pseudo atoms in which the atomic electron-density distribution is written as the sum of the free atomic electron-density distribution plus an expansion into deformation functions with Slater-type orbital radial dependence.

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A Stochastic Model for X-ray Diffraction from Imperfect Crystals

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Abstract

A model of crystal defects is developed to describe the diffraction of X-rays from imperfect crystals containing defect surfaces and crystal grains. The model, which is based on continuum theory for an isotropic homogeneous elastic medium, leads to a stochastic first-order differential equation, known as a Langevin equation. The solution of this equation is used to derive a correlation function for the strain-dependent term in the formula for the crystal reflectance. A consequence of the model is that the kinematic reflectivity of an imperfect crystal is given by the convolution between the perfect-crystal reflectivity and a function that transforms between a Gaussian and a Lorentzian depending on a correlation length in the crystal.

Introduction

X-ray rocking curves obtained from thin crystalline films or superlattices may show complicated features that are characteristic of the correlations between the crystal structures in the films. However, in the presence of defects causing severe distortions, many of the features are lost and the result is usually a broad Gaussian-like curve, the width of which is taken as a measure of the quality of the crystal. The loss of structure in the rocking curve can be interpreted as a loss of information about the nature of the crystal, which suggests that it should be possible to model such a curve with only a few parameters. For example, the theory of X-ray diffraction by Zachariasen (1967) only involves the size of the mosaic-crystal grains and the half-width of the distribution function for the grain orientations. The statistical theories of X-ray diffraction by Kato (1980) and Becker & Al Haddad (1990) contain two correlation lengths that relate to the statistical nature of the crystal imperfections.

Davis (1991) suggested that a first-order stochastic differential equation could model the effects of a class of crystal imperfections on the strain-dependent term in the equation for the crystal reflectance. This model was used to derive a partial differential equation describing dynamical diffraction in a crystal containing point-like defects and crystal grains that are misoriented with respect to the perfect lattice.

In this paper, the first-order stochastic equation is derived from continuum theory for a homogeneous isotropic elastic solid containing defects. This equation is related to the Markov process used by Becker & Al Haddad (1989) to derive an order parameter for their dynamical theory and it involves parameters similar to those in the mosaic-crystal theory of Darwin, as used by Zachariasen (1967). The solution

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of the stochastic equation leads to a correlation function that, together with an equation for the crystal reflectance, provides a kinematic description of X-ray diffraction from the imperfect crystal. The reflectivity is obtained as a convolution between the perfect-crystal reflectivity and the Fourier transform of the correlation function. The properties of the convolving function are discussed.

Crystal reflectance

A simple formula for the crystal reflectance can be derived from the Takagi–Taupin equations (Takagi, 1962, 1969; Taupin 1964), which describe the dynamical diffraction of X-rays from a distorted crystal. By projecting the propagation paths of the transmitted and the diffracted waves onto some coordinate axis in the crystal, such as one parallel to the surface normal of the crystal with the coordinate t, the reflectance $R(t)$ can be defined as the ratio of the diffracted- and transmitted-wave amplitudes at t. This is a complex quantity since it contains information on the relative phases of the waves. Because the transmitted and diffracted waves travel along different paths in the crystal it is necessary to assume that the crystal properties are constant over the plane at fixed t. Then a first-order differential equation for the reflectance can be written,

$$\mathrm{d}R/\mathrm{d}t = i\alpha(\chi_h - 2\beta R + \chi_{-h}R^2). \qquad (1)$$

Here $\alpha = -\pi k/\gamma_h$, with $1/k = \lambda$ the X-ray wavelength; γ_o and γ_h are the direction cosines of the transmitted and diffracted waves with respect to the coordinate axis; $\chi_h = C\chi'_h$ and $\chi_{-h} = -C(\gamma_h/\gamma_o)\chi'_{-h}$, where C is a polarization factor and χ'_h and χ'_{-h} are the Fourier components of the dielectric susceptibilities associated with the reciprocal-lattice vectors $\mathbf{h}$ and $-\mathbf{h}$, respectively. The resonance parameter, β, is given by

$$\beta = n^2(k_h^2 - k^2)/2k^2 - n\hat{\mathbf{k}}_h \cdot \nabla(\mathbf{h}\cdot\mathbf{u})/k \equiv \langle\beta\rangle + \beta_\xi, \qquad (2)$$

where $n = (1+\chi'_o)^{1/2}$ is the refractive index for X-rays, $\mathbf{k}$ and $\mathbf{k}_h$ are the wavevectors of the transmitted and diffracted waves in the crystal interior, with $\mathbf{k}_h = \mathbf{k}+\mathbf{h}$ and $\hat{\mathbf{k}}_h$ the unit vector in direction $\mathbf{k}_h$, and $\mathbf{u}$ is the displacement due to strain of a point in the lattice from its relaxed position. In the present model for the imperfect crystal, the defects introduce random fluctuations in the strain as a function of position in the crystal. The strain-dependent term in (2) can then be separated into an average term and a fluctuating term. The average term, together with the first term in (2), is written as $\langle\beta\rangle$, which is a function of the angle of incidence of the X-ray beam. The fluctuating part, β_ξ, depends on a random variable ξ, the statistical properties of which are determined below.

The reflectance equation (1) has been solved numerically for strained heterostructures (Bensoussan, Malgrange & Sauvage-Simkin, 1987) but, in general, if β is an arbitrary function of t it is not possible to solve it explicitly in terms of quadratures and the elementary functions of analysis (Bellman & Kalaba, 1965; Brand, 1966). However, for crystals, such as thin films, in which the change in the amplitude of the transmitted wave may be small, an approximate solution can be obtained by omitting the quadratic term in (1). This leads to a *kinematic* equation, the solution of which is

$$R(t) = \exp\left[-i2\alpha\int_0^t \beta(t')\,\mathrm{d}t'\right] \times \int_0^t i\alpha\chi_h(t')\exp\left[i2\alpha\int_0^{t'}\beta(t'')\,\mathrm{d}t''\right]\mathrm{d}t', \qquad (3)$$

where it has been assumed that $R(0)=0$. This is appropriate for thin films when there is no reflection from the substrate. Note that in the kinematic approximation the assumption of constant crystal properties across the plane at fixed t is not necessary.

In general, $\langle\beta\rangle$ is complex to take account of the absorption of X-rays. In the case where there is no absorption associated with the strain fluctuations in the crystal, β_ξ is real and the average reflectivity, $\langle R^*R\rangle$, from an imperfect crystal is given by

$$\langle R^*R\rangle = \exp\left[-i2\alpha\int_0^t(\langle\beta\rangle - \langle\beta\rangle^*)\,\mathrm{d}t'\right] \times \int_0^t\int_0^t \alpha^2\chi_h(t')\chi_h^*(t'') \times \exp\left[i2\alpha\left(\int_0^{t'}\langle\beta\rangle\,\mathrm{d}t - \int_0^{t''}\langle\beta\rangle^*\,\mathrm{d}t\right)\right] \times \left\langle\exp\left(i2\alpha\int_{t''}^{t'}\beta_\xi\,\mathrm{d}t\right)\right\rangle \mathrm{d}t'\,\mathrm{d}t''. \qquad (4)$$

If β_ξ is Gaussian distributed then it can be shown (see, for example, Risken, 1984) that

$$\left\langle\exp\left(i2\alpha\int_{t''}^{t'}\beta_\xi\,\mathrm{d}t\right)\right\rangle = \exp\left[-2\alpha^2\int_{t''}^{t'}\int_{t''}^{t'}\langle\beta_\xi(t_1)\beta_\xi(t_2)\rangle\,\mathrm{d}t_1\,\mathrm{d}t_2\right], \qquad (5)$$

which involves the correlation $\langle\beta_\xi(t_1)\beta_\xi(t_2)\rangle$ between the fluctuating terms of the resonance parameter.

The statistical properties of β_ξ depend on the nature of the defects in the crystal. It will be assumed that the defects are of two general types: (i) defect surfaces, such as stacking faults, which will be modelled by surface distributions of point defects; (ii) volume defects, which are taken to be the crystal grains with lattice planes rotated through small angles relative to the perfect lattice. The defects are taken to be randomly distributed throughout the crystal and to cause

random displacements **u**. The two defect types will be incorporated into a single equation that models randomly oriented crystal grains bounded by surfaces of defects. The aim is to obtain an expression for the two-point correlation function required in (5). The models are based on continuum theory for an infinite homogeneous isotropic elastic body (see Eshelby, 1956).

Surface-defect model

A point defect at $\mathbf{r}'$ producing a spherically symmetric deformation induces an elastic displacement

$$\mathbf{u}(\mathbf{r}) = c_d(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3, \tag{6}$$

where c_d is the *strength* of the defect. If there is a distribution of such defects,

$$\rho(\mathbf{r}') = \sum_n c_n \delta(\mathbf{r}'-\mathbf{r}_n), \tag{7}$$

where the sum is over defect sites located at $\mathbf{r}_n$ and $\delta(\,)$ is the Dirac delta function, then the displacement arising from the combined action of these defects is

$$\mathbf{u}(\mathbf{r}) = \int \rho(\mathbf{r}')(\mathbf{r}-\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|^3 \, \mathrm{d}^3r'. \tag{8}$$

This has the same form as the electric field from a distribution of point charges. Application of the Gauss law yields the strain

$$\nabla \cdot \mathbf{u}(\mathbf{r}) = 4\pi\rho(\mathbf{r}) = 4\pi \sum_n c_n \delta(\mathbf{r}-\mathbf{r}_n). \tag{9}$$

In this model, a stacking fault or a plane of defects is represented by a surface distribution of point defects described by (7). Because the strain depends on the delta function in (9), the interaction between the X-ray beam and the point defect in the surface is localized at the defect site. It will be shown in a later section that a consequence of this point-like interaction is that the scattering of X-rays from the defect surfaces is similar to that of Huang scattering from point defects. Furthermore, the point-like behaviour will be seen to occur in the limit as a correlation length approaches zero.

The imperfect crystal considered here is assumed to contain a large number of defect surfaces, randomly located and randomly oriented. As it propagates through the crystal, a pencil beam of diffracted X-rays will cross many of these surfaces and it will be influenced by the strains in the region about each crossing point. The effect of a large number of these surfaces at some depth t in the crystal on the intensity of a broad X-ray beam is obtained by taking an average of the effect on an ensemble of independent pencil beams.

Consider then a size scale such that the defect surface appears locally flat and integrate over a small cylindrical volume of upper surface area Δa and infinitesimal thickness δt_d with its axis parallel to the unit normal $\hat{\mathbf{s}}$ to the defect surface, as shown in Fig. 1. If the contribution from distantly located defects to the strain over this volume is taken to be negligible in comparison with the contribution from the defects within the volume, then

$$\begin{aligned}\int \nabla \cdot \mathbf{u}(\mathbf{r}) \, \mathrm{d}V &\simeq [\partial(\mathbf{u}\cdot\hat{\mathbf{s}})/\partial t_d]\Delta a \delta t_d \\ &\simeq [\partial u/\partial t_d]\Delta a \delta t_d. \end{aligned} \tag{10}$$

The last expression follows since, by arguments of symmetry and local flatness, the local defects produce a displacement $\delta\mathbf{u}$ parallel to $\hat{\mathbf{s}}$. In this case the component of the strain in (10) in some other direction specified by a constant vector $\mathbf{h}$ is simply given by multiplying (10) by the direction cosine, $\mathbf{h}\cdot\hat{\mathbf{s}}/h$. Furthermore, by a change of coordinates from the local thickness t_d, which depends on the local-defect-surface normal, to some global coordinate t in a direction specified by a unit vector $\hat{\mathbf{k}}_h$, where $t = t_d/\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}$, the strain becomes

$$\begin{aligned}\partial(\mathbf{h}\cdot\mathbf{u})/\partial t = [(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})/\Delta a\delta t_d] \\ \times 4\pi \int \sum_n c_n \delta(\mathbf{r}-\mathbf{r}_n)\, \mathrm{d}V. \end{aligned} \tag{11}$$

The sum over the defects can be partitioned into a sum over the defects j within the surface and a sum over the defect surfaces i at a depth t_{di}. Since the integration volume has an infinitesimal thickness, the integral in (11) becomes

$$\begin{aligned}\int \sum_n c_n \delta(\mathbf{r}-\mathbf{r}_n)\, \mathrm{d}V &= \int\int \sum_j c_j \delta(x-x_j)\delta(y-y_j)\, \mathrm{d}x\, \mathrm{d}y \\ &\quad \times \sum_i \delta(t_d - t_{di})\, \delta t_d \\ &= \Delta a \delta t_d c \sum_i \delta[\mathbf{k}_h\cdot\hat{\mathbf{s}}(t-t_i)], \end{aligned} \tag{12}$$

where c represents the defect strength per unit area. This can be thought of as the amount by which the lattice is displaced across the defect surface. Note that the change of coordinates within the delta function has no effect unless $\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}} = 0$, which will be assumed to occur so rarely as to be negligible. The strain can then be written as

$$\begin{aligned}\partial(\mathbf{h}\cdot\mathbf{u})/\partial t &= 4\pi c(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}) \sum_i \delta(t-t_i) \\ &\equiv 4\pi[\langle\varepsilon(t)\rangle + \delta\varepsilon(t)]. \end{aligned} \tag{13}$$

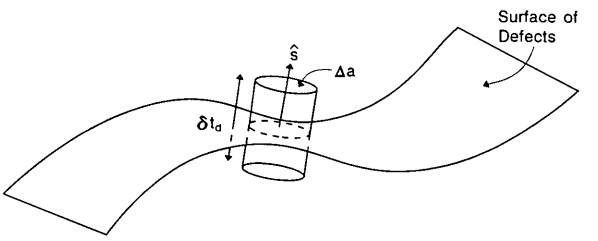

Fig. 1. The geometry for calculating the displacement from a smooth surface distribution of point defects.

This expression involves the local surface orientation and the defect-surface strength, which take random values throughout the crystal. The strain has been separated into an average term, $\langle\varepsilon(t)\rangle$, and a fluctuating term, $\delta\varepsilon(t)$, where $\langle\delta\varepsilon(t)\rangle=0$. If the directions of the defect-surface normals are independent of the defect-surface strengths then the average becomes

$$\langle\varepsilon(t)\rangle=\langle(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})\rangle\left\langle c\sum_i\sigma(t-t_i)\right\rangle$$
$$=\langle(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})\rangle\rho(t), \tag{14}$$

where $\rho(t)$ is the average defect strength per unit volume at depth t. If the elastic displacement is integrated over the crystal surface, the average of ρ over the entire crystal can be related to the volume change of the crystal arising from the defects,

$$\Delta V=\int_s\mathbf{u}\cdot\mathrm{d}\boldsymbol{S}=\int_V\nabla\cdot\mathbf{u}\,\mathrm{d}V$$
$$=4\pi\times3(1-\nu)/(1+\nu)\langle\rho\rangle V, \tag{15}$$

where Poisson's ratio, ν, is included to take account of the boundary conditions for the elastic forces at the crystal surface (Eshelby, 1954, 1956).

The two-point correlation for $\delta\varepsilon(t)$ as a function of t is given by

$$\langle\delta\varepsilon(t)\delta\varepsilon(t')\rangle$$
$$=\left\langle c[\mathbf{h}\cdot\hat{\mathbf{s}}(t)][\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}(t)]\,c[\mathbf{h}\cdot\hat{\mathbf{s}}(t')]\right.$$
$$\left.\times[\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}(t')]\sum_i\sum_j\delta(t-t_i)\delta(t'-t_j)\right\rangle-\langle\varepsilon\rangle^2$$
$$=\left\langle c^2(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})(\mathbf{h}\cdot\hat{\mathbf{s}}')(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}')\right.$$
$$\left.\times\sum_i\delta(t-t_i)\delta(t'-t_i)\right\rangle$$
$$+\left\langle c^2(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})(\mathbf{h}\cdot\hat{\mathbf{s}}')(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}')\right.$$
$$\left.\times\sum_i\sum_{j\neq i}\delta(t-t_i)\delta(t'-t_j)\right\rangle-\langle\varepsilon\rangle^2, \tag{16}$$

where the sum has been divided into the terms for which $j=i$ and those for which $j\neq i$. Note that the surface normals are not necessarily the same at different depths and are written as functions of t. In the term for which $j=i$, the sum is zero unless $t'=t$, whereas, in the term for $j\neq i$, the sum is zero unless $t'\neq t$. If these conditions are represented by delta functions and it is assumed that defect surfaces at different depths are independent then

$$\langle\delta\varepsilon(t)\delta\varepsilon(t')\rangle$$
$$\simeq\delta(t-t')\left\langle c^2(\mathbf{h}\cdot\hat{\mathbf{s}})^2(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})^2\sum_i\delta(t-t_i)^2\right\rangle$$
$$+[1-\delta(t-t')]\left\langle c(\mathbf{h}\cdot\hat{\mathbf{s}})(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}})\sum_i\delta(t-t_i)\right\rangle$$
$$\times\left\langle c(\mathbf{h}\cdot\hat{\mathbf{s}}')(\hat{\mathbf{k}}_h\cdot\hat{\mathbf{s}}')\sum_j\delta(t'-t_j)\right\rangle-\langle\varepsilon\rangle^2$$
$$=\delta(t-t')\left[\left\langle c^2(\mathbf{h}\cdot\hat{\mathbf{s}})^2(\hat{\mathbf{k}}_h\cdot\hat{\sigma})^2\sum_i\delta(t-t_i)^2\right\rangle-\langle\varepsilon\rangle^2\right]. \tag{17}$$

Here it can be seen that the fluctuating terms are delta-function correlated with depth. Furthermore, it will be assumed that $\delta\varepsilon$ is Gaussian distributed.

Volume-defect model

The volume defects are taken to be the randomly oriented crystal grains that compose the imperfect crystal. Each grain contains no strains other than a small rotation, related to the displacement by

$$\boldsymbol{\omega}=\tfrac{1}{2}(\nabla\times\mathbf{u}), \tag{18}$$

where ω_k is the angle of rotation about axis k. For such grains, the following relations hold for all cyclic permutations of the indices:

$$\partial u_j/\partial x_i=-\partial u_i/\partial x_j=\omega_k, \tag{19}$$
$$\partial u_x/\partial x=\partial u_y/\partial y=\partial u_z/\partial z=0. \tag{20}$$

Consider, as before, a pencil beam of diffracting radiation propagating in a direction specified by the constant unit vector $\hat{\mathbf{k}}_h$. Then the gradient along this direction of the component of the displacement, $\mathbf{h}\cdot\mathbf{u}$, where $\mathbf{h}$ is a constant vector, is given by

$$(\hat{\mathbf{k}}_h\cdot\nabla)(\mathbf{h}\cdot\mathbf{u})=\partial u_y/\partial x(\hat{k}_{hx}h_y-\hat{k}_{hy}h_x)$$
$$+\partial u_z/\partial y(\hat{k}_{hy}h_z-\hat{k}_{hz}h_y)$$
$$+\partial u_x/\partial z(\hat{k}_{hz}h_x-\hat{k}_{hx}h_z)$$
$$=\boldsymbol{\omega}\cdot(\hat{\mathbf{k}}_h\times\mathbf{h}). \tag{21}$$

Let the shape of the ith crystal grain be specified by $S_i(\mathbf{r})$, where $S_i(\mathbf{r})=1$ if $\mathbf{r}$ represents an interior point of the grain and $S_i(\mathbf{r})=0$ if $\mathbf{r}$ represents an exterior point and let $\boldsymbol{\omega}_i$ be the rotation vector for this grain. The rotation vector in (21) can then be represented by a sum over the crystal grains,

$$\boldsymbol{\omega}(\mathbf{r})=\sum_i\boldsymbol{\omega}_iS_i(\mathbf{r}). \tag{22}$$

The gradient of (21) in the direction of $\hat{\mathbf{k}}_h$ is then

$$(\hat{\mathbf{k}}_h \cdot \nabla)[\hat{\mathbf{k}}_h \cdot \nabla(\mathbf{h} \cdot \mathbf{u})] = \sum_i [(\hat{\mathbf{k}}_h \cdot \boldsymbol{\omega}_i)(\hat{\mathbf{k}}_h \times \mathbf{h}) \cdot \nabla S_i(\mathbf{r}) + \hat{\mathbf{k}}_h \cdot (\hat{\mathbf{k}}_h \times \mathbf{h}) \times (\nabla S_i(\mathbf{r}) \times \boldsymbol{\omega}_i)]. \quad (23)$$

The pencil beam of X-rays, with a small cross section, will sample a subset of all the grains in the crystal so that the sum over the i grains in (23) can be replaced by a sum over the subset of n grains that are intercepted by the beam. The coordinate $\mathbf{r}$ can also be replaced by the position t that measures distances in the crystal along the path of the X-ray beam. Furthermore, the gradients of $S_n(\mathbf{r})$ are zero in both the interior and the exterior of grain n and become infinite at the grain boundary. If t_n^+ represents the location of the upper boundary of grain n and $\hat{\mathbf{s}}_n^+$ represents the outwardly directed unit normal to the upper surface and t_n^- and $\hat{\mathbf{s}}_n^-$ are the corresponding parameters for the lower boundary then the gradients of $S_n(\mathbf{r})$ can be replaced by these normal vectors and by delta functions that locate the two grain surfaces intercepted by the X-ray beam. Since $\hat{\mathbf{k}}_h \cdot \nabla = \partial/\partial t$, (23) becomes

$$\begin{aligned}\partial^2/\partial t^2[\mathbf{h} \cdot \mathbf{u}(t)] &= -\sum_n [(\hat{\mathbf{k}}_h \cdot \boldsymbol{\omega}_n)(\hat{\mathbf{k}}_h \times \mathbf{h}) \cdot \hat{\mathbf{s}}_n^+ \\ &\quad + \hat{\mathbf{k}}_h \cdot (\hat{\mathbf{k}}_h \times \mathbf{h}) \times (\hat{\mathbf{s}}_n^+ \times \boldsymbol{\omega}_n)]\delta(t - t_n^+) \\ &\quad - \sum_n [(\hat{\mathbf{k}}_h \cdot \boldsymbol{\omega}_n)(\hat{\mathbf{k}}_h \times \mathbf{h}) \cdot \hat{\mathbf{s}}_n^- \\ &\quad + \hat{\mathbf{k}}_h \cdot (\hat{\mathbf{k}}_h \times \mathbf{h}) \times (\hat{\mathbf{s}}_n^- \times \boldsymbol{\omega}_n)]\delta(t - t_n^-) \\ &\equiv \sum_n [\Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^+)\delta(t - t_n^+) \\ &\quad + \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^-)\delta(t - t_n^-)] \\ &\equiv \langle \varepsilon(t) \rangle + \delta\varepsilon(t). \end{aligned} \quad (24)$$

Here the terms involving the scalar and vector products have been represented by Ω. As with surfaces of point defects, the expression for the displacements associated with the crystal grains has been separated into an average term and a fluctuating term. These terms depend on the locations of the grain boundaries, the directions of the surface normals of the grains and the grain orientations, all of which take random values throughout the crystal. The direction from which the rotations of the crystal grains are reckoned is arbitrary and for convenience it is chosen so that the average term in (24) is zero, *i.e.* $\langle \varepsilon \rangle = 0$.

The derivation of the correlations of the fluctuating terms proceeds along similar lines to that for defect surfaces. The correlations between $\delta\varepsilon(t)$ and $\delta\varepsilon(t')$ can be obtained from (24) and involve the products of two sums over n and m. As in (16), these can be separated into terms for which $m = n$ and those for which $m \neq n$. The $m = n$ term is zero unless $t' = t$. This condition can be represented by a delta function. However, care is required in treating the term for which $m \neq n$ because there is a correlation between adjacent crystal grains that share a common boundary. To take account of this, let the grains be numbered consecutively with the crossings of the pencil beam and further separate the sums into terms involving adjacent boundaries. The correlation can then be written in the form

$$\begin{aligned}\langle \delta\varepsilon(t)\delta\varepsilon(t') \rangle &= \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^+)^2 \delta(t - t_n^+)\delta(t' - t_n^+) \right\rangle \\ &\quad + \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^-)^2 \delta(t - t_n^-)\delta(t' - t_n^-) \right\rangle \\ &\quad + \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^+)\Omega(\boldsymbol{\omega}_{n+1}, \hat{\mathbf{s}}_{n+1}^-) \right. \\ &\quad \left. \times \delta(t - t_n^+)\delta(t' - t_{n+1}^-) \right\rangle \\ &\quad + \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^-)\Omega(\boldsymbol{\omega}_{n-1}, \hat{\mathbf{s}}_{n-1}^+) \right. \\ &\quad \left. \times \delta(t - t_n^-)\delta(t' - t_{n-1}^+) \right\rangle, \end{aligned} \quad (25)$$

where the double sum has been split into terms involving the same boundary, adjacent boundaries and non-connected boundaries. The latter has not been shown in (25) because it averages to zero since non-connected boundaries are independent. The surface normals and the locations of adjacent grain boundaries are related by $\hat{\mathbf{s}}_n^+ = -\hat{\mathbf{s}}_{n+1}^-$ and $t_n^+ = t_{n+1}^-$. From (24) it follows that

$$\Omega(\boldsymbol{\omega}_{n+1}, \hat{\mathbf{s}}_{n+1}^-) = \Omega(\boldsymbol{\omega}_{n+1}, -\hat{\mathbf{s}}_n^+) = -\Omega(\boldsymbol{\omega}_{n+1}, \hat{\mathbf{s}}_n^+). \quad (26)$$

With the use of (26) and the fact that the sums are zero unless $t' = t$, the correlation takes the form

$$\begin{aligned}&\langle \delta\varepsilon(t)\delta\varepsilon(t') \rangle \\ &= \delta(t - t') \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^+) \right. \\ &\quad \left. \times [\Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^+) - \Omega(\boldsymbol{\omega}_{n+1}, \hat{\mathbf{s}}_n^+)]\delta(t - t_n^+) \right\rangle \\ &\quad + \delta(t - t') \left\langle \sum_n \Omega(\boldsymbol{\omega}_n, \hat{\mathbf{s}}_n^-) \right. \\ &\quad \left. \times [\Omega(\omega_n, \hat{\mathbf{s}}_n^-) - \Omega(\omega_{n-1}, \hat{\mathbf{s}}_n^-)]\delta(t - t_n^-) \right\rangle. \end{aligned} \quad (27)$$

Since the grain boundaries are taken as discontinuous and independent, the fluctuation $\delta\varepsilon$ is delta-function correlated with position and, as before, it is assumed to be Gaussian distributed. The effect on the intensity of a broad X-ray beam diffracted from many misoriented crystal grains is obtained by averaging the effect on an ensemble of independent pencil beams.

Imperfect crystals

The imperfections considered here are a combination of misoriented crystal grains and defect surfaces. In general, the crystal-grain boundaries will coincide with the defect surfaces and the two defect types will be correlated. Because the forms of the defect equations are similar, each depending on a Gaussian-distributed delta-function-correlated random variable, the model for the imperfect crystal is obtained by a linear combination of (13) and (24). Note that, over a length scale l in a crystal grain that has been rotated by $\boldsymbol{\omega}$, the lattice points have relative displacements of $l|\boldsymbol{\omega}|$. This means that the displacements arising from small rotations of crystal grains are correlated over distances scaled by l. The quantity $l|\boldsymbol{\omega}|$ may be thought of as the *strength* of the defect and it is similar to the point-defect strength per unit area, c, which gives the displacement across an infinitesimally thick defect surface. Bearing this in mind and remembering that β_ξ is the fluctuating part of $(n/k)\partial(\mathbf{h}\cdot\mathbf{u})/\partial t$, one can write the linear combination of (13) and (24) as

$$l\,\mathrm{d}/\mathrm{d}t[\beta_\xi(t)]+\beta_\xi(t)=\sigma\xi(t), \tag{28}$$

which is a first-order differential equation involving the stochastic variable ξ. The parameter l is a *correlation length* and σ is the sum of the root-mean-square deviations from the means of the defect *strengths*, including the geometric factors [see (17) and (27)]. Equation (28) is a Langevin equation (Van Kampen 1976; Risken, 1984), which is usually associated with the study of Brownian motion (see, for example, Uhlenbeck & Ornstein, 1930).

The correlation function for β_ξ is derived from the solution of (28) by using the fact that ξ is delta-function correlated, which yields

$$\langle\beta_\xi(t)\beta_\xi(t+\tau)\rangle=(\sigma^2/2l)\exp(-|\tau|/l), \tag{29}$$

where a transient term has been omitted, leaving the stationary correlation that only depends on the relative positions, τ. Substitution of (29) into (5) with $\tau=t'-t''$ gives

$$\left\langle\exp\left(i2\alpha\int_{t''}^{t'}\beta_\xi\,\mathrm{d}t\right)\right\rangle$$

$$=\exp\{-2\alpha^2\sigma^2l[|\tau|/l+\exp(-|\tau|/l)-1]\}$$

$$\equiv(1/2\pi)\int_{-\infty}^{\infty}\gamma(\kappa)\exp(-i\kappa\tau)\,\mathrm{d}\kappa, \tag{30}$$

which defines the Fourier transform of a function $\gamma(\kappa)$. When this is substituted into (4), the double integral can be separated into a product of two integrals that are complex conjugates,

$$\begin{aligned}\langle R^*R\rangle=&\int_{-\infty}^{\infty}\mathrm{d}\kappa[\gamma(\kappa)/2\pi]\left\{\exp\left(-i2\alpha\int_0^t\langle\beta\rangle\,\mathrm{d}t'\right)\right.\\&\times\int_0^t i\alpha\chi_h(t')\exp\left[i\int_0^{t'}(2\alpha\langle\beta\rangle-\kappa)\,\mathrm{d}t\right]\mathrm{d}t'\Bigg\}\\&\times\left\{\exp\left(i2\alpha\int_0^t\langle\beta\rangle^*\,\mathrm{d}t'\right)\int_0^t-i\alpha\chi_h^*(t'')\right.\\&\times\exp\left[-i\int_0^{t''}(2\alpha\langle\beta\rangle^*-\kappa)\,\mathrm{d}t\right]\mathrm{d}t''\Bigg\}\\=&\int_{-\infty}^{\infty}[\gamma(\kappa)/2\pi]|R(2\alpha\langle\beta\rangle-\kappa)|^2\,\mathrm{d}\kappa.\end{aligned} \tag{31}$$

Equations (31) give the result that the average reflectivity of the imperfect crystal is a convolution of the reflectivity of a perfect crystal with the function $\gamma(\kappa)$, where the perfect-crystal reflectivity depends on the average parameter $\langle\beta\rangle$. The effects of non-random strains, such as might be encountered in strained-layer superlattices, and the average of the strains arising from the defects are included in the perfect-crystal rocking curve and the effects of the random fluctuating strains are introduced through $\gamma(\kappa)$.

Note that the result (31) and definition of $\gamma(\kappa)$, through the Fourier transform of the phase term on the left side of (30), are independent of the defect model. The only requirements are that the kinematic solution (3) is valid and that the defect correlations are stationary, *i.e.* depend only on τ. The defect model with the assumption of Gaussian-distributed defects is required to relate the defect parameters, l and σ, to $\gamma(\kappa)$ *via* (30).

To obtain $\gamma(\kappa)$ explicitly requires the Fourier inversion of (30) and involves incomplete gamma functions. Of greater interest is the inversion of (30) in the limit of very large crystal grains, $l\to\infty$, and point-like defects, $l\to0$. In the following discussion it is useful to note that the kinematic reflectivity for an infinitely thick perfect crystal is a delta function at the Bragg angle,

$$|R(2\alpha\langle\beta\rangle-\kappa)|^2\to\delta(2\alpha\langle\beta\rangle-\kappa), \tag{32}$$

so that, if κ is replaced by $2\alpha\langle\beta\rangle$ in the function $\gamma(\kappa)$ in (31), the kinematic reflectivity for an infinitely thick imperfect crystal is obtained.

For large crystal grains the exponent in (30) is expanded to second order in τ/l, yielding

$$\begin{aligned}&-2\alpha^2\sigma^2l[|\tau|/l+\exp(-|\tau|/l)-1]\\&\cong-2\alpha^2\sigma^2l(|\tau|/l+1-|\tau|/l+\tau^2/2l^2-1)\\&=-2\alpha^2(\sigma^2/2l)\tau^2.\end{aligned} \tag{33}$$

If this approximation is substituted in (30), with κ replaced by $2\alpha\langle\beta\rangle$, the inverse transform gives the

reflectivity,

$$\langle R^*R\rangle \to \gamma(2\alpha\langle\beta\rangle) = \tfrac{1}{2}(\pi/4\alpha^2\upsilon^2)^{1/2}\exp(-\langle\beta\rangle^2/2\upsilon^2), \quad (34)$$

where $\upsilon^2=\sigma^2/2l$ is the variance of the distribution of the β_ξ terms. The rocking curve described by (34) is a Gaussian curve. This merely echoes the fact that each infinitely thick crystal grain has an orientation that is selected from a Gaussian distribution, which was assumed in the derivation of (30). For a finite crystal, the perfect-crystal reflectance is convolved with this Gaussian distribution, with $\kappa/2\alpha$ replacing $\langle\beta\rangle$.

For point-like defects, $l\to 0$ so that

$$-2\alpha^2\sigma^2 l[|\tau|/l+\exp(-|\tau|/l)-1]\to -2\alpha^2\sigma^2|\tau| \quad (35)$$

and the reflectivity of the infinite crystal takes the form

$$\langle R^*R\rangle \to \gamma(2\alpha\langle\beta\rangle)=\sigma^2/(\alpha^2\sigma^4+\langle\beta\rangle^2). \quad (36)$$

This is a Lorentzian function that exhibits the $1/\beta^2$ dependence found in the diffuse intensity for Huang scattering from point defects (Huang, 1947). The similarity is expected since both Huang scattering and the surface-defect model described here are based on the spherically symmetric deformation given by (6). The form of the phase term obtained from (30) with the approximation (35) is the same as that chosen by Becker & Al Haddad (1989, 1990) in their statistical dynamical theory for purely mosaic crystals.

For nonzero but finite correlation lengths, the perfect-crystal rocking curves are convolved with the function $\gamma(\kappa)$ which, on the basis of the previous discussion, will have a form that lies somewhere between a Gaussian and a Lorentzian function. This correlation function changes between these two extremes as the correlation length l is varied.

Discussion

The present description of the defects in crystals, based on continuum theory, contains many approximations and assumptions. The random properties of the crystal are assumed to be stationary, *i.e.* independent of depth in the crystal, and Gaussian distributed at each plane for given t. While somewhat restrictive, these assumptions should be valid in many crystals, particularly thin films grown by metal organic chemical vapour deposition or molecular beam epitaxy, where many aspects of the growth procedures, such as lattice mismatches or thermal-expansion differences between the substrates and the thin films, introduce imperfections that lead to disorder throughout the film (see, for example, Liaw, Chou & Chang, 1990).

A number of assumptions were involved in the calculation of the strains from defect surfaces; these could break down for strong and closely spaced defects. For example, in deriving (10) it was assumed that the local defects produce a displacement parallel to the defect-surface normal $\hat{\mathbf{s}}$. For a severely distorted defect surface this may not be the case. However, this will only alter the relationships between $\mathbf{h}$, $\hat{\mathbf{k}}$, $\hat{\mathbf{s}}$ and the defect strength parameter σ and it will not alter (28), which forms the basis of the correlation function for the defect model.

The Takagi–Taupin equations are approximations in themselves, where second- and higher-order terms have been neglected. In particular, the strain gradient should satisfy [Takagi (1969), equation (93)]

$$n|\nabla^2(\mathbf{h}\cdot\mathbf{u})|/k \simeq \mathrm{d}\beta_\xi/\mathrm{d}t \simeq \sigma/l \ll |\chi'_h|/\lambda. \quad (37)$$

This condition will be satisfied for all but extremely distorted crystals.

The X-ray beam is treated as an ensemble of non-interfering pencil beams with well defined propagation directions, which implies that the X-rays are plane waves. The assumption of a well defined propagation direction of the diffracting beam, $\hat{\mathbf{k}}_h$, relative to the lattice suggests that the model does not treat X-rays that scatter from the defects into other directions. However, a change in the propagation direction of an X-ray through an angle $\delta\theta$ relative to the perfect lattice is equivalent to an X-ray crossing into a crystal grain with a tilt $-\delta\theta$, where $\delta\theta$ is small (Fig. 2). The defect model accounts for this, but now the correlation length l must be interpreted as a length scale between the changes of direction of an X-ray beam

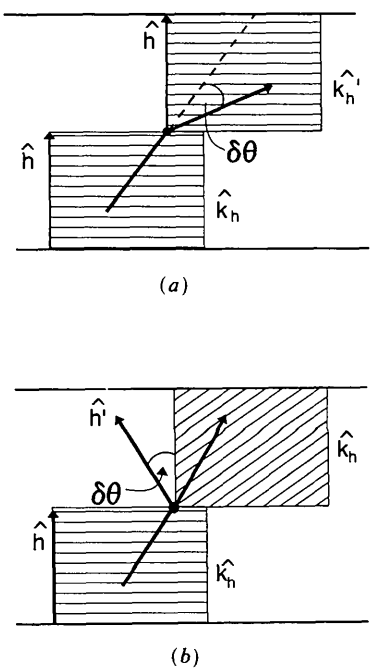

Fig. 2. The equivalence between (*a*) an X-ray scattered through a small angle $\delta\theta$ at a defect and (*b*) an X-ray entering a grain rotated by $-\delta\theta$. The angle has been exaggerated for clarity.

relative to the local lattice vector. It then gives a measure of the crystal-grain size or the distance between points in the crystal that scatter the X-rays.

It is likely that the major influence on this model is the kinematic assumption, which will fail for thicker films when the extinction of the transmitted beam is important. This means that the reflectance becomes large and the quadratic term in (1) cannot be neglected. In such instances, dynamical models (Kato, 1980; Becker & Al Haddad, 1990; Davis, 1991) must be used.

Concluding remarks

A stochastic model for crystal defects has been developed that leads to a correlation function that is used to calculate the reflectivity of imperfect crystals containing defect planes and crystal grains. A solution for the kinematical reflectivity has been given involving a convolution between the perfect-crystal reflectivity and a function depending on two parameters related to the crystal defects. This function takes the limiting form of a Gaussian or a Lorentzian function depending on a correlation length. In a subsequent paper, the fit of this kinematic solution to experimental data will be discussed. The defect model has been incorporated previously in a model for dynamical X-ray diffraction that leads to a partial differential equation for a probability density describing the crystal reflectance (Davis, 1991).

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Cubic Cylinder Packings

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Abstract

Five basic cubic packings of symmetry-related cylinders are described. Four are stable packings and two were described by O'Keeffe & Andersson [*Acta Cryst.* (1977). A**33**, 914–923]. The possible symmetries of rods that can replace the cylinders in crystal structures are identified. Replacing cylinders by bundles of cylinders produces a total of 23 cubic cylinder packings, of which 18 are stable.

Introduction

The study of packings of objects such as spheres or polyhedra (representing atoms or groups of atoms) has played an essential role in descriptive crystal chemistry for a long time. More recently, packings of cylinders (representing rods of atoms) have been used similarly. Some cylinder packings and their applications to crystal chemistry were described by O'Keeffe & Andersson (1977) - hereinafter OKA - who described eight packings. The term cylinder packing is used here to refer to infinite packings of cylinders in which every cylinder is related to all the others by crystallographic symmetry operations. Two cubic packings were found to be particularly useful in descriptive crystal chemistry when the cylinders were replaced by rods of atoms. These packings were referred to as 'body-centered cubic rod packing' and

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