Comparison of the results obtained by both optical-diffraction and X-ray-diffraction methods lends support to the suggestion made by Edmunds & Hinde, in connection with $AuCu_3$, that ordering progresses through the general interchange of nearest-neighbour atoms so that like atoms tend to avoid each other. However, it seems unlikely that reduction in strain energy contributes to the ordering forces in $CdMg_3$ as the atoms of Cd and Mg have almost identical radii, although there remains the possibility that the constituent ions of the alloy may differ appreciably in radii.

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Scattering of X-rays by Defect Structures. II. An Extension of the Theory

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An earlier theory of the scattering of X-rays by a crystal containing defects is extended to the case where atoms are displaced by comparatively large amounts from their mean positions. It is assumed that a displaced atom is influenced to about the same extent by a number of defects.

In an earlier paper (Cochran, 1956; referred to here as Part I) it was shown that the intensity of X-ray scattering from a crystal containing defects depends in a simple way on the Fourier transforms of the defects considered separately. The theory given in that paper is believed to be accurate, no matter how large the displacements of the atoms from their positions in the corresponding perfect crystal, in the situation where each atom is affected by no more than one defect. The theory also applies to the more important case where each atom is influenced by a large number of defects, provided that the displacement $\mathbf{u}$ of an atom is small enough for the approximation

$$\exp [2\pi i\mathbf{u}\cdot\mathbf{S}]-1 = 2\pi i\mathbf{u}\cdot\mathbf{S}$$

to apply, $\mathbf{S}$ being a vector in reciprocal space, as defined in Part I. Taking $S = 1{\cdot}3$ Å^{-1} (the limit of Cu $K\alpha$ radiation) requires $\mathbf{u}$ to be less than about 0·02 Å, a very restrictive condition. In applying this theory to the problem of the scattering of X-rays by a structure containing interstitial atoms, considerably larger displacements are encountered. We have therefore extended the theory to the situation where the displacements may be large, and are brought about by the simultaneous operation of a large number of defects, randomly distributed throughout the crystal. The theory of Part I took account of possible changes, by replacement, of the scattering factors of atoms; the present theory is restricted to defects made up of atomic displacements.

The intensity from the crystal containing defects will be

$$|T_{C+\Delta}(\mathbf{S})|^2 = \sum_p \sum_q f_p f_q \exp [2\pi i(\mathbf{R}_p-\mathbf{R}_q)\cdot\mathbf{S}] \times \exp [2\pi i(\mathbf{u}_p-\mathbf{u}_q)\cdot\mathbf{S}] \,. \quad (1)$$

The notation is largely as in Part I. $\mathbf{R}_p$ locates an atom whose scattering factor is f_p, and which is displaced by $\mathbf{u}_p$. Defects $\delta_1, \ldots, \delta_n$, together with the perfect crystal C, make up a defective crystal $C+\Delta$ whose Fourier transform is $T_{C+\Delta}(\mathbf{S})$. If $\boldsymbol{\varepsilon}_{1p}, \ldots, \boldsymbol{\varepsilon}_{np}$ are the displacements of the pth atom produced by $\delta_1, \ldots, \delta_n$ acting separately, $\mathbf{u}_p$ is given by

$$\mathbf{u}_p = \sum_{j=1}^{n} \boldsymbol{\varepsilon}_{jp} \,,$$

that is, the principle of superposition is assumed. The coordinate parameters of an atom in the average unit cell of $C+\Delta$ are assumed to be the same as they were in the perfect crystal C, possibly after allowance for expansion of the lattice as in Part I. We define u as the component of $\mathbf{u}$ in the direction of $\mathbf{S}$, and ε similarly. Since u will *not* be used to denote $|\mathbf{u}|$, no confusion need arise.

Our fundamental assumption, which can be justified by appeal to the central limit theorem, is that the random distribution of the defects δ_j, which will result in the displacement components $\varepsilon_1, \ldots, \varepsilon_n$ varying in a random manner, will cause $u = \sum_{j=1}^{n} \varepsilon_j$ to have a Gaussian distribution, as will $u_p - u_q$. Corresponding to a fixed value of $\mathbf{R}_p - \mathbf{R}_q$, and therefore to a fixed value of $f_p f_q$, there are N^1 values of $u_p - u_q$, and these N^1 points will have a Gaussian distribution about zero, with variance $\overline{(u_p-u_q)^2}$. (The actual value of N^1 need not concern us; it tends to N, the number of unit cells in the crystal, when $\mathbf{R}_p - \mathbf{R}_q$ is small.) We now replace this distribution of points on a line by a continuous distribution

$$\frac{N^1}{(2\pi\,\overline{(u_p-u_q)^2})^{\frac{1}{2}}} \exp\left[-\frac{u^2}{2\,\overline{(u_p-u_q)^2}}\right] . \tag{2}$$

Expression (1) may be rewritten as

$$|T_{C+\Delta}(\mathbf{S})|^2 = \Sigma f_p f_q \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \times (\Sigma \exp\,[2\pi i(\mathbf{u}_p - \mathbf{u}_q)\cdot\mathbf{S}]) \,, \tag{3}$$

the outer sum being over all values of $\mathbf{R}_p - \mathbf{R}_q$, while the inner is over all values of p and q for which $\mathbf{R}_p - \mathbf{R}_q$ is constant. We now replace the summation within brackets of (3) by the equivalent integration involving (2), which is

$$\int_{-\infty}^{+\infty} \frac{N^1}{(2\pi\,\overline{(u_p-u_q)^2})^{\frac{1}{2}}} \exp\left[-\frac{u^2}{2\,\overline{(u_p-u_q)^2}}\right] \exp\,[2\pi i u S]\,du = N^1 \exp\,[-2\pi^2 S^2\,\overline{(u_p-u_q)^2}] \,. \tag{4}$$

Thus (1), via (3) and (4), may be written

$$|T_{C+\Delta}(\mathbf{S})|^2 = \sum_p \sum_q f_p f_q \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \times \exp\,[-2\pi^2 S^2\,\overline{(u_p-u_q)^2}] \,. \tag{5}$$

This expression will be recognized as one which occurs in the theory of thermal diffuse scattering (James, 1948), where, however, the second exponential results from averaging $\exp\,[2\pi i(\mathbf{u}_p - \mathbf{u}_q)\cdot\mathbf{S}]$ over all values of the time, on which u_p and u_q depend in that case. Our derivation shows that (5) is of more general application. This equation may be written as

$$|T_{C+\Delta}(\mathbf{S})|^2 = \sum_p \sum_q f_p^1 f_q^1 \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \times \exp\,[4\pi^2 S^2\,\overline{u_p u_q}] \,, \tag{6}$$

where $f_p^1 = f_p \exp\,[-2\pi^2 S^2 \overline{u_p^2}]$ and $f_q^1 = f_q \exp\,[-2\pi^2 S^2 \overline{u_q^2}]$. It is quite possible for $\overline{u_p^2}$ not to equal $\overline{u_q^2}$. Most of the applications of the theory will be to crystals of simple structure in which the atoms are equivalent, and we may take $f^1 = f \exp\,[-M]$, where $M = 2\pi^2 S^2 \overline{u^2}$. We now expand the second exponential of (6) as far as the second term. The approximation involved is less serious than that involved when the method of Part I is applied to this situation. This gives

$$\begin{aligned} |T_{C+\Delta}(\mathbf{S})|^2 &= \exp\,[-2M] \sum_p \sum_q f_p f_q \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \\ &\quad + 4\pi^2 S^2 \exp\,[-2M] \sum_p \sum_q f_p f_q \overline{u_p u_q} \\ &\quad \times \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \,. \end{aligned} \tag{7}$$

The first term will be recognized as the Laue–Bragg intensity $J_1(\mathbf{S})$, the second as the diffuse intensity $J_2(\mathbf{S})$.

So far the result is not particularly novel; it is an obvious generalization of part of the theory of thermal diffuse scattering as given by James (1948). We now have to express this result in terms of the Fourier transforms of the individual defects, as in Part I. Since $u_p = \sum_{j=1}^{n} \varepsilon_{jp}$, and the defects which produce the displacements are randomly distributed, we have

$$\overline{u_p u_q} = \sum_{j=1}^{n} \overline{\varepsilon_{jp}\varepsilon_{jq}} \tag{8}$$

and

$$M \equiv 2\pi^2 S^2 \overline{u^2} = 2\pi^2 S^2 \sum_{j=1}^{n} \overline{\varepsilon_j^2} \,. \tag{9}$$

We now consider the intensity given by a crystal containing only one defect δ_j. It was shown in Part I that the diffuse intensity is then $|T_{\delta j}(\mathbf{S})|^2$, where

$$T_{\delta j}(\mathbf{S}) = \sum_p f_p \exp\,[2\pi i \mathbf{R}_p\cdot\mathbf{S}]\,(\exp\,[2\pi i \varepsilon_{jp} S] - 1) \,. \tag{10}$$

We now, however, expand the term in brackets, deliberately retaining only one term, and write

$$T_{\delta j}(\mathbf{S}) = 2\pi i S \sum_p f_p \varepsilon_{jp} \exp\,[2\pi i \mathbf{R}_p\cdot\mathbf{S}] \,, \tag{11}$$

from which

$$|T_{\delta j}(\mathbf{S})|^2 = 4\pi^2 S^2 \sum_p \sum_q f_p f_q \overline{\varepsilon_{jp}\varepsilon_{jq}} \times \exp\,[2\pi i(\mathbf{R}_p - \mathbf{R}_q)\cdot\mathbf{S}] \,. \tag{12}$$

Comparing (12) with the second term of (7), and using (8), we see that

$$J_2(\mathbf{S}) = \exp\,[-2M] \sum_{j=1}^{n} |T_{\delta j}(\mathbf{S})|^2 \,. \tag{13}$$

(We may note that if the approximation $\overline{u_p^2} = \overline{u_q^2}$ is not justifiable in a particular case, (7) can be expressed in terms of f_p^1 and f_q^1, and it is only necessary to redefine (11) with f_p^1 replacing f_p, thus

$$T_{\delta j}^1(\mathbf{S}) = 2\pi i S \sum_p f_p^1 \varepsilon_{jp} \exp\,[2\pi i \mathbf{R}_p \cdot \mathbf{S}] \,,$$

to obtain the more exact result

$$J_2(\mathbf{S}) = \sum_{j=1}^{n} |T_{\delta j}^1(\mathbf{S})|^2 \,. \tag{13a}$$

In what follows it will be assumed that this is an unnecessary refinement.)

The result (13) expresses the diffuse intensity in terms of the Fourier transforms of the individual defects. It differs from that given in Part I in two respects:

(1) The factor $\exp\,[-2M]$ did not appear previously. This is understandable, as the displacements were necessarily taken to be small in the case where atoms were influenced by more than one defect.

(2) It is now specifically *required* that $T_{\delta j}(\mathbf{S})$ should be calculated from (11), and not from (10). The former will be much the simpler for numerical calculations.

The factor $\exp[-2M]$ can also be expressed in terms of the Fourier transforms of the individual defects. The theory of Part I gave the changed Laue–Bragg intensity as

$$1 + \frac{1}{N} \sum_{j=1}^{n} \left\{ \frac{T_{\delta j}(\mathbf{H})}{F(\mathbf{H})} + \frac{T_{\delta j}^*(\mathbf{H})}{F^*(\mathbf{H})} \right\} . \tag{14}$$

$\mathbf{H}$ is the value assumed by $\mathbf{S}$ at a reciprocal-lattice point, $F(\mathbf{H})$ is the structure factor. Expanding the bracket of (10) now as far as the *second* term, we have

$$T_{\delta j}(\mathbf{H}) = \sum_p f_p \exp\,[2\pi i \mathbf{R}_p \cdot \mathbf{H}]\,(2\pi i \varepsilon_{jp} H - 2\pi^2 \varepsilon_{jp}^2 H^2) \,. \tag{15}$$

The first term in the bracket makes no contribution since $\overline{\varepsilon_{jp}} = 0$, and on introducing again the assumption that $\overline{\varepsilon_{jp}^2}$ is the same for all atoms, we have

$$\begin{aligned} T_{\delta j}(\mathbf{H}) &= -2\pi^2 \overline{\varepsilon_j^2} H^2 \sum_p f_p \exp\,[2\pi i \mathbf{R}_p \cdot \mathbf{H}] \\ &= -2\pi^2 \overline{\varepsilon_j^2} H^2 N F(\mathbf{H}) \,, \end{aligned}$$

so that

$$T_{\delta j}(\mathbf{H})/F(\mathbf{H}) = -2\pi^2 \overline{\varepsilon_j^2} H^2 N \,. \tag{16}$$

The same expression is found for $T_{\delta j}^*(\mathbf{H})/F^*(\mathbf{H})$. Thus the changed Laue–Bragg intensity, as given by (14) in this case, is

$$1 - 4\pi^2 H^2 \sum_{j=1}^{n} \overline{\varepsilon_j^2} \,,$$

which, in our present notation, is simply $1-2M$. We therefore have the useful rule that where (14), with each $T_{\delta j}(\mathbf{H})$ expanded as far as terms in ε_j^2, gives a result $1-2M$, the more exact result in the particular case where each atom is influenced by a large number of defects, is $\exp\,[-2M]$.

It has been verified that expression (13) leads quite directly to the expression given by James (1948, p. 208) for the intensity of thermal diffuse scattering. In the accompanying paper (Cochran & Kartha, 1956) we apply (13) to the calculation of the diffuse scattering from a crystal containing interstitial atoms.

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