The variance of the joint p.d.f. can be split into two terms. The first term contains the variances of all positions and depends on temperature, the second contains the distances of the split positions from their centre of gravity and is independent of temperature. This allows the average distance of a split position from the centre of gravity to be determined by extrapolating the harmonic temperature factor to 0 K (assuming the vibrations at 0 K are negligible).

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Dynamical X-ray Diffraction from Crystals with Precipitates. I. Theory of the Bragg Case

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Abstract

The optical coherence approach has been used for computing the reflection curves of crystals with spherical precipitates in the Bragg case and the curves were compared with those obtained from the usual kinematical theory. It has been shown that the asymmetry of the curves depends on the sign of the volume change caused by defects. Near their maximum the shape of the curves is not dependent on the type of deformation field of the precipitates and it depends on the properties of the perfect crystal. In comparison with the kinematical theory it has been demonstrated that the difference between the results of the dynamical theory and those of the kinematical theory are significant only near the maximum of the reflection curves.

1. Introduction

In dislocation-free silicon crystals grown by the Czochralski method structural transformations take place during the technological process, namely precipitates of other phases or other microdefects can occur. The defects affect the electrical properties of the semiconductors or they can cause the formation of dislocation loops.

X-ray methods of investigating microdefect formation are advantageous owing to their non-destructivity. The theoretical description of X-ray diffraction from crystals with randomly distributed small defects has been given in the kinematical approximation in the theory of diffuse scattering in papers by Dederichs (1971), Larson & Schmatz (1980) and Trinkaus (1972). The kinematical theory enables us

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to compute the angle distribution of the scattered intensity and the contribution of the defects to the reflection curves of the crystal.

Within the dynamical theory this problem was solved in a coherent approximation by Dederichs (1972), who assumed the degree of coherence of the diffracted wave to be the same as that of the primary wave. Then the first approximation of the diffracted intensity is equivalent to the intensity diffracted by the perfect crystal with a modified value of the static Debye–Waller factor (so-called quasiperfect crystal).

In papers by Kato (1980) the problem of the dynamical diffraction from a randomly disordered crystal was solved for the case of a narrow incident beam. Olekhnovich & Olekhnovich (1981) found the dynamical correction of the angular distribution of the diffracted intensity. In a previous paper (Holý, 1982*a*) the diffraction from crystals with small defects was described within the dynamical theory by means of the formalism of the function of the mutual coherence. It has been shown that the degree of coherence of the X-rays is decreased by the diffraction from crystals with randomly distributed defects, which causes changes in the shape of the reflection curve and in the angular distribution of the diffracted intensity. The general ideas were applied to the case of the diffraction from the crystal with randomly distributed small amorphous spheres in the Laue case of diffraction (Holý, 1982*b*) and in the Bragg case as well (Holý, 1983).

The aim of this paper is the theoretical description of the dynamical X-ray diffraction from crystals containing small spherical precipitates that deform elastically the surrounding lattice. This paper contains the theory of the Bragg-case diffraction; the Laue case will be described in paper II.

2. The diffracted intensity in the first and second approximations

The computational procedure is based on the results of the paper by Holý (1983), referred to as paper 1. The first and second approximations of the diffracted intensity are determined by the first and second iterational solutions of the integral equation for the mutual coherence function of the waves in the crystal. As in paper 1 we shall assume that the dynamical wavefield in the quasiperfect crystal is scattered by the defects kinematically, thus, Green's function $\hat{G}$ in (1.2) is replaced by its kinematical limit $\hat{G}^K$ (1.16). The error introduced by this assumption will be estimated in the *Discussion*.

The formula for the first approximation of the diffracted intensity was derived in paper 1.

$$I_h^{(1)} = I_h^{(0)} + \tfrac{1}{4}K^2|\chi_h|^2 \frac{c}{V_c} I_e \int\limits_{\substack{\text{reciprocal}\\ \text{space}}} \mathrm{d}\boldsymbol{q} \frac{|v(\boldsymbol{q})|^2}{|q_h - \kappa_h|^2} \qquad (1)$$

holds, where $I_h^{(0)}$ is the intensity diffracted by the quasiperfect crystal, I_e is the intensity of the incident wave, χ_h is the hth component of the crystal polarizability, c is the defect concentration normalized to unity (we assume $c \ll 1$) and V_c is the volume of the unit cell. The quantity $v(\boldsymbol{q})$ is given by

$$v(\boldsymbol{q}) = \int\limits_{\substack{\text{real}\\ \text{space}}} \mathrm{d}\boldsymbol{r} V(\boldsymbol{r}) \exp(2\pi i \boldsymbol{q}\,.\,\boldsymbol{r}), \qquad (2)$$

where

$$V(\boldsymbol{r}) = \exp[-2\pi i \boldsymbol{h}\,.\,\boldsymbol{l}(\boldsymbol{r})] - 1, \qquad (3)$$

$\boldsymbol{h}$ is the diffraction vector and $\boldsymbol{l}(\boldsymbol{r})$ is the displacement field in the vicinity of the defect. The vector $\boldsymbol{k}_0 + \boldsymbol{h} + \boldsymbol{\kappa}$ is the wave vector of the diffracted waves inside the crystal.

$$|\boldsymbol{k}_0| = |\boldsymbol{k}_h| = |\boldsymbol{k}_0 + \boldsymbol{h}| = K(1 + \chi_0/2)$$

holds and

$$\kappa_j = \boldsymbol{\kappa}\,.\,\boldsymbol{k}_j/\mathrm{Re}\,|\boldsymbol{k}_j|;\, j = 0, h.$$

The Debye–Waller factor of the quasiperfect crystal is

$$e^{-L} = \exp\left[\frac{c}{V_c}\int \mathrm{d}\boldsymbol{r}\, V(\boldsymbol{r})\right]. \qquad (4)$$

The second approximation of the diffracted intensity is given by (1.17). Replacing Green's function $\hat{G}$ by $\hat{G}^K$ we obtain

$$I_h^{(2)} = I_h^{(1)} + I_h^{(0)} \frac{K^2}{2} \frac{c}{V_c} \times \mathrm{Re}\left[\frac{\chi_h \chi_{-h}}{\kappa_h} \int\limits_{\substack{\text{reciprocal}\\ \text{space}}} \mathrm{d}\boldsymbol{q} \frac{|v(\boldsymbol{q})|^2}{q_0 - \kappa_x \sin(2\theta)/\gamma_h}\right], \qquad (5)$$

where γ_h is the direction cosine of the vector $\mathrm{Re}(\boldsymbol{k}_h)$ with respect to the internal normal to the crystal surface, κ_x is the component of $\boldsymbol{\kappa}$ parallel to the surface.

3. The deformation field of the precipitate

Let us consider spherical precipitates with a spherically symmetrical deformation field (Eshelby, 1956).

$$\boldsymbol{l}(\boldsymbol{r}) = \begin{cases} A\,\boldsymbol{r}/|\boldsymbol{r}|^3 & \text{for } |\boldsymbol{r}| > R_d \\ \text{random value for } |\boldsymbol{r}| \le R_d. \end{cases} \qquad (6)$$

R_d is the defect radius, $4\pi A$ is the change in the volume of the crystal caused by a single defect neglecting the influence of the crystal surface. The quantity $V(\boldsymbol{r})$ averaged over all atom configurations in the defects is

$$V(\boldsymbol{r})=\begin{cases}\exp\left(-2\pi i A\boldsymbol{h}\,.\,\boldsymbol{r}/|\boldsymbol{r}|^3\right)-1 & \text{for } |\boldsymbol{r}|>R_d\\ -1 & \text{for } |\boldsymbol{r}|\leq R_d.\end{cases} \tag{7}$$

For such a complicated form of $V(\boldsymbol{r})$ the integrals (1) and (5) cannot be evaluated analytically. In order to enable a direct computation of these integrals the actual structure of the crystal at points $\boldsymbol{r}$, where $R_d < |\boldsymbol{r}| \leq R = (2\pi A h)^{1/2}$ will be replaced by the amorphous structure. Then the following approximation can be used (Dederichs, 1971).

$$V(\boldsymbol{r})=\begin{cases}-2\pi i A\boldsymbol{h}\,.\,\boldsymbol{r}/|\boldsymbol{r}|^3 & \text{for } |\boldsymbol{r}|>R=(2\pi A h)^{1/2}\\ -1 & \text{for } |\boldsymbol{r}|\leq R.\end{cases} \tag{8}$$

It will be shown in §4 that this approximation does not affect the shape of the reflection curve near its maximum.

The Debye–Waller factor can be computed from (4) and (7) or approximately from (4) and (8). The exact computation gives

$$e^{-L}=\exp\{-P_d[1-3S(w)]\}, \tag{9}$$

where

$$S(w)=\sum_{n=1}^{\infty}\frac{(-1)^n w^{2n}}{(2n+1)!(4n-3)}, \quad w=2\pi A h/R_d^2 \tag{10}$$

and $P_d=(4/3)\pi R_d^3(c/V_c)$ is the relative amorphous volume of the crystal. The series (10) converges and its value is

$$S(w)=\frac{1}{3}-\frac{\sin w}{5w}-\frac{2\cos w}{15}+\frac{4}{15}[w\sin w-(2\pi)^{1/2}w^{3/2}C(w^{1/2})], \tag{11}$$

$$C(x)=\frac{2}{(2\pi)^{1/2}}\int_0^x \cos t^2\,\mathrm{d}t$$

is the Fresnel integral. Using the approximate relation (8) we get

$$e^{-L}=e^{-P}, \quad P=\frac{4}{3}\pi R^3\frac{c}{V_c}, \tag{12}$$

where P is the relative volume of spheres with radius R with respect to the crystal volume. The numerical considerations show that for realistic parameters of defects both formulas (9) and (12) give $e^{-L}\simeq 1$ with an accuracy better than several percent.

For $v(\boldsymbol{q})$ it follows from (2) and (8) that

$$v(\boldsymbol{q})=\frac{2A\boldsymbol{h}\,.\,\boldsymbol{q}}{q^3}\frac{\sin(2\pi qR)}{R}-\frac{\sin(2\pi qR)-2\pi qR\cos(2\pi qR)}{2\pi^2q^3}. \tag{13}$$

4. The reflection curves of crystals with precipitates

Formulas (1) and (5) can be rewritten in the forms

$$I_h^{(1)}=I_h^{(0)}+\tfrac{1}{4}K^2|\chi_h|^2\frac{c}{V_c}I_e\frac{\operatorname{Im}[Q_h(\kappa_h)]}{\operatorname{Im}(\kappa_h)} \tag{14}$$

and

$$I_h^{(2)}=I_h^{(1)}+\tfrac{1}{2}K^2I_h^{(0)}\frac{c}{V_c}\times\operatorname{Re}\left[\frac{\chi_h\chi_{-h}}{\kappa_h}Q_0\left(\kappa_x\frac{\sin(2\theta)}{\gamma_h}\right)\right], \tag{15}$$

respectively, where

$$Q_j(\xi)=\int_{\substack{\text{reciprocal}\\ \text{space}}}\mathrm{d}\boldsymbol{q}\frac{|v(\boldsymbol{q})|^2}{q_j-\xi}, \quad j=0,h. \tag{16}$$

The explicit evaluation of Q_j has been deposited.* Formulas (14) and (15) are the basis of the numerical computation of the reflection curves.

Let us consider properties of these curves near their maxima. If

$$2\pi|\boldsymbol{\kappa}|R\ll 1 \tag{17}$$

holds, then the value of Q_j can be replaced by its limit

$$\lim_{\xi\to 0}Q_j(\xi).$$

If ξ is complex, then

$$\lim_{\xi\to 0}Q_j(\xi)=\text{v.p.}\int_{\substack{\text{reciprocal}\\ \text{space}}}\mathrm{d}\boldsymbol{q}\frac{|v(\boldsymbol{q})|^2}{q_j}+i\pi\,\operatorname{sign}[\operatorname{Im}(\xi)]\int_{\boldsymbol{q}_\perp.\operatorname{Re}(\boldsymbol{k}_j)=0}\mathrm{d}\boldsymbol{q}_\perp|v(\boldsymbol{q}_\perp)|^2, \tag{18}$$

where v.p. denotes the principal value of the integral. Thus, the first approximation of the diffracted intensity near the maximum of the reflection curve is approximately given by

$$I_h^{(1)}\simeq I_h^{(0)}+\tfrac{1}{4}K^2|\chi_h|^2\frac{c}{V_c}I_e\frac{2\pi^2(R^4+8\pi^2A^2h^2)}{|\operatorname{Im}(\kappa_h)|}. \tag{19}$$

The numerical computation of the reflection curves was carried out by means of exact formulas (14) and (15). The values of A and P were chosen so as to

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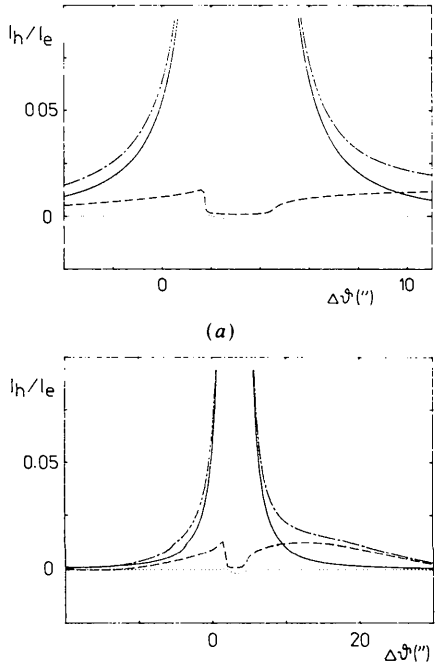
* This material has been deposited with the British Library Lending Division as Supplementary Publication No. SUP39537 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

correspond to typical precipitates SiO_2 in Czochralski-grown Si. Since the amorphous spheres used in our model have the radius $R=(2\pi Ah)^{1/2}\gg R_d$, it is necessary to choose $P\gg P_d$. The reflection curves of the crystal with precipitates in 422 Cu $K\alpha_1$ symmetrical Bragg-case diffraction are plotted in Figs. 1(*a*), (*b*). Fig. 1(*a*) shows the region near the exact Bragg position where (17) is valid; the whole curve is demonstrated in Fig. 1(*b*). Fig. 2 shows the comparison of the contribution to the reflection curve in the first approximation with the intensity computed in the kinematical approximation by means of the theory of diffuse scattering (Dederichs, 1971).

4. Discussion

In the region of validity of approximation (17) the form of the first iteration contribution to the reflection curve is not dependent on the type of the deformation field of the microdefects and it is determined only by the dynamical absorption coefficient $\mathrm{Im}\,(\kappa_h)$ and by $c(R^4+8\pi^2A^2h^2)$. Thus, the defect parameters can affect only the absolute value of this contribution but not the shape of the reflection curve. From the random positions of the defects it follows that the value of the contribution of the first iteration to the intensity is proportional to the amount of irradiated defects, which is inversely proportional to the absorption coefficient of the waves inside the quasiperfect crystal.



(*b*)

Fig. 1. The reflection curve (Cu $K\alpha_1$ 422 symmetrical Bragg case on Si) of the quasiperfect crystal (full line), the contribution of the first approximation ($I_h^{(1)}-I_h^{(0)}$, dashed line) and of the second approximation ($I_h^{(2)}-I_h^{(1)}$, dotted line). The whole reflection curve $I_h^{(2)}$ is plotted as dot-and-dashed line. The parameters of the defects $A=2000\ \mathrm{nm}^3$, $P=0{\cdot}01$. (*a*) shows the region of the maximum of $I_h^{(0)}$, (*b*) the whole reflection curve.

If (17) is not valid, the shape of the reflection curve depends on the type of the deformation field and it is sensitive to the value of R. In contrast to the area near the maximum, where the reflection curve was not essentially affected by approximation (8), far from the maximum assumption (8) causes an essential error in the diffracted intensity. In this region the curve shows an asymmetry depending on the sign of A. If $A>0$ (the defect compresses the surrounding lattice) the diffracted intensity is greater for positive deviations of the angle of incidence from the Bragg position than for negative deviations. If $A<0$ the asymmetry is opposite.

From Fig. 2 it is obvious that the dynamical approach yields corrections to the kinematical diffraction curve that are essential only in the close vicinity of the maximum of the reflection curve of the quasiperfect crystal. The tails of the curve can therefore be computed kinematically.

In the maximum of the reflection curve the contribution of the second iteration is essential. This contribution can be interpreted as the decrease in the intensity diffracted from the quasiperfect crystal owing to the defects and it corresponds to the second approximation in the coherent diffraction theory (Dederichs, 1972).

Deriving formulas (1) and (5) we have replaced Green's function $\hat{G}$ in (1.1) by its kinematical limit $\hat{G}^K$. It was shown in paper 1 that the error caused by this assumption is negligible if

$$PR^2<10^{-2}\ \mu\mathrm{m}^2. \qquad (20)$$

This estimate is valid in the case of precipitates if (8) holds. The differences between our results and those from usual kinematical theory are essentially only in

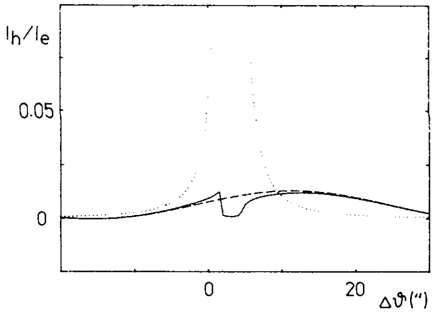


Fig. 2. The comparison of the first approximation $I_h^{(1)}-I_h^{(0)}$ (full line) with the intensity of the diffuse scattering computed from the kinematical theory (dashed line). The reflection curve of $I_h^{(0)}$ is plotted as a dotted line, the parameters of the diffraction and of the defects are the same as in Fig. 1.

the close vicinity of the maximum of the reflection curve, where, however, the shape of the reflection curve is not dependent on the type of the deformation field of the defects.

The results obtained enable us to explain the contrast of the growth striations with microdefects in double-crystal topography. From the above results it is obvious that for all angles of incidence of the primary wave the intensity diffracted from the region with the microdefects is greater than that from the perfect crystal. Thus, in the case of diffraction which is not sensitive to the variation of the mean lattice parameter in the striations, the striations with microdefects have a black contrast.

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Printing Sets of Structure Factors for Coping with Orientation Ambiguities and Possible Twinning by Merohedry

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Abstract

Any crystal whose point group is a subgroup of index p of its lattice symmetry (merohedral crystals, $p = 2$, 4 or 8) can be referred to p non-equivalent possible settings of the cordinate axes. These possible settings are tabulated, for all 44 oriented point groups and for each setting s, as the triplet of indices $h_sk_sl_s$ into which the original hkl transforms, together with the relevant transformation operation. At least one such set of suitable observed structure factors should be published with every structure description for merohedral crystals so that the chosen setting can be identified. A list of the types of reflections unsuitable for orientation purposes is given. A unique orientation of the coordinate axes could be reached experimentally, without structural knowledge, by attributing to the largest I_{obs}, indices hkl in a specified asymmetric domain of the point-group symmetry of the lattice. The table also serves as a complete collection of possible twin laws in twinning by merohedry; each transformed symbol $h_sk_sl_s$ represents the reflection which, on the diffraction pattern of the twin, contributes its intensity to that of hkl.

Introduction

When measuring physical properties of crystals previously described in the literature, it is essential to identify, among the possible crystal settings, the one that was used for the structure solution. The crystallographer who collects diffraction intensities for a crystal of known structure is confronting the same problem. As long as the intensity data were tabulated in the original publication, the retrieval of the crystal setting was straightforward: the reciprocal axes were simply chosen in such a way that the intensities of the indexed reflections would match those of the published ones.

At the present time intensity data are no longer published, being instead deposited in manuscript form in some archival center. As a consequence, ambiguities in the identification of the axial setting arise in all crystals but those with the same point-group symmetry as their lattice symmetry (holosymmetric crystals) or with all its symmetry axes (holoaxial hemisymmetry, column 2 in Table 1) provided the latter are referred to a right-handed coordinate system, RHCS. This situation exists even if metric

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