serve between the orthorhombic a and b directions at temperatures up to 520° C. In effect this means that the 'pseudo-tetragonal' unit cell retains a small but constant shear about its b_0 axis, producing a slight departure of the monoclinic β angle from 90°.

Above 520° C. increased thermal motion permits movement of the displaced ions into sites more typical of the simple lattice possessing an unmodified unit cell. It is probable that the observed dilatation of the crystal lattice in the c_0 direction and the removal of the residual shear distortion mentioned above accompanies or perhaps precedes this process.

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Scattering of X-rays by Defect Structures

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The intensity of X-ray scattering from a crystal containing defects is shown to depend in a simple way on the Fourier transforms of the defects considered separately. An example of the application of the theory is worked out.

1. Introduction

General theories of the coherent scattering of X-rays by a crystal which is disordered or contains imperfections have been given by Zachariasen (1945), and by Matsubara (1952). The effects of imperfections of a particular kind have often been calculated, for example for 'impurity' atoms (Huang, 1947) and for screw dislocations (Wilson, 1952). The general theory given here has the same starting-point as that of Matsubara, but is developed in a different way. The results are equivalent to those of Zachariasen, but are more easily applied to particular problems, as is shown by some examples.

2. General theory

We consider a spherical crystal of radius $\mathscr{R}$, containing N units cells. If we denote the crystal by C, and its Fourier transform by T_C, then

$$T_C(\mathbf{S}) = T_L(\mathbf{S})F(\mathbf{H})\,. \tag{2·1}$$

$\mathbf{S}$ is a vector in reciprocal space, $\mathbf{H}$ a vector to a point of the reciprocal lattice. $T_L(\mathbf{S})$ is the transform of a lattice bounded by a sphere, and, as is well known, it has an appreciable value only within about $\mathscr{R}^{-1}$ of $\mathbf{S} = \mathbf{H}$. The transform of the contents of one unit cell, $F(\mathbf{S})$, which varies comparatively slowly with $\mathbf{S}$, has therefore been replaced in (2·1) by the structure factor $F(\mathbf{H})$.

We now imagine a defect Δ to be introduced into the crystal to produce an imperfect crystal $C+\Delta$. This defect will in general be an assemblage of both positive and negative atoms—negative at points from which atoms have been displaced, positive at points to which they have been displaced. We thus have

$$T_{C+\Delta}(\mathbf{S}) = T_C(\mathbf{S})+T_\Delta(\mathbf{S})\,. \tag{2·2}$$

The transform of the defect, $T_\Delta(\mathbf{S})$, will be given by

$$T_\Delta(\mathbf{S}) = \sum_L \sum_m \big(f'_{m,L}\exp\,[2\pi i(\mathbf{R}'_L+\mathbf{r}'_{m,L})\cdot\mathbf{S}] - f_m \exp\,[2\pi i(\mathbf{R}_L+\mathbf{r}_m)\cdot\mathbf{S}]\big)\,. \tag{2·3}$$

In this expression, the outer sum is over all unit cells and the inner over all atoms in one unit cell. $\mathbf{R}_L$ locates a particular unit cell in the crystal, and $\mathbf{r}_{m,L}$ a particular atom in that unit cell. The defect is taken to consist of the replacement of atoms of scattering factor f at $\mathbf{R}+\mathbf{r}$ by others of scattering factor f' at $\mathbf{R}'+\mathbf{r}'$.

We next introduce $F_M(\mathbf{H})$, the structure factor of the average unit cell of $C+\Delta$. Thus

$$F_M(\mathbf{H}) = \frac{1}{N}\sum_L \sum_m f'_{m,L}\exp\,[2\pi i(\mathbf{r}'_{m,L})\cdot\mathbf{S}]\,. \tag{2·4}$$

From (2·3) and (2·4) it follows that

$$T_\Delta(\mathbf{H}) = N(F_M(\mathbf{H})-F(\mathbf{H}))\,. \tag{2·5}$$

Next we define

$$T_M(\mathbf{S}) = T_L(\mathbf{S})F_M(\mathbf{H})\,; \tag{2·6}$$

T_M is thus the transform of a crystal of radius $\mathscr{R}$, composed of identical average unit cells. Combining (2·2), (2·5) and (2·6):

$$T_{C+\Delta}(\mathbf{S}) = T_M(\mathbf{S})+\{T_\Delta(\mathbf{S})-(1/N)\,T_L(\mathbf{S})\,T_\Delta(\mathbf{H})\}\,. \quad (2{\cdot}7)$$

When the first term on the right is large, the second is zero, and conversely. The intensity from the defective crystal (apart from constant factors) is thus

$$|T_{C+\Delta}(\mathbf{S})|^2 = |T_M(\mathbf{S})|^2+|\{T_\Delta(\mathbf{S})-(1/N)\,T_L(\mathbf{S})\,T_\Delta(\mathbf{H})\}|^2. \quad (2{\cdot}8)$$

The first term on the right is the Laue–Bragg intensity

$$J_1(\mathbf{S}) = |T_M(\mathbf{S})|^2\,. \quad (2{\cdot}9)$$

The second must represent the diffuse intensity

$$J_2(\mathbf{S}) = |\{T_\Delta(\mathbf{S})-(1/N)\,T_L(\mathbf{S})\,T_\Delta(\mathbf{H})\}|^2\,. \quad (2{\cdot}10)$$

Except within about $\mathscr{R}^{-1}$ of $\mathbf{S} = \mathbf{H}$, we have

$$J_2(\mathbf{S}) = |T_\Delta(\mathbf{S})|^2\,. \quad (2{\cdot}10a)$$

Equation (2·9) expresses a well known result. Equation (2·10), while no doubt equivalent to Zachariasen's (1945) result, is in a form which is suitable for detailed calculation in particular cases. Equation (2·10*a*) is accurate for all practical purposes, and expresses a result which might have been anticipated, namely that the diffuse intensity depends on the transform of the difference between the imperfect and perfect crystals. We note from (2·10) that $J_2(\mathbf{H}) = 0$, in agreement with Zachariasen's conclusion that there is no diffuse intensity *exactly* at reciprocal-lattice points.

The change in Laue–Bragg intensity can also be expressed in terms of $T_\Delta(\mathbf{S})$. A short calculation gives the fractional change of intensity in going from C to $C+\Delta$ as

$$\frac{|F_M(\mathbf{H})|^2-|F(\mathbf{H})|^2}{|F(\mathbf{H})|^2} = \frac{1}{N}\left(\frac{T_\Delta(\mathbf{H})}{F(\mathbf{H})}+\frac{T^*_\Delta(\mathbf{H})}{F^*(\mathbf{H})}\right)+\frac{1}{N^2}\left(\frac{|T_\Delta(\mathbf{H})|}{|F(\mathbf{H})|}\right)^2. \quad (2{\cdot}11)$$

(The second term will be neglected in subsequent use of this result.) It is worth noting that (2·11) gives the change in *height* of the Laue–Bragg maxima. One can no longer define integrated intensity precisely, since Laue–Bragg and diffuse intensity cannot be separated from one another.

In almost all instances it will be the case that Δ can be regarded as arising from the simultaneous presence of a large number of relatively small defects, which may or may not be identical, but are in any case centred on different points in the crystal. If each atom in the crystal is affected by no more than one defect, we can take

$$\Delta = \sum_{j=1}^{n} \delta_j\,, \quad (2{\cdot}12)$$

where each δ_j is a defect centred in the crystal at a point $\mathbf{R}_j$, so that

$$T_\Delta(\mathbf{S}) = \sum_{j=1}^{n} T_{\delta j}(\mathbf{S}) \exp\,[2\pi i\mathbf{R}_j\cdot\mathbf{S}]\,, \quad (2{\cdot}13)$$

and therefore

$$T_\Delta(\mathbf{H}) = \sum_{j=1}^{n} T_{\delta j}(\mathbf{H})\,. \quad (2{\cdot}14)$$

Equations (2·12), (2·13) and (2·14) thus apply exactly, no matter how large the displacement of atoms around a defect may be, provided that the influence of a defect is limited in range, and the concentration of defects small. If the defects consist only in the replacement of atoms, without displacement, the results apply without any restriction. In the more interesting cases which occur in practice, however, no upper limit can be set to the range of influence of a defect, as is shown by the expansion (or contraction) of the lattice in proportion with the defect concentration. Each atom must be imagined to be influenced by each defect δ_j in the crystal. In such cases equation (2·12) is true as an approximation, as we now proceed to show.

It is necessary to assume that the effects produced combine linearly, i.e. the net displacement of any atom is the sum of the displacements that would be produced by each defect δ_j acting alone, and that the same is true for the net expansion of the lattice. Consider the contribution $t_{\delta j}$ of a single atom to $T_{\delta j}$. It is given by

$$t_{\delta j} = (-1+\exp\,[2\pi i(\boldsymbol{\varepsilon}_j-\boldsymbol{\eta}_j)\cdot\mathbf{S}])\,f\,. \quad (2{\cdot}15)$$

$\boldsymbol{\varepsilon}_j$ is the actual displacement of the atom from the position occupied in C. However, we now take as our reference crystal not C, but a perfect crystal expanded to have the same lattice as the mean lattice of $C+\delta_j$. The movement of the lattice point nearest to the atom in question, resulting from this expansion, is taken to be $\boldsymbol{\eta}_j$. Equation (2·15) then follows. The contribution, t_Δ, of this atom to T_Δ will be

$$t_\Delta = \left(-1+\exp\left[2\pi i\left\{\sum_{j=1}^{n}(\boldsymbol{\varepsilon}_j-\boldsymbol{\eta}_j)\right\}\cdot\mathbf{S}\right]\right)f\,. \quad (2{\cdot}16)$$

Clearly we must now take as our reference crystal a perfect crystal expanded to have the same lattice as the mean lattice of $C+\Delta$. Even then, $t_\Delta \neq \sum_{j=1}^{n} t_{\delta j}$ *unless* the net displacement of the atoms from the mean lattice is at every stage small enough for the approximation

$$t_{\delta j} = 2\pi i(\boldsymbol{\varepsilon}_j-\boldsymbol{\eta}_j)\cdot\mathbf{S} \quad (2{\cdot}15a,\ \text{cf. } 2{\cdot}15)$$

to apply. When this is true, a slight extension of the above argument shows that (2·12), (2·13) and (2·14) still apply as approximations which hold if the atomic displacements from the mean lattice are small. In what follows we assume this to be true.

Returning now to equation (2·14), we substitute the value of $T_\Delta(\mathbf{H})$ given there in (2·11), and obtain for the fractional change in Laue–Bragg intensity

$$\frac{1}{N}\left\{\frac{\sum_{j=1}^{n} T_{\delta j}(\mathbf{H})}{F(\mathbf{H})}+\frac{\sum_{j=1}^{n} T^*_{\delta j}(\mathbf{H})}{F^*(\mathbf{H})}\right\}. \qquad (2\cdot17)$$

If all the defects are the same, this is simply

$$\frac{n}{N}\left\{\frac{T_\delta(\mathbf{H})}{F(\mathbf{H})}+\frac{T^*_\delta(\mathbf{H})}{F^*(\mathbf{H})}\right\}. \qquad (2\cdot17a)$$

In working out the diffuse intensity, we consider for simplicity of explanation the case where the defects δ are the same. From (2·10a), using (2·13) in the form

$$T_\Delta(\mathbf{S}) = T_\delta(\mathbf{S})\sum_{j=1}^{n}\exp\left[2\pi i\mathbf{R}_j\cdot\mathbf{S}\right],$$

we have

$$J_2(\mathbf{S}) = |T_\delta(\mathbf{S})|^2\left\{n+\sum_{\substack{i,j=1\\ i\neq j}}^{n}\cos 2\pi(\mathbf{R}_i-\mathbf{R}_j)\cdot\mathbf{S}\right\}. \qquad (2\cdot18)$$

The average value of the expression in brackets is n. The second term will cause the actual value to fluctuate between zero and a few times n. If the points $\mathbf{R}_j$ are distributed completely at random throughout the crystal, such fluctuations will occur over distances of the order $\mathscr{R}^{-1}$, and would in practice be quite unobservable. We therefore have the simple result

$$J_2(\mathbf{S}) = n|T_\delta(\mathbf{S})|^2. \qquad (2\cdot19)$$

When the defects δ_j are not all the same, a similar argument shows that, under the same conditions of random distribution of defects,

$$J_2(\mathbf{S}) = \sum_{j=1}^{n}|T_{\delta j}(\mathbf{S})|^2. \qquad (2\cdot20)$$

3. An example of the application of the theory

This problem has already been solved by Huang (1947). Each defect δ consists in the replacement of an atom of scattering factor f_1 by another of scattering factor f_2 in a crystal of, for example, copper. Surrounding atoms at $\mathbf{r}$ are taken to be displaced by $c\mathbf{r}/r^3$. Referring the face-centred cubic crystal, of cubic cell dimension a, to a primitive trigonal unit cell, we have

$$T_\delta(\mathbf{S}) = f_2-f_1+f_1\left\{\sum_L\left(-\cos 2\pi\mathbf{R}_L\cdot\mathbf{S}\right.\right.$$
$$\left.\left.+\cos 2\pi\mathbf{R}_L\cdot\mathbf{S}(1+c/R_L^3)\right)\right\}, \qquad (3\cdot1)$$

$$T_\delta(\mathbf{H}) = f_2-f_1-2f_1\sum_L\sin^2\left((c\pi/R_L^3)\mathbf{R}_L\cdot\mathbf{H}\right). \qquad (3\cdot2)$$

Since c is relatively small, the factor inside the summation can be replaced by $((c\pi/R_L^3)R_L\cdot\mathbf{H})^2$. From a result given by Born & Misra (1940), which is also used by Huang, it then follows that

$$T_\delta(\mathbf{H}) = (f_2-f_1)-f_1\frac{4\cdot22\pi^2c^2H^2}{(\tfrac{1}{2}a)^4}. \qquad (3\cdot3)$$

We then have

$$T_\Delta(\mathbf{H}) = n\left\{(f_2-f_1)-f_1\frac{4\cdot22\pi^2c^2H^2}{(\tfrac{1}{2}a)^4}\right\} \qquad (3\cdot4)$$

and $F(\mathbf{H}) = f_1$.

The fractional change of Laue–Bragg intensity is then given by (2·17a) as

$$\frac{2n}{N}\left\{\left(\frac{f_2}{f_1}-1\right)-\frac{4\cdot22\pi^2c^2H^2}{(\tfrac{1}{2}a)^4}\right\}. \qquad (3\cdot5)$$

Apart from terms involving $(n/N)^2$, this result is the same as that given by Huang.

To calculate the diffuse intensity, we return to equation (3·1), which may be written as

$$T_\delta(\mathbf{S}) = f_2-f_1+f_1\sum_L\left\{-\tfrac{1}{2}((2\pi c/R_L^3)\mathbf{R}_L\cdot\mathbf{S})^2\cos 2\pi\mathbf{R}_L\cdot\mathbf{S}\right.$$
$$\left.-((2\pi c/R_L^3)\mathbf{R}_L\cdot\mathbf{S})\sin 2\pi\mathbf{R}_L\cdot\mathbf{S}\right\}. \qquad (3\cdot6)$$

To a first approximation, the term in c^2/R_L^6 can be neglected compared with that in c/R_L^3, giving

$$T_\delta(\mathbf{S}) = f_2-f_1-f_1\sum_L((2\pi c/R_L^3)\mathbf{R}_L\cdot\mathbf{S})\sin 2\pi\mathbf{R}_L\cdot\mathbf{S}. \qquad (3\cdot6a)$$

Now, by a well known result in Fourier theory, the sum over all lattice points in (3·6a) can be replaced by the integral

$$I(\mathbf{S}) = \frac{2\pi c}{v}\int_{r_0}^{\mathscr{R}}\frac{\mathbf{r}\cdot\mathbf{S}}{r^3}\sin 2\pi\mathbf{r}\cdot\mathbf{S}\,dV_r, \qquad (3\cdot7)$$

on the understanding that $I(\mathbf{S})$ is to be set down with origin at each point of the reciprocal lattice (see Ekstein, 1945). v is the volume of the primitive unit cell, that is $v = \tfrac{1}{4}a^3$. The lower limit of the integral is $r_0 > 0$ since the atom at $\mathbf{R}_L = 0$ is not displaced. The integral $I(\mathbf{S})$ can be evaluated directly, and the final result is

$$T_\delta(\mathbf{S}) = f_2-f_1-Sf_1\sum_{\mathbf{H}}\frac{4\pi c}{v|\mathbf{S}-\mathbf{H}|}\cos(\mathbf{S},\mathbf{S}-\mathbf{H})$$
$$\times\left\{\frac{\sin 2\pi r_0|\mathbf{S}-\mathbf{H}|}{2\pi r_0|\mathbf{S}-\mathbf{H}|}-\frac{\sin 2\pi\mathscr{R}|\mathbf{S}-\mathbf{H}|}{2\pi\mathscr{R}|\mathbf{S}-\mathbf{H}|}\right\}. \qquad (3\cdot8)$$

The value of r_0 has not yet been specified, and in fact the value of (3·8) is independent of r_0 provided the latter is just less than $a/\sqrt{2}$, the shortest interatomic distance. The series in (3·8) will converge most rapidly if r_0 is chosen to be as large as possible, and putting $r_0 = a/\sqrt{2}$ we may approximate in the neighbourhood of a particular reciprocal-lattice point by retaining only the first term of the series to give

$$T_\delta(\mathbf{S}) = (f_2-f_1) - \frac{4\pi c S f_1}{v|\mathbf{S}-\mathbf{H}|}\cos(\mathbf{S}, \mathbf{S}-\mathbf{H}) \times \left\{\frac{\sin \sqrt{2}.\pi a|\mathbf{S}-\mathbf{H}|}{\sqrt{2}.\pi a|\mathbf{S}-\mathbf{H}|}\right\}. \qquad (3{\cdot}9)$$

(The term $\sin 2\pi\mathscr{R}|\mathbf{S}-\mathbf{H}|/2\pi\mathscr{R}|\mathbf{S}-\mathbf{H}|$ in (3·8) need be considered only when $|\mathbf{S}-\mathbf{H}| \simeq \mathscr{R}^{-1}$.)

Our expression for the diffuse intensity near $\mathbf{S} = \mathbf{H}$ is therefore

$$J_2(\mathbf{S}) = n\left[(f_2-f_1) - \frac{4\pi c S f_1}{v|\mathbf{S}-\mathbf{H}|}\cos(\mathbf{S}, \mathbf{S}-\mathbf{H}) \times \frac{\sin \sqrt{2}.\pi a|\mathbf{S}-\mathbf{H}|}{\sqrt{2}.\pi a|\mathbf{S}-\mathbf{H}|}\right]^2. \qquad (3{\cdot}10)$$

This result is not identical with Huang's, which is not surprising in view of the approximations made in both cases. Both qualitatively and quantitatively, however, it gives results very close to those given by Huang's expression for $J_2(\mathbf{S})$, the main features being (*a*) an increase of diffuse intensity with S^2; (*b*) a concentration of diffuse intensity near $\mathbf{S} = \mathbf{H}$, falling off somewhat more rapidly than $|\mathbf{S}-\mathbf{H}|^{-2}$; (*c*) almost zero intensity in a plane passing through each reciprocal-lattice point, the normal to the plane being the direction of $\mathbf{H}$.

4. Other applications

Possible applications of the theory, to problems not already solved, which suggest themselves are:

(i) The calculation of the diffuse intensity from neutron-irradiated crystals of, for example, boron carbide. It has been shown by Tucker & Senio (1955) that the defect consists mainly in the removal of the central carbon atom of a chain of three, resulting in an inward movement, predominantly in the *c* direction, of surrounding atoms. On the basis of the above theory, the following qualitative predictions can be made about the distribution of diffuse intensity:

(*a*) As this displacement of atoms presumably extends over neighbouring unit cells, the diffuse intensity will be concentrated around reciprocal-lattice points.

(*b*) If all the atoms in a neighbouring unit cell are affected in nearly the same way and to nearly the same extent, the diffuse intensity around a reciprocal-lattice point will be nearly proportional to the Laue–Bragg intensity.

(*c*) The diffuse intensity surrounding an (00*l*) reciprocal-lattice point will be particularly strong, but should fall to zero, or at least to a low minimum, on a plane passing through the point (00*l*) with normal along *c**. Other reciprocal-lattice points will show this feature to a lesser extent, (*hk*0) points should not show it at all.

These predictions are made on the assumption that the displacement of atoms along *c* is the only defect present. However, the displaced carbon atom, and helium and lithium atoms produced by the reaction of boron atoms with bombarding neutrons, presumably occupy interstitial sites and thereby produce further displacements which complicate the picture. Conclusions (*a*) and (*b*) should, however, remain valid, and the feature mentioned in (*c*) might not be completely masked. Detailed calculation must await more precise knowledge of the nature of the defect.

(ii) Calculation of the intensity of scattering from simple crystals containing Frenkel defects, that is vacant sites plus interstitial atoms. Detailed calculations are in progress, and it appears that the effects to be expected are qualitatively similar to those discussed in § 3.

This work may be regarded as an extension of work by P. B. Hirsch (unpublished) on the low-angle scattering of X-rays by defect structures. I am grateful to Dr Hirsch for allowing me to read his notes on the subject.

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