various averages of equation (3). Each atomic site of the crystal lattice is assumed to be occupied by a spherically symmetrical distortion center. The distortion center may be one of two kinds, depending on whether the site is occupied by an A or B atom. The lattice is assumed to be strained by each such distortion center as though it were a continuous, perfectly elastic, isotropic medium, hence according to an inverse square law. It is assumed that the deviation of an atom from its undistorted position is given by the vector sum of the individual strains caused by each distortion center in the crystal. Then

$$\mathbf{R}_n = \mathbf{a}_n+\sum_j c_j\mathbf{r}_{nj}/|\mathbf{r}_{nj}|^3\,.$$

The summation is taken over all sites j in the crystal except site n, and the coefficient c_j is either c_A or c_B depending on whether site j is occupied by an A atom or a B atom. Each distortion center j produces a change in volume in the sample

$$\Delta V_j = 4\pi r^2\Delta r = 4\pi r^2 c_j/r^2 = 4\pi c_j\,,$$

and, since it is the average lattice which is being discussed, the net change in volume due to all the distortion centers must be zero, and hence

$$m_A c_A+m_B c_B = 0\,. \tag{4}$$

We now proceed to evaluate the various components of equation (3). For an A atom at site m and a B atom at n, we express $(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)$ by

$$(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n) = \left[c_B\frac{\mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3}+\sum_{j\neq m,n} c_j\frac{\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}\right] -\left[c_A\frac{\mathbf{r}_{nm}}{|\mathbf{r}_{nm}|^3}+\sum_{j\neq m,n} c_j\frac{\mathbf{r}_{nj}}{|\mathbf{r}_{nj}|^3}\right].$$

Since $\mathbf{r}_{nm} = -\mathbf{r}_{mn}$, we may write

$$\langle\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)\rangle_{AB}^{mn} = (c_A+c_B)\frac{\mathbf{k}\cdot\mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} +\sum_{j\neq m,n}\langle c_j\rangle_{AB}^{mn}\mathbf{k}\cdot\left[\frac{\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}-\frac{\mathbf{r}_{nj}}{|\mathbf{r}_{nj}|^3}\right]. \tag{5}$$

Because there is no order, the average value of c_j is independent of the kind of atoms at sites m and n, and hence $\langle c_j\rangle = m_A c_A+m_B c_B = 0$, and (5) reduces to

$$\langle\mathbf{k}\cdot(\boldsymbol{\delta}_m-\boldsymbol{\delta}_n)\rangle_{AB}^{mn} = (c_A+c_B)\frac{\mathbf{k}\cdot\mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3}\,. \tag{6}$$

We now consider the second and third averages of (3) and start with an A atom at m and a B atom at n:

$$(\mathbf{k}\cdot\boldsymbol{\delta}_m)^2 = \left[c_B\frac{\mathbf{k}\cdot\mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3}+\sum_{j\neq m,n} c_j\frac{\mathbf{k}\cdot\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}\right]^2.$$

Since $\langle c_j\rangle = 0$ for $j \neq m, n$, we obtain

$$\langle(\mathbf{k}\cdot\boldsymbol{\delta}_m)^2\rangle_{AB}^{mn} = c_B^2\frac{(\mathbf{k}\cdot\mathbf{r}_{mn})^2}{|\mathbf{r}_{mn}|^6}+(m_A c_A^2+m_B c_B^2) \times\sum_{j\neq m,n}\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6}\,.$$

Adding and subtracting a term for $j = n$ similar to those in the sum, and writing similar terms for $\langle(\mathbf{k}\cdot\boldsymbol{\delta}_n)^2\rangle_{AB}^{mn}$, and expressing c_B in terms of c_A by equation (4), we obtain finally

$$\tfrac{1}{2}\langle(\mathbf{k}\cdot\boldsymbol{\delta}_m)^2\rangle_{AB}^{mn}+\tfrac{1}{2}\langle(\mathbf{k}\cdot\boldsymbol{\delta}_n)^2\rangle_{AB}^{mn} =\left(1-\frac{m_A}{m_B}\right)^2\frac{c_A^2}{2}\frac{(\mathbf{k}\cdot\mathbf{r}_{mn})^2}{|\mathbf{r}_{mn}|^6}+\frac{m_A}{m_B}c_A^2\sum_{j\neq m}\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6}\,. \tag{7}$$

The summation which occurs here has been evaluated by Born & Misra (1940). Using their value for a close-packed cubic crystal, and introducing the abbreviation $2M'$, we have

$$2M' = \frac{m_A}{m_B}c_A^2\sum_{j\neq m}\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6} = \frac{m_A c_A^2}{m_B}\,\frac{33{\cdot}7\,|k|^2}{a_0^4}\,, \tag{8}$$

where a_0 is the cubic unit cell edge.

We now evaluate the last average of (3) and again start with an A atom at m and a B atom at n. We have

$$(\mathbf{k}\cdot\boldsymbol{\delta}_m)(\mathbf{k}\cdot\boldsymbol{\delta}_n) = \left[c_B\frac{\mathbf{k}\cdot\mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3}+\sum_{j\neq m,n} c_j\frac{\mathbf{k}\cdot\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}\right]\left[c_A\frac{\mathbf{k}\cdot\mathbf{r}_{nm}}{|\mathbf{r}_{nm}|^3}+\sum_{j\neq m,n} c_j\frac{\mathbf{k}\cdot\mathbf{r}_{nj}}{|\mathbf{r}_{nj}|^3}\right].$$

Since $\langle c_j\rangle = 0$ for $j \neq m, n$ this reduces to

$$\langle(\mathbf{k}\cdot\boldsymbol{\delta}_m)(\mathbf{k}\cdot\boldsymbol{\delta}_n)\rangle_{AB}^{mn} = -c_A c_B\frac{(\mathbf{k}\cdot\mathbf{r}_{mn})^2}{|\mathbf{r}_{mn}|^6} +(m_A c_A^2+m_B c_B^2)\sum_{j\neq m,n}\frac{\mathbf{k}\cdot\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}\frac{\mathbf{k}\cdot\mathbf{r}_{nj}}{|\mathbf{r}_{nj}|^3}\,. \tag{9}$$

A method for the precise evaluation of the summation of equation (9) has not been deduced. Huang (1947) has approximated it by an integral with the further approximation that the lower limit of integration is taken as the value which will give the correct result for $2M'$ when this quantity is evaluated as an integral. Using Huang's result, expressing c_B in terms of c_A, and introducing the abbreviation H_{mn}, we have

$$H_{mn} = (m_A c_A^2 + m_B c_B^2) \sum_{j \neq m,n} \frac{\mathbf{k} \cdot \mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3} \frac{\mathbf{k} \cdot \mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}$$
$$= \frac{m_A}{m_B} c_A^2 \frac{4\pi |k|^2}{a_0^3} \left[\frac{2 \sin^2 \psi}{|\mathbf{r}_{mn}|} - \frac{a_0^2 \sin^2 \psi}{3 |\mathbf{r}_{mn}|^3} + \frac{2\, a_0^2 \cos^2 \psi}{3 |\mathbf{r}_{mn}|^3} \right]. \quad (10)$$

The angle ψ is the angle between the vectors $\mathbf{k}$ and $\mathbf{r}_{mn}$, and the result is specialized for a close-packed cubic crystal of cubic unit cell size a_0. A similar result may be obtained for other types of crystals.

The results of equations (6)–(10) may now be substituted into (3), and c_B expressed in terms of c_A by equation (4):

$$I_{AB}^{mn} = 2 m_A m_B N f_A f_B \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}]$$
$$\times \left\{ 1 + i c_A \frac{(m_B - m_A)}{m_B} \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} - c_A^2 \frac{(m_A^2 - 4 m_A m_B + m_B^2)}{2 m_B^2} \right.$$
$$\left. \times \frac{(\mathbf{k} \cdot \mathbf{r}_{mn})^2}{|\mathbf{r}_{mn}|^6} - 2M' + H_{mn} \right\}. \quad (11)$$

Similar expressions may be deduced for I_{AA}^{mn} and I_{BB}^{mn}:

$$I_{AA}^{mn} = m_A^2 N f_A^2 \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}] \left\{ 1 + 2 i c_A \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \right.$$
$$\left. + c_A^2 \left(\frac{m_A - 2 m_B}{m_B} \right) \frac{(\mathbf{k} \cdot \mathbf{r}_{mn})^2}{|\mathbf{r}_{mn}|^6} - 2M' + H_{mn} \right\}; \quad (12)$$

$$I_{BB}^{mn} = m_B^2 N f_B^2 \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}] \left\{ 1 - 2i \frac{m_A c_A}{m_B} \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \right.$$
$$\left. + c_A^2 m_A \left(\frac{m_B - 2 m_A}{m_B^2} \right) \frac{(\mathbf{k} \cdot \mathbf{r}_{mn})}{|\mathbf{r}_{mn}|^6} - 2M' + H_{mn} \right\}. \quad (13)$$

The three expressions may be combined to give I^{mn}, the contribution to the intensity of all atom pairs such that $\mathbf{a}_m - \mathbf{a}_n = \mathbf{r}_{mn}$ is a constant. The third terms in each bracket combine to give a term which is proportional to $(f_A - f_B)$ and rather similar in form to the part of H_{mn} involving $\cos^2 \psi$. If the ratio of f_A and f_B is not greater than 4, the third term may be neglected relative to H_{mn}, in view of the approximations involved in H_{mn}. Dropping the third term, I^{mn} is now summed over all values of r_{mn} to obtain the total intensity in electron units. The expression for I^{mn} applies only for $m \neq n$; for the case $m = n$, $I^{mm} = N (m_A f_A^2 + m_B f_B^2)$:

$$\frac{I}{N} = (m_A f_A^2 + m_B f_B^2) + 2 i m_A c_A (m_A f_A + m_B f_B)(f_A - f_B)$$
$$\times \sum_{n \neq m} \frac{\mathbf{k} \cdot \mathbf{r}_{mn}}{|\mathbf{r}_{mn}|^3} \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}] + (m_A f_A + m_B f_B)^2$$
$$\times \sum_{n \neq m} (1 - 2M' + H_{mn}) \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}]. \quad (14)$$

It is within the approximations made to write $1 - 2M' = \exp [-2M']$, which we do to facilitate comparison with the theory for thermal motion. In that part of (14), involving $1 - 2M'$, we add and subtract a similar term for $n = m$. We represent the interatomic vector by $r_{mn} = l_1 \mathbf{a}_1' + l_2 \mathbf{a}_2' + l_3 \mathbf{a}_3'$, where $\mathbf{a}_1'$, $\mathbf{a}_2'$ and $\mathbf{a}_3'$ are half the usual cubic cell vectors and $l_1 l_2 l_3$ are integers whose sum must be even for a close-packed cubic crystal. The vector $\mathbf{k}$ may be written

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

where the $\mathbf{b}_1'$ are reciprocal to the $\mathbf{a}_1'$ and $h_1 h_2 h_3$ are continuous variables.

With these changes and some re-arrangement, (14) can be written as the sum of five terms:

$$\frac{I}{N} = (m_A f_A + m_B f_B)^2 \exp [-2M']$$
$$\times \sum_{l_1 l_2 l_3} \exp [2\pi i (l_1 h_1 + l_2 h_2 + l_3 h_3)]$$
$$+ (m_A f_A + m_B f_B)^2 (1 - \exp [-2M'])$$
$$+ m_A m_B (f_A - f_B)^2 - (m_A f_A + m_B f_B)(f_A - f_B) \sum_{l_1 l_2 l_3} \frac{2 m_A c_A}{|r(l_1 l_2 l_3)|^3}$$
$$\times 2\pi (l_1 h_1 + l_2 h_2 + l_3 h_3) \sin 2\pi (l_1 h_1 + l_2 h_2 + l_3 h_3)$$
$$+ (m_A f_A + m_B f_B)^2 \sum_{n \neq m} H_{mn} \exp [i \mathbf{k} \cdot \mathbf{r}_{mn}]. \quad (15)$$

The first part gives rise to the sharp crystalline reflections, unbroadened by the strains of the size effect, but reduced in intensity by a factor $\exp [-2M']$. This effect is entirely analogous to that of thermal motion.

The second part of the intensity expression also has an analogue in the diffraction theory of thermal motion. It is identical in form with the temperature diffuse scattering for a crystal in which the atoms are assumed to vibrate independently of each other. This term conserves the intensity lost by the fundamental crystalline reflections as the crystal is changed from a state of perfect long-range order to a state of no order.

The third component is the Laue monotonic diffuse scattering which conserves the intensity associated with superstructure reflections of a perfectly ordered crystal.

The size-effect modulation of the diffuse scattering predicted by Warren *et al.* (1951) is given by the fourth part of (15). This term is a consequence of the fact that AA, AB, and BB pairs of atoms have different average interatomic distances for the same coordination shell. It is seen that its magnitude depends not only on the distortion constant but also on the difference in the atomic scattering factors of the two kinds of atoms. The modulations increase in amplitude in reciprocal space linearly with the distance from the origin. A result of the theory is that the magnitude of each $l_1 l_2 l_3$ modulation is determined.

Huang (1947) has evaluated the summation which occurs in the final part of (15). With the aid of his result, this contribution to the intensity may be written

$$\frac{I_H}{N} = (m_A f_A + m_B f_B)^2 \, 32 \pi^2 \frac{m_A c_A^2}{m_B a_0^6} \frac{|k|^2}{|2\pi g|^2} \left\{ \left(5 \frac{(\mathbf{g} \cdot \mathbf{k})^2}{|\mathbf{g}|^2 |\mathbf{k}|^2} - \frac{5}{3} \right) \right.$$
$$\left. \times \frac{\sin (2\pi a_0 |g|)}{2\pi a_0 |g|} + \left(\frac{5}{3} - \frac{(\mathbf{g} \cdot \mathbf{k})^2}{|\mathbf{g}|^2 |\mathbf{k}|^2} \right) \cos (2\pi a_0 |g|) \right\}. \quad (16)$$

The vector $\mathbf{g}$ is a vector from the nearest reciprocal-lattice point to the point in reciprocal space at which the diffuse intensity is being measured.

It is seen from (16) that the Huang diffuse scattering, because of its inverse-square dependence on $|\mathbf{g}|$, is large only near the fundamental reflections. Huang has pointed out that, for $\mathbf{g}$ perpendicular to $\mathbf{k}$, it is very small. Hence the Huang diffuse scattering is concentrated near the reciprocal-lattice points in the vicinity of a line from the origin through each lattice point. This, too, is similar to the result of the temperature diffuse scattering theory. The Huang scattering results from averages of terms of the type $(\mathbf{k}\cdot\delta_m)(\mathbf{k}\cdot\delta_n)$. That the time average of such cross terms is not zero for thermal displacements accounts for the concentration of the temperature diffuse scattering in the vicinity of the Bragg reflections. However, it is in general true that temperature diffuse scattering is distributed in a much more nearly spherically symmetrical way about the Bragg peaks.

3. Diffraction theory for an alloy with short-range order

For an alloy with short-range order, it is not possible to develop a rigorous theory involving only the distortion constants c_A and c_B and the short-range-order coefficients α_j. It is still true that $m_Ac_A+m_Bc_B = 0$, but, since the atoms are not randomly distributed among the atomic sites, $\langle c_j\rangle_{AB}^{mn}$ does not vanish. Its value depends on the probability of finding a particular kind of atom at site j after having specified the occupants of the two sites m and n. Such a probability is independent of the usual short-range-order probability; if it could be measured experimentally, there would result a more complete description of the atomic arrangement than is possible from the usual short-range-order parameters.

For large crystals, the total number of AB pairs whose sites m and n satisfy the condition that $\mathbf{r}_{mn}$ is a constant, is given by $2m_Bp_{mn}N$, where p_{mn} is the probability of finding an A atom at site n if there is a B atom at site m. With short-range order, equation (3) becomes

$$I_{AB}^{mn} = 2m_Bp_{mn}Nf_Af_B\exp[i\mathbf{k}\cdot\mathbf{r}_{mn}]\{1+i\langle\mathbf{k}\cdot(\delta_m-\delta_n)\rangle_{AB}^{mn} -\tfrac{1}{2}\langle(\mathbf{k}\cdot\delta_m)^2\rangle_{AB}^{mn}-\tfrac{1}{2}\langle(\mathbf{k}\cdot\delta_n)^2\rangle_{AB}^{mn}+\langle(\mathbf{k}\cdot\delta_m)(\mathbf{k}\cdot\delta_n)\rangle_{AB}^{mn}\}. \tag{17}$$

We define quantities ε_{AB}^{mn}, ε_{AA}^{mn} and ε_{BB}^{mn}, which may be functions of the composition and the degree of short-range order:

$$\left.\begin{aligned}\mathbf{k}\cdot\mathbf{r}_{mn}\varepsilon_{AB}^{mn} &= \langle\mathbf{k}\cdot(\delta_m-\delta_n)\rangle_{AB}^{mn},\\ \mathbf{k}\cdot\mathbf{r}_{mn}\varepsilon_{AA}^{mn} &= \langle\mathbf{k}\cdot(\delta_m-\delta_n)\rangle_{AA}^{mn},\\ \mathbf{k}\cdot\mathbf{r}_{mn}\varepsilon_{BB}^{mn} &= \langle\mathbf{k}\cdot(\delta_m-\delta_n)\rangle_{BB}^{mn}.\end{aligned}\right\} \tag{18}$$

Consider now the second average of (17):

$$\langle(\mathbf{k}\cdot\delta_m)^2\rangle_{AB}^{mn} = \sum_{j\neq m}\langle c_j^2\rangle_{AB}^{mn}\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6} + \sum_{j\neq m}\sum_{i\neq j}\langle c_jc_i\rangle_{AB}^{mn}\frac{\mathbf{k}\cdot\mathbf{r}_{mj}}{|\mathbf{r}_{mj}|^3}\frac{\mathbf{k}\cdot\mathbf{r}_{mi}}{|\mathbf{r}_{mi}|^3}. \tag{19}$$

We are interested in this expression when site n is far from site m, and hence the neighbors of m are independent of the occupancy of site n. If p'_{mj} is the probability of finding a B atom at j when there is an A atom at m, the first average can be written

$$\langle c_j^2\rangle_{AB}^{mn} = \langle c_j^2\rangle_A^m = (1-p'_{mj})c_A^2+p'_{mj}c_B^2.$$

The second average can be evaluated only by assuming that the occupancy of positions i and j are independent and hence $\langle c_jc_i\rangle = \langle c_j\rangle\langle c_i\rangle$. Making use of the fact that the sum over a complete surrounding shell $\sum_i\langle c_i\rangle(\mathbf{k}\cdot\mathbf{r}_{mj})/|\mathbf{r}_{mj}|^3$ must be zero, since neighbors of m occur in diametrically opposite pairs, and that $\langle c_j\rangle_A^m = (1-p'_{mj})c_A+p'_{mj}c_B$, equation (19) becomes

$$2M'_A = \langle(\mathbf{k}\cdot\delta_m)^2\rangle_A^m = \sum_{j\neq m}c_A^2(1-\alpha_{mj})\left(\frac{m_A}{m_B}+\alpha_{mj}\right)\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6}, \tag{20}$$

where the short-range-order parameter is given by $\alpha_{mj} = 1-p'_{mj}/m_B$. Similarly,

$$2M'_B = \langle(\mathbf{k}\cdot\delta_m)^2\rangle_B^m = \sum_{j\neq m}c_A^2\left(\frac{m_A}{m_B}\right)^2(1-\alpha_{mj})\left(\frac{m_B}{m_A}+\alpha_{mj}\right)\frac{(\mathbf{k}\cdot\mathbf{r}_{mj})^2}{|\mathbf{r}_{mj}|^6}. \tag{21}$$

For small values of the short-range-order parameter α_{mj}, the values of $2M'_A$ and $2M'_B$ do not differ greatly from the $2M'$ given by (8). Although different values of M'_A and M'_B are to be expected, it does not seem safe to rely on the differences given by (20) and (21) in view of the approximations involved in the derivation. In what follows we will restrict ourselves to the case of a small degree of short-range order and approximate M'_A and M'_B by the value of M' given by (8).

The final average of equation (17), which gives rise to the Huang diffuse scattering, has been evaluated in a very approximate form for an alloy with no short-range order. The effect of a small amount of order is probably within the approximations which have been made, and we will use the same approximate form for an alloy with a small amount of order.

With the abbreviation $\eta = f_B/f_A$, we rewrite (15) in a form suitable for a small degree of short-range order:

$$\begin{aligned}\frac{I}{Nf_A^2} = {} & (m_A+m_B\eta)^2 \exp\,[-2M'] \\ & \times \sum_{l_1l_2l_3} \exp\,[2\pi i(l_1h_1+l_2h_2+l_3h_3)] \\ & +(m_A+m_B\eta)^2(1-\exp\,[-2M']) \\ & +m_Am_B(1-\eta)^2\{1+\sum_{l_1l_2l_3\neq 0}\alpha(l_1l_2l_3) \\ & \times \exp\,[-2M'+H(l_1l_2l_3)]\cos 2\pi(l_1h_1+l_2h_2+l_3h_3)\} \\ & -\sum_{l_1l_2l_3}\beta(l_1l_2l_3)2\pi(l_1h_1+l_2h_2+l_3h_3)\sin 2\pi(l_1h_1+l_2h_2+l_3h_3) \\ & +(m_A+m_B\eta)^2\sum_{n\neq m} H_{mn}\exp\,[i\mathbf{k}\cdot\mathbf{r}_{mn}]\,; \qquad (22)\end{aligned}$$

where

$$\begin{aligned}\beta(l_1l_2l_3) = {} & m_A[1-p'(l_1l_2l_3)]\varepsilon_{AA}(l_1l_2l_3) \\ & +2m_Bp(l_1l_2l_3)\eta\varepsilon_{AB}(l_1l_2l_3)+m_B[1-p(l_1l_2l_3)]\eta^2\varepsilon_{BB}(l_1l_2l_3)\,.\end{aligned}$$

Because the weighted average of the distances between AB, AA, and BB pairs must conform to the average lattice constant, there exists a relation among the ε's:

$$\begin{aligned}& m_A[1-p'(l_1l_2l_3)]\varepsilon_{AA}(l_1l_2l_3)+2m_Bp(l_1l_2l_3)\varepsilon_{AB}(l_1l_2l_3) \\ & \qquad +m_B[1-p(l_1l_2l_3)]\varepsilon_{BB}(l_1l_2l_3) = 0\,.\end{aligned}$$

With the aid of this relation we may write

$$\begin{aligned}\beta(l_1l_2l_3) = {} & (1-\eta)\{m_A[1-p'(l_1l_2l_3)]\varepsilon_{AA}(l_1l_2l_3) \\ & -m_B[1-p(l_1l_2l_3)]\eta\varepsilon_{BB}(l_1l_2l_3)\}\,.\end{aligned}$$

In addition to the effect of short-range order on the size-effect modulations, the Laue monotonic diffuse scattering of equation (15) has been replaced by the usual short-range-order Fourier series. However, because of the size effect, we see that the apparent values of the short-range parameters are slightly smaller than their true value by a factor $\exp\,[-2M'+H(l_1l_2l_3)]$. The size effect on the short-range-order diffuse peaks is to cause them to be broadened, the effect being more pronounced for peaks further from the origin of reciprocal space.

4. Experimental verification of the theory

It has been shown that we may expect to detect the size effect in the diffraction pattern of an alloy in what we may consider to be four ways: (*a*) The Bragg maxima are of reduced integrated intensity; (*b*) the short-range-order peaks at higher $\sin\theta/\lambda$ are broader; (*c*) there is the Huang diffuse scattering concentrated near the crystalline reflections and along a line from the reflection through the origin of reciprocal space; and (*d*) there are the size-effect modulations of the diffuse scattering.

To measure the size-effect reduction of the integrated intensity, peak areas were measured with a Norelco diffractometer for two powder samples of Cu_3Au. The first was quenched from above 600° C. and therefore had no long-range order, while the second was annealed just below T_c and slowly cooled to room temperature to give a nearly perfect long-range order. Except for the size-effect reduction $\exp\,[-2M']$ and a small difference in their Debye temperatures, the integrated intensities of the fundamental reflections from these two samples should be the same. To avoid difficulties with extinction and surface roughness and to observe the effect where it should be largest, high-angle reflections of Mo $K\alpha$ radiation were used.

The ratio of the peak areas of the disordered sample to that of the ordered sample for the same reflection should give

$$A_O/A_D = \exp\,[-\Delta(2M)](1-2M')\,;$$

$\Delta(2M)$ is the difference in the Debye factors for ordered and disordered Cu_3Au. We have replaced $\exp\,[-2M']$ by $(1-2M')$, the form in which it was actually derived. Fig. 1 shows a plot of the quantity

$$\{1-(A_O/A_D)\exp\,[\Delta(2M)]\} = 2M'$$

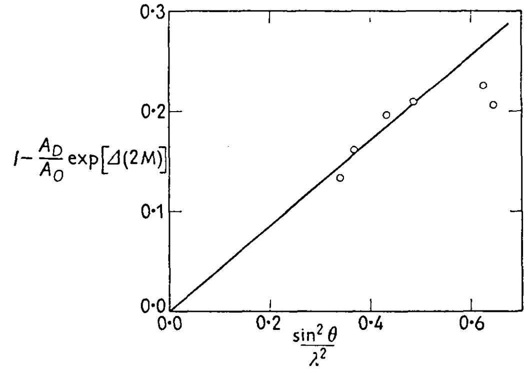

Fig. 1. Plot of $1-(A_D/A_O)\exp\,[\Delta(2M)]$ vs. $\sin^2\theta/\lambda^2$ for high-order fundamental reflections from Cu_3Au powder using Mo $K\alpha$. A_D is the peak area for a disordered sample quenched from 600° C., and A_O is that for a highly ordered sample.

as a function of $\sin^2\theta/\lambda^2$, $\Delta(2M)$ having been computed to be $0{\cdot}074\sin^2\theta/\lambda^2$ from the Debye temperatures given by Quimby (1954). From the slope of this line and with the aid of equation (8), we may write

$$0{\cdot}43\,\frac{\sin^2\theta}{\lambda^2} = \frac{m_Ac_A^2}{m_B}\,\frac{33{\cdot}7}{a_0^4}\left(\frac{4\pi\sin\theta}{\lambda}\right)^2.$$

With $a_0 = 3{\cdot}74$ Å, there results a value of c_A of 0·072 Å³.

To measure the size effect on the diffuse scattering, we must first consider how to separate the final four parts of equation (22). The second part is quite small and structureless, and, with a knowledge of c_A as determined from integrated intensity measurements, one may compute it and subtract it off. The significant part of the diffuse scattering, I'_D, then is the sum of the short-range-order scattering (I_{SRO}), the size-effect modulations (I_M), and the Huang scattering (I_H). Shown in Fig. 2(*a*) is a plot of measured values of I'_D/Nf_A^2 as a function of h_1 along the h_100 axis in reciprocal space as determined from a single crystal

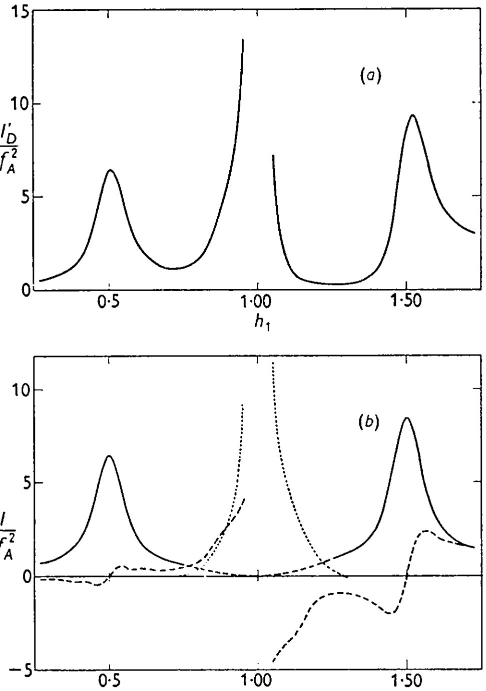

Fig. 2. (a) Variation of the diffuse intensity I'_D along the $h_1 00$ axis in reciprocal space for a single crystal of Cu_3Au quenched from 600° C. (b) The three components of I'_D/Nf_A^2 for Cu_3Au along the $h_1 00$ line in reciprocal space. Solid line: I_{SRO}/Nf_A^2; dashed line: I_M/Nf_A^2; dotted line: I_H/Nf_A^2.

of Cu_3Au. Here h_1 is a continuous variable which has the value $h_1 = 1$ at the 200 Bragg maximum. The sample was quenched from above 600° C. so that there was no long-range order. Copper $K\alpha$ radiation, monochromated by a LiF crystal bent according to Chipman (1956), was used. Balanced Ni–Co filters eliminated the half-wavelength radiation from the monochromator. The intensity measurements were corrected for air scattering and converted to absolute units by comparison with the scattered intensity from a sample of lucite ($C_5H_8O_2$) at a large scattering angle. Under these conditions the atoms of lucite may be considered to scatter independently of each other. The data were corrected for temperature diffuse scattering by making measurements at room temperature, and at −115° C., assuming the thermal diffuse scattering to be proportional to the absolute temperature. The data were corrected for Compton modified radiation, and a Hönl dispersion correction was applied to the atomic scattering factors used.

Along the $h_1 00$ axis we may write

$$\frac{I'_D}{Nf_A^2} = m_A m_B (1-\eta)^2 \sum_{l_1 l_2 l_3} \alpha(l_1 l_2 l_3) \cos 2\pi h_1 l_1 - \sum_{l_1 l_2 l_3} \beta(l_1 l_2 l_3)(2\pi h_1 l_1) \sin 2\pi h_1 l_1 + (m_A + m_B \eta)^2\, 32\pi^2 \times \frac{m_A c_A^2}{m_B a_0^6} \frac{h_1^2}{(\Delta h_1)^2} \left[\frac{10}{3} \frac{\sin 4\pi(\Delta h_1)}{4\pi \Delta h_1} + \frac{2}{3} \cos 4\pi(\Delta h_1) \right].$$

The quantity Δh_1 is the absolute value of the difference between h_1 and the value it takes on at the nearest fundamental reflection. For the moment we neglect the size effect on the short-range-order parameters which causes them to appear slightly smaller than their true value.

In the neighborhood of the superstructure position $h_1 = 0{\cdot}5$ it may be safely assumed that the Huang scattering is negligibly small. Hence $I'_D N f_A^2$, except for its dependence on the slowly varying η, is the sum of an even function about $h_1 = 0{\cdot}5$ and h_1 times an odd function. Therefore the difference between I'_D/Nf_A^2 at $h_1 = 0{\cdot}5 + x$ and at $h_1 = 0{\cdot}5 - x$ is independent of I_{SRO} and allows the determination of I_M/Nf_A^2. This may then be subtracted from I'_D/Nf_A^2 to obtain I_{SRO}/Nf_A^2. A similar separation may be accomplished in the vicinity of $h_1 = 1{\cdot}5$.

The short-range-order peak so obtained may then be extrapolated into the neighborhood of the fundamental reflection ($h_1 = 1$) where it is known to be small and slowly varying. The difference between I'_D/Nf_A^2 and this extrapolated curve gives the sum of I_M/Nf_A^2 and I_H/Nf_A^2 and hence h_1 times an odd function plus h_1^2 times an even function. A separation of these two quantities similar to that described above is then possible. Fig. 2(b) shows the three components of I'_D separated as described above. The size-effect on the short-range-order diffuse scattering (b) is to cause the apparent values of the short-range-order parameters to be smaller than their true value by a factor $\exp[-2M' + H(l_1 l_2 l_3)]$. Since $H(l_1 l_2 l_3)$ decreases and approaches zero with increasing $l_1 l_2 l_3$, the ratio of the apparent to the true value of $\alpha(l_1 l_2 l_3)$ should approach the limiting value $\exp[-2M']$. But the fluctuations in inter-site vectors due to thermal motion affect the short-range-order scattering in precisely the same way as those resulting from the size-effect. Though we have corrected the diffraction pattern for temperature diffuse scattering, this diffuse scattering is associated with the fundamental reflections, as is the Huang scattering in the case of the size effect. Hence the ratio of the apparent to the true value of $\alpha(l_1 l_2 l_3)$ should approach $\exp[-2(M+M')]$. The value of $2M$ at room temperature as determined from the Debye temperature (Quimby, 1954) for Cu_3Au at room temperature with no long-range order is $2M = 1{\cdot}03 \sin^2\theta/\lambda^2$. Hence $2(M+M') = 1{\cdot}46 \sin^2\theta/\lambda^2$. At the superstructure position $h_1 h_2 h_3 = \frac{1}{2}00$, $\exp[-2(M+M')]$ is very nearly unity. However at $\frac{1}{2}00$, its value is 0·79.

Fourier coefficients of the quantity

$$I_{SRO}/[Nf_A^2 m_A m_B (1-\eta)^2]$$

along the $h_1 00$ axis were determined for the $\frac{1}{2}00$ and $\frac{3}{2}00$ peaks. These coefficients are given by $A(l_1) = \sum_{l_2 l_3} \alpha'(l_1 l_2 l_3)$, where the $\alpha'(l_1 l_2 l_3)$ are apparent coefficients neglecting the $\exp[-(2M+2M')+H]$ correction. Shown in Table 1 are the ratios of the corresponding $A(l_1)$ for the $\frac{3}{2}00$ peak to that of the $\frac{1}{2}00$ peak.

Table 1

l_1	$A(l_1)(\frac{3}{2}00)/A(l_1)(\frac{1}{2}00)$
0	0·98
1	0·90
2	0·80
3	0·82
4	0·82
5	0·81

The values in Table 1 indicate that for the more distant neighbors the $\alpha(l_1l_2l_3)$ for the $\frac{3}{2}00$ peak are reduced by approximately the expected value $\exp[-2(M+M')] = 0{\cdot}79$. This is not a critical test of the value of $2M'$ since $2M'$ is only about 30% of the value of $2(M+M')$. The values do, however, suggest the need for a correction factor for distant-neighbor short-range-order coefficients when obtained from peaks well out in reciprocal space. The existence of such a correction factor for the effect of thermal vibrations has been suggested (Muldawer, 1952).

The measurements of the Huang diffuse scattering (*c*) along the h_100 axis are shown in Fig. 3, compared with the function

$$K(m_A+m_B\eta)^2\,\frac{h_1^2}{(\Delta h)^2}\left[\frac{10}{3}\,\frac{\sin 4\pi(\Delta h_1)}{4\pi(\Delta h_1)}+\frac{2}{3}\cos 4\pi(\Delta h_1)\right],$$

where the constant K was chosen to obtain a reasonable fit with experiment. The value of K used corresponds to a value of c_A of 0·10 Å^3. With the approximations made to obtain the theoretical expression for the Huang scattering, this seems to be in reasonable agreement with the value of $c_A = 0{\cdot}072$ Å^3 obtained from the integrated intensity measurements.

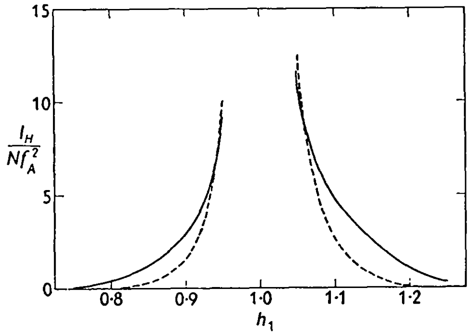

Fig. 3. Variation of the Huang diffuse scattering along the h_100 line in reciprocal space in the vicinity of the 200 reflection for a single crystal of Cu_3Au quenched from 600° C. Solid line: measured; dashed line: calculated.

A contour map of the total unmodified diffuse intensity, corrected for temperature diffuse scattering, for Cu_3Au in the vicinity of the 200 Bragg reflection is shown in Fig. 4. The quantity plotted is intensity in electron units per atom divided by f_A^2, and contour lines are drawn at intervals of 0·5. The map corresponds to the h_1h_20 plane in reciprocal space. The data for this map are an extension of the h_100 data discussed earlier and were obtained in the same way.

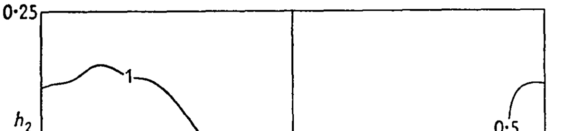

Fig. 4. Contour plot of the measured I_D/Nf_A^2 in the h_1h_20 plane in the vicinity of the 200 reflection for a single crystal of Cu_3Au quenched from 600° C. The plotted values are corrected for temperature diffuse scattering and they represent mainly the Huang diffuse scattering and the size-effect modulations.

It is seen that the radial distribution of the diffuse scattering near the crystalline reflection predicted by the Huang theory is observed. That the total diffuse scattering on the far side of the 200 reflection is less than that nearer the origin results from the fact that the size-effect modulations are positive on one side and negative on the other.

Along the h_100 axis the modulations of the diffuse intensity caused by the size-effect (*d*) may be considered as a periodic function multiplied by h_1. We may write

$$I'_M = I_M/[Nf_A^2h_1(\eta-1)(m_A+m_B\eta)] = -\sum_{l_1} B(l_1)\sin 2\pi h_1l_1\,,$$

where the Fourier coefficient $B(l_1)$ is given by

$$B(l_1) = \sum_{l_2l_3}(2\pi l_1)(\beta(l_1l_2l_3)/[(\eta-1)(m_A+m_B\eta)]\,.$$

The summation is taken over all $\beta(l_1l_2l_3)$ which share a common value of l_1. Division by $(\eta-1)(m_A+m_B\eta)$ is intended to minimize the dependence of I'_M on η.

If the effect of short-range order on the modulations is neglected, they may be computed from a knowledge of the distortion constant c_A. For a crystal with no order, $\beta(l_1l_2l_3) = (m_A+m_B\eta)(1-\eta)2m_Ac_A/|r(l_1l_2l_3)|^3$, as is apparent from equation (15). One may then readily compute the Fourier coefficients $B(l_1)$ of I'_M. Shown in Table 2 is a comparison of the measured values of $B(l_1)$ as determined from the data of Fig. 2(*b*) with those computed neglecting the effect of order

Table 2

l_1	Observed $B(l_1)$	Calculated $B(l_1)$
1	0·598	0·515
2	0·374	0·446
3	0·536	0·352
4	0·230	0·237
5	0·264	0·132
6	0·112	—
7	0·170	—
8	0·090	—

with $c_A = 0{\cdot}072$ Å^3. The contributions to $B(l_1)$ from the 600 coordination shell and all higher-order shells have been neglected in the calculations, thus accounting for the small computed value of B_5 and no computed values for B_6, B_7, and B_8.

There is rough general agreement. However, the theory has failed to predict that $B(l_1)$, for even l_1, is small, as was observed. That this is so is a consequence of the shift to slightly higher 2θ of the short-range-order peaks.

5. Discussion

The integrated intensities of the fundamental reflections are decreased by a factor exp $[-2B' \sin^2 \theta/\lambda^2]$ due to the difference in size of the atoms, and by a factor exp $[-2B \sin^2 \theta/\lambda^2]$ due to thermal vibrations. From the present set of measurements on Cu_3Au quenched from 600° C. and measured at room temperature, $B' = 0{\cdot}22$ Å^2 and $B = 0{\cdot}52$ Å^2. The size effect is therefore roughly half the thermal effect. A previous measurement by a different method (Herbstein, Borie & Averbach, 1956) gave for disordered Cu_3Au $B' = 0{\cdot}17$ Å^2. Measurements on a disordered sample of 15 atomic % gold in copper (Coyle & Gale, 1955) gave $B' = 0{\cdot}32$ Å^2.

Since $2B' = 16\pi^2 m_A c_A^2\ 33{\cdot}7/[m_B a_0^4]$, the measured value of $2B'$ gives the magnitude of the distortion constant c_A, and from $m_A c_A + m_B c_B = 0$ we obtain the magnitude of c_B. In the present case the correct sign is obvious, $c_A = -0{\cdot}072$ Å^3 and $c_B = +0{\cdot}022$ Å^3. If the radius of an atom differs from that of the average atom by Δr, then from the definition of c, $\Delta r/r = c/r^3$. For Cu_3Au, $(\Delta r/r)_{Cu} = -0{\cdot}031$ and $(\Delta r/r)_{Au} = +0{\cdot}095$. From the lattice constants of Cu, Au and Cu_3Au, and assuming that the Cu and Au atoms maintain in the alloy the same size as in the pure element, we obtain $(\Delta r/r)_{Cu} = -0{\cdot}032$ and $(\Delta r/r)_{Au} = 0{\cdot}091$. In this case the assumption that the atoms maintain their size in the alloy would have predicted distortion constants c_A and c_B in good agreement with those found from the exp $[-2M']$ reduction in intensity. However, it is probably not safe to assume that this relation will be maintained in all alloys.

The elastic model which has been used assumes that an A atom at position m is characterized by a distortion constant c_A, and that neighboring atoms are displaced by the A atom at m in a manner characterized by c_A, independent of the kind of neighboring atom. For an alloy system in which the nearest neighbor AB distance is closely the average of the AA and BB distances, the model is probably a good approximation.

Next to the reduction in the intensities of the fundamentals by the factor exp $[-2M']$, the simplest effect of the difference in size of the atoms to observe experimentally is the modulation in the diffuse intensity. Within experimental error the magnitude of the modulations was correctly predicted by the same distortion constants obtained from exp $[-2M']$. We therefore have a relation between the two effects such that either one can be predicted approximately from the other. In detail, however, there is still a discrepancy. There is an outward shift of the short-range-order peaks which can be considered as produced by the modulation term. This effect is not adequately explained by the equation which we have derived on the basis that short-range order can be neglected. There is probably a great deal of important information about the fine structure of short-range order to be obtained from this remaining discrepancy.

The Huang diffuse scattering is the most difficult size effect to observe experimentally, since it is concentrated near the strong fundamental reflections and in the region where the temperature diffuse scattering is a maximum. As observed in this work, the measurements are probably good enough to verify the qualitative correctness of the expression for the Huang diffuse scattering, but neither the measurements nor the theory are good enough to allow quantitative information about the distortion to be obtained from the measured Huang diffuse scattering.

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