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Diffuse X-ray Scattering from Self Interstitials in a General Lattice

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Abstract

A general theory for diffuse X-ray scattering from self interstitials in a lattice containing more than one atom per unit cell is presented. Expressions for Laue scattering at the defect and the scattering from the strongly distorted region around the defect are unaffected by the number of atoms in the unit cell. However, the larger diffuse scattering contribution from terms linear in the lattice distortions depend on the number of atoms in the unit cell. The general expression is calculated using a lattice statics technique. An expression is also given for the Huang diffuse scattering in a general lattice using the continuum theory of linear elasticity. As an example, Huang diffuse scattering calculated from the lattice statics method and elasticity theory is compared in zinc, an h.c.p. lattice with two atoms per unit cell.

1. Introduction

The existing theories of diffuse X-ray scattering from cubic lattices (Krivoglaz, 1969; Dederichs, 1973) are inadequate for analyzing the diffuse scattering data from self-interstitials in a lattice containing more than one atom in the unit cell. In this paper we present a modified theory of diffuse scattering for point defects in a general lattice.

Following a method due to Kanzaki (1957) and using the modified dynamical matrix, we find an expression for the Fourier transformed displacement field of the defect. The Fourier transform is then used to obtain an expression for the diffuse X-ray scattering cross section in a general lattice. A general expression for the Huang diffuse scattering is also obtained using the continuum theory of linear elasticity. For lattices with one atom per unit cell, these expressions reduce to the well known formulas of diffuse scattering.

2. Theory

Consider a low concentration C (number per unit volume) of point defects distributed at random in a perfect lattice. Assuming a linear superposition of the strain fields around the point defects and neglecting the interference between the scattering contributions from different defects (the 'single defect approximation'), the diffuse X-ray scattering cross section can be written as

$$I_D = C|F(\mathbf{Q})|^2, \tag{1}$$

where

$$F(\mathbf{Q}) = f_Q^D + f\sum_n [\exp(i\mathbf{Q}.\mathbf{u}_n) - 1]\exp(i\mathbf{Q}.\bar{\mathbf{R}}_n). \tag{2}$$

$F(\mathbf{Q})$ is the defect structure factor; f_Q^D represents the scattering at the defect and f is the atomic scattering factor of the atoms in a perfect lattice. $\bar{\mathbf{R}}_n$ is the position vector of an atom n in the average lattice, *i.e.* in a lattice homogeneously relaxed by all the other defects and $\mathbf{u}_n$ is the static displacement of the atom n due to the defect singled out. The scattering vector $\mathbf{Q}$ satisfies the relationship $\mathbf{Q} = \mathbf{q} + \mathbf{h}$, where $\mathbf{h}$ is a reciprocal-lattice vector and $\mathbf{q}$ a vector within the first Brillouin zone. Equation (1) can be rewritten in the form

$$I_D = C\Big|f_Q^D + f\sum_n [\exp(i\mathbf{Q}.\mathbf{u}_n) - 1 - i\mathbf{Q}.\mathbf{u}_n]\exp(i\mathbf{Q}.\bar{\mathbf{R}}_n) + if\mathbf{Q}.\sum_n \mathbf{u}_n \exp(i\mathbf{Q}.\bar{\mathbf{R}}_n)\Big|^2. \tag{3}$$

Let us now look into the evaluation of each of the three terms in (3). We will point out as we go along the differences arising due to the lattice containing more than one atom in the unit cell.

The first term f_Q^D in (3) contains only the scattering at the defect (Dederichs, 1973) and its evaluation will be independent of the number of atoms in the unit cell of the perfect lattice. The next term, the first sum in (3), contains terms of second and higher order in the displacements $\mathbf{u}_n$ and has a finite contribution only from the strongly distorted immediate neighbourhood of the defect. Since the displacements of the atoms around the defect have to be calculated explicitly by the methods of lattice statics, the mode of evaluation of this

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term also will not depend on the number of atoms in the unit cell.

The second sum of (3) has a finite contribution from all the atoms of the lattice and contains terms of first order in displacements. To calculate this term, we need an expression for the Fourier transform of the displacement field. We proceed as follows using a method due to Kanzaki (1957).

In the harmonic approximation the total potential energy of the perfect lattice φ, distorted under the application of applied external force **K** (Maradudin, Montroll, Weiss & Ipatova, 1971) can be written as

$$\varphi - \varphi_0 = -\sum_{lk\alpha} K_\alpha(lk)\, u_\alpha(lk) + \tfrac{1}{2} \sum_{\substack{lk\alpha \\ l'k'\beta}} \varphi_{\alpha\beta}(lk; l'k')\, u_\alpha(lk)\, u_\beta(l'k') \tag{4}$$

where

$$\varphi_{\alpha\beta}(lk;l'k') = \left.\frac{\partial^2 \varphi}{\partial u_\alpha(lk)\, \partial u_\beta(l'k')}\right|_0 . \tag{5}$$

The subscript zero implies that the derivatives are evaluated at the equilibrium configuration. Expanding u_α in a series of plane waves

$$u_\alpha(lk) = \sum_q u_\alpha(\mathbf{q}) \exp[-i\mathbf{q}.\mathbf{x}(lk)], \tag{6}$$

where $\mathbf{x}(lk) = \mathbf{x}(l) + \mathbf{x}(k)$ stands for the position vector of the kth atom in the lth unit cell.

$$\varphi - \varphi_0 = -\sum_{lk\alpha} K_\alpha(lk) \sum_q u_\alpha(\mathbf{q}) \exp[-i\mathbf{q}.\mathbf{x}(lk)] + \tfrac{1}{2} \sum_{\substack{lk\alpha \\ l'k'\beta}} \varphi_{\alpha\beta}(lk;l'k') \sum_q u_\alpha(\mathbf{q}) \times \exp[-i\mathbf{q}.\mathbf{x}(lk)] \sum_{q'} u_\beta(\mathbf{q}') \times \exp[-i\mathbf{q}', \mathbf{x}(l'k')]. \tag{7}$$

Since $u_\alpha(\mathbf{q})$ is independent of the indices l and k, the first term in (7) can be written as

$$-\sum_{q\alpha} u_\alpha(\mathbf{q}) \sum_{lk} K_\alpha(lk) \exp[-i\mathbf{q}.\mathbf{x}(lk)] = -\sum_{q\alpha} u_\alpha(\mathbf{q})\, K_\alpha(\mathbf{q}), \tag{8}$$

where

$$K_\alpha(\mathbf{q}) = \sum_{lk} K_\alpha(lk) \exp[-i\mathbf{q}.\mathbf{x}(lk)]$$

is the Fourier transform of the applied external forces.

Since $\varphi_{\alpha\beta}$ depends on l and l' only through their difference, the second term in (7) can be written

$$\tfrac{1}{2} \sum_{\substack{l-l' \\ kk' \\ \alpha\beta}} \varphi_{\alpha\beta}(lk;l'k') \sum_{qq'} u_\alpha(\mathbf{q})\, u_\beta(\mathbf{q}') \times \exp\{-i\mathbf{q}'.[\mathbf{x}(l') - \mathbf{x}(l)]\} \exp\{-i[\mathbf{q}.\mathbf{x}(k) + \mathbf{q}'.\mathbf{x}(k')]\} \sum_l \exp[-i(\mathbf{q}+\mathbf{q}').\mathbf{x}(l)]. \tag{9}$$

We now use the relationship

$$\sum_l \exp[-i(\mathbf{q}+\mathbf{q}').\mathbf{x}(l) = N\Delta(\mathbf{q}+\mathbf{q}'). \tag{10}$$

Here $\Delta(\mathbf{q}+\mathbf{q}')$ equals zero unless $(\mathbf{q}+\mathbf{q}')$ is zero or a reciprocal-lattice vector, in which case it equals unity. N represents the total number of unit cells in the lattice. Since all $\mathbf{q}$ vectors lie in the first Brillouin zone, we have $\mathbf{q} = -\mathbf{q}'$. Equation (9) can then be written as

$$\begin{aligned} &\frac{N}{2} \sum_{\substack{l-l' \\ k\alpha \\ k'\beta}} \varphi_{\alpha\beta}(lk;l'k') \times \sum_q u_\alpha(\mathbf{q})\, u_\beta(-\mathbf{q}) \exp\{-i\mathbf{q}.[\mathbf{x}(lk) - \mathbf{x}(l'k')]\} \\ &= \frac{N}{2} \sum_{\substack{q \\ \alpha\beta}} u_\alpha(\mathbf{q})\, u_\beta(-q) \times \sum_{\substack{l-l' \\ kk'}} \varphi_{\alpha\beta}(lk;l'k') \exp\{-i\mathbf{q}.[\mathbf{x}(lk) - \mathbf{x}(l'k')]\} \\ &= \frac{N}{2} \sum_{\substack{q \\ \alpha\beta}} u_\alpha(\mathbf{q})\, u_\beta(-\mathbf{q}) \times \sum_{kk'} C_{\alpha\beta}(kk';\mathbf{q})\, (m_k\, m_{k'})^{1/2}, \end{aligned} \tag{11}$$

where $C_{\alpha\beta}$ represents the modified dynamical matrix (Maradudin *et al.*, 1971) and m_k the mass of the kth atom in the unit cell.

Using (8) and (11), (7) can be written as

$$\varphi - \varphi_0 = -\sum_{q\alpha} K_\alpha(\mathbf{q})\, u_\alpha(\mathbf{q}) + \frac{N}{2} \sum_{\substack{q \\ \alpha\beta}} u_\alpha(\mathbf{q})\, u_\beta(-q) \times \sum_{kk'} (m_k\, m_{k'})^{1/2}\, C_{\alpha\beta}(kk';+\mathbf{q}). \tag{12}$$

Making use of the equilibrium condition

$$\frac{\partial \varphi}{\partial u_\alpha(\mathbf{q})} = 0, \tag{13}$$

we find

$$K_\alpha(\mathbf{q}) = N \sum_\beta u_\beta(-\mathbf{q}) \sum_{kk'} (m_k m_{k'})^{1/2} C_{\alpha\beta}(kk';\mathbf{q}) \tag{14}$$

which gives

$$u_\beta(\mathbf{q}) = \frac{1}{N} \sum_{\substack{\alpha \\ kk'}} \exp\{-i\mathbf{q}.[\mathbf{x}(k) - \mathbf{x}(k')]\} \times \frac{D^{-1}_{\alpha\beta}(kk';-\mathbf{q})}{(m_k m_{k'})^{1/2}} K_\alpha(-\mathbf{q}), \tag{15}$$

where $D_{\alpha\beta}$ is the dynamical matrix.

Equation (15) is an expression for the Fourier transform of the displacement field in a lattice with more than one atom per unit cell. Substituting (15) into (3) gives the expression for the diffuse X-ray scattering cross section in a general lattice

$$I_D = C \Big| f^D_Q + f \sum_n [\exp(i\mathbf{Q}.\mathbf{u}_n) - 1 - i\mathbf{Q}.\mathbf{u}_n] \exp(i\mathbf{Q}.\bar{\mathbf{R}}_n) + (if/N) \sum_k \exp[i\mathbf{h}.\mathbf{x}(k)] \sum_\beta Q_\beta \times \sum_{\substack{\alpha \\ k'}} \exp\{-i\mathbf{q}.[\mathbf{x}(k) - \mathbf{x}(k')]\} \times \frac{D^{-1}_{\alpha\beta}(kk';-\mathbf{q})}{(m_k m_{k'})^{1/2}} K_\alpha(-\mathbf{q}) \Big|^2 \tag{16}$$

We observe that the main difference arising due to the lattice containing γ ($\gamma > 1$) atoms in the unit cell is that the dynamical matrix D is no longer a 3×3 matrix. But it can be represented by a $\gamma \times \gamma$ supermatrix, elements of which are 3×3 matrices (Dewames, Wolfram & Lehman, 1965). The contribution from each element of the supermatrix to the diffuse scattering cross section has to be appropriately weighted by a phase factor and the masses of the atoms in the unit cell. For lattices with one atom per unit cell, (16) reduces to the well known formulas of diffuse scattering for these lattices.

3. Huang diffuse scattering

In this section, we investigate how the expressions for Huang diffuse scattering (HDS) is modified when the lattice contains more than one atom in the unit cell. HDS, which appears close to Bragg peaks, depends on the long-range displacement field of the point defect and can be calculated using the continuum theory of linear elasticity. Close to Bragg peaks, $\mathbf{q} \ll \mathbf{h}$, (1) can be approximated by

$$I_D = C \Big| f^D_Q - f \sum_n (1 - \cos \mathbf{h}.\mathbf{u}_n) \exp(i\mathbf{Q}.\bar{\mathbf{R}}_n) + if\mathbf{h}.\sum_n \mathbf{u}_n \exp(i\mathbf{h}.\bar{\mathbf{R}}_n) \Big|^2. \tag{17}$$

In the following we restrict our attention to HDS [third term in (17)], which makes the main contribution at small q values. The summation in (17) can be split into two sums: one over the atoms in the unit cell and other over all the unit cells of the lattice. We have then for HDS cross section

$$I_{\mathrm{HDS}} = C \Big| if\mathbf{h} \sum_l \sum_k \mathbf{u}(lk) \exp\{i\mathbf{h}.[\mathbf{x}(l) + \mathbf{x}(k)]\} \Big|^2. \tag{18}$$

Since all the atoms in a unit cell will be displaced equally in the elastic displacement field of the point defect, $\mathbf{u}(lk)$ is independent of the sublattice index k and may be replaced by $\mathbf{u}(l)$. Equation (18) then reduces to

$$I_{\mathrm{HDS}} = C \Big| if\mathbf{h}.\sum_k \exp[i\mathbf{h}.\mathbf{x}(k)] \sum_l \mathbf{u}(l) \exp[i\mathbf{q}.\mathbf{x}(l)] \Big|^2 \cong C \Big| i\Big\{f \sum_k \exp[i\mathbf{h}.\mathbf{x}(k)]\Big\} \frac{\mathbf{h}.\mathbf{u}(\mathbf{q})}{V_C} \Big|^2, \tag{19}$$

where $\mathbf{u}(\mathbf{q})$ is the Fourier transform of the elastic displacement field of the point defect and V_C denotes the volume of the unit cell. We note that the presence of more than one atom in the unit cell has resulted in the appearance of an additional phase factor.

4. Huang diffuse scattering in zinc

As an example, we calculate the HDS from a self interstitial in zinc, an h.c.p. lattice with two atoms per unit cell, using both (16) and (19). Since the elastic constants and the atomic force constants are related, a comparison of HDS as calculated by these two different methods will provide a good check on the theory developed in the preceding sections.

Of the four self-interstitial configurations permitted by the symmetry of an h.c.p. lattice, octahedral (O), tetrahedral (T) and a dumbbell aligned along the c axis (S_c) have tetragonal symmetry, while the crowdions (C) have orthorhombic symmetry. As the crowdion has been ruled out experimentally (Ehrhart & Schonfeld, 1979) we restrict our attention to the O, T and S_c configurations. In the following, all equivalent orientations of a given defect configuration are assumed to be equally populated and their contribution to HDS is averaged.

Using (19), HDS averaged over all possible orientations of a given defect configuration can be written as

$$I_{\mathrm{HDS}} = C\left\{\frac{f}{V_C}\sum_k \exp\left[i\mathbf{h}.\mathbf{x}(k)\right]\right\}^2 \sum_{\nu=1}^{5} \gamma_\nu \pi_\nu. \qquad (20)$$

π_ν represent the five independent parameters in the tensor $\overline{p_{ij}p_{kl}}$, which is an average over the product of dipole force tensors p. γ_ν can be calculated from the elastic constants and the direction of $\mathbf{q}$ and $\mathbf{h}$.*

In order to compute HDS using (16), we require Kanzaki forces due to the defect, the dynamical matrix and the perfect-lattice Green functions for zinc. Since the interstitial in zinc has a large relaxation volume (3·6 atomic volumes), the defect forces are expected to be long range. Kanzaki forces, extending up to the third neighbour around the defect, were calculated using the experimental values of the force dipole tensor (Ehrhart *et al.*, 1979).* We computed the dynamical matrix and the lattice Green functions for zinc (Khanna, 1982) using a modified axially symmetric force constant model due to Dewames *et al.* (1965).

For the sake of comparison, the HDS was computed for the O, T and S_c configurations near the 002 reflection in the [001] direction. Since the experimental value of dipole force tensor was used for the computation, all of them yielded identical HDS close to Bragg peaks. This is to be expected since these defects have the same long-range symmetry. The computed HDS also showed the expected $1/q^2$ behaviour very close to Bragg peaks.

From elasticity theory, the HDS close to a 002 reflection in the [001] direction is

$$I_{\mathrm{HDS}} = C\left|\frac{f}{V_C}\sum_k \exp\left[i\mathbf{h}.\mathbf{x}(k)\right]\right|^2 \left(\frac{h}{q}\right)^2 \frac{p_{33}^2}{C_{33}^2}. \qquad (21)$$

Substituting the computed value of I_{HDS} for a given p_{33} in (21) we get $C_{33} = 67{\cdot}8$ GN m^{-2}. This is exactly the value quoted by Dewames *et al.* (1965) based on their atomic force constants. Thus the general theory valid over the entire q space correctly predicts the Huang diffuse scattering close to Bragg peaks.

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* A list of γ_ν for some high-symmetry reflections and directions and specific forms of π_ν and a table containing general expressions for the dipole force tensor components have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36990 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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On Structure Refinement Using Data from a Twinned Crystal

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Abstract

Refinements leading to accurate structural parameters are possible by using the measured data F_o^2 of a twinned crystal with exactly superimposed reciprocal lattices and accumulating the sum for the n twin domains, $\sum_i^n \alpha_i |kF_{ci}|^2$, of the calculated squared structure factors, $|kF_{ci}|^2$, weighted according to the fractional contribution α_i of twin i to the total squared structure factor $|kF_c|^2$. The derivatives with respect to structural parameters and the overall scale factor (k) may be

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