the cumulative numbers of seminvariants:

$$\mathcal{N}_{ijk} = N_{jk}\mathcal{P}^{\text{trial}}_{ijk} \quad (6)$$

$$\mathcal{N}^{\text{theor}}_{ijk} = N_{jk}\mathcal{P}^{\text{theor}}_{ijk}. \quad (7)$$

Suppose now that the theoretical distribution corresponds exactly to the true distribution of seminvariants, then a suitable random variable to test is

$$D_{jk} = \sup_i |\mathcal{N}^{\text{theor}}_{ijk} - \mathcal{N}_{ijk}|. \quad (8)$$

Maximal admissible deviations, $D^{\text{crit}}_{jk} = |\mathcal{N}^{\text{theor}}_{ijk} - \mathcal{N}_{ijk}|_{\max}$, at significance level 0·01, are dependent on the number of seminvariants N_{jk} in the tested region; these are given in Table 1.

The $|\mathcal{N}^{\text{theor}}_{rjk} - \mathcal{N}_{rjk}|$ values for the last interval of ψ values are identically zero because $\mathcal{N}^{\text{theor}}_{rjk} = \mathcal{N}_{rjk} = N_{jk}$, where N_{jk} is the number of seminvariants in the jth region of the kth distribution. Therefore, only $(r-1)$ first intervals of ψ values are tested for maximal differences between cumulative distributions. If in some region and interval the theoretical distribution does not correspond to the true distribution, then the critical values taken from Table 1 must be increased.*

In the case of special seminvariants there are only two possible seminvariant values and also only two intervals. Thus, the number of seminvariants in the second interval is uniquely determined by the number of seminvariants in the first interval and in this case

* The optimal values D^{crit}_{jk} have to be selected by experience for each type of theoretical distribution.

Table 1. *Critical values* $D^{crit}_{jk} = |\mathcal{N}^{theor}_{ijk} - \mathcal{N}_{ijk}|_{max}$ *of the Kolmogorov–Smirnov test at the* 0·01 *significance level*

N_{jk}	2	6	10	15	20	40	>40
D^{crit}_{jk}	2	4	5	6	7	10	$1{\cdot}63\sqrt{N_{jk}}$

only one difference $D_{jk} = |N^{\text{theor}}_{1jk} - N_{1jk}|$ is tested against Table 1 for one region of magnitudes. For centrosymmetric structures the efficiency of the Kolmgorov test based on testing

$$D_{jk} = |P^{\text{theor}}_{+jk} - P^{\text{trial}}_{+jk}|_{\max}$$

may be compared with that of the coefficient

$$K = \sum w_{ijk}(P^{\text{theor}}_{+jk} - P^{\text{trial}}_{+jk})^2 / \sum w_{ijk}$$

used in the x^2 test [equation (19) in paper II] under a restrictive condition that the only contribution to the summation is a maximal difference, *i.e.* $K' = (P^{\text{theor}}_{+jk} - P^{\text{trial}}_{+jk})^2_{\max}$. Thus, the Kolmogorov test is expected to have worse discriminative abilities than the x^2 test, but its convenience may be seen in its simplicity.

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Diffraction Scattering at Angles Far From the Bragg Angle and the Structure of Thin Subsurface Layers

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Abstract

It has been shown that by measuring the angular dependence of X-ray diffraction scattering far from the Bragg peak, information on the structure perfection of thin subsurface layers can be directly obtained. This is associated with the fact that the waves generated in the crystal bulk compensate one another, and the intensity of rocking-curve tails is due mainly to scattering in the subsurface layer. The typical thickness of a scattering layer is related to the deviation angle by a simple relationship: $\Delta z \simeq L_{\text{ex}}\omega_0/\alpha$, where α is the deviation angle of the specimen from the exact Bragg position, ω_0 the diffraction maximum width, and L_{ex} the extinction length. The method of three-crystal diffractometry permitted the observation for the first time with a conventional X-ray source of a distorted layer with a thickness of ~10 nm.

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Introduction

X-ray diffraction is a powerful method for studying the perfection of crystal structures. While Laue-case diffraction provides information on the crystal bulk, Bragg-case diffraction gives information about layers whose thicknesses (up to several μm) are comparable with the extinction length, L_{ex}, which determines the penetration depth of X-rays, provided the exact Bragg condition is satisfied. The deviation from the exact Bragg position results in deeper penetration of X-rays, which is determined by the photoelectric absorption coefficient. Hence, it is natural to draw the conclusion that an X-ray diffraction method can be used to study layers whose thicknesses are equal to or somewhat greater than the extinction length. However, in some cases, the use of more precise measurements permits one to investigate even thinner layers (Cathcart, Petersen & Sparks, 1969; Afanas'ev, Kovalchuk,
Kovjev & Kohn, 1977).

In actual fact, the potentialities of X-ray diffraction methods in studying thin surface layers are much greater. In the following, it will be shown that the intensity of the rocking-curve tail is due mainly to scattering in the subsurface layer. This is associated with the fact that the waves arising in the crystal bulk compensate one another. The characteristic thickness of a scattering layer is given by a simple relationship with the parameter of deviation angle α:

$$\Delta z \simeq L_{ex}\omega_0/\alpha. \tag{1}$$

The method of three-crystal diffractometry (TCD) (Iida & Kohra, 1979; Afanas'ev *et al.*, 1981) permits us to study separately different kinds of diffraction scattering from the crystal under investigation and to follow the behavior of the rocking-curve tail at deviation angles $|\alpha| = |\theta - \theta_B| \gg 0$. This method provides reliable measurements of both intensities and shapes of diffraction scattering peaks (the main peak and the pseudopeak) at deviation angles α exceeding the value of ω_0 by more than two orders of magnitude, even when one uses standard X-ray sources.

As will be shown below, the angular dependence of the main peak intensity gives us directly the information about the perfection of subsurface layers of thickness 10 nm and, thus, about the thicknesses of transitional layers. Now, let us consider the problem in more detail.

Theory

Two functions are necessary for a complete description of structural changes occurring in a disturbed surface layer. The first, $\varphi(z)$, characterizes the displacement of atomic planes from their positions in an ideal lattice and the other, $e^{-w(z)}$, or the so-called Debye–Waller factor, describes atomic disorder in crystal planes. In other words, the latter function describes the degree of amorphization of a specimen. If an X-ray beam falls onto a crystal at angle α sufficiently exceeding ω_0, it is possible to use the kinematical approximation of the diffraction scattering. Then, we can write the following relationship between the amplitudes of incident (E_0) and scattered (E_h) waves:

$$R(\alpha) = \frac{E_h}{E_0} = \frac{-iK\chi_h}{2|\gamma_h|}\int_0^\infty \exp(iK/2|\gamma_h|) \times(\chi_0 - a)z \exp[i\varphi(z) - w(z)]\,dz, \tag{2}$$

where $|\mathbf{K}| = 2\pi/\lambda$, $\gamma_h = \cos(\mathbf{K}, \mathbf{n})$ and $a = \alpha 2 \sin 2\theta_B$, $\mathbf{n}$ is the inner normal to the exit surface of the crytstal, χ_0, χ_h are the Fourier components of the polarizability, and z is the distance from the entrance surface of the crystal.

It is $P_R(\alpha) = |R(\alpha)|^2$ that determines the intensity of the main peak. Let $\varphi(z)$ and $w(z)$ be changed at a relatively slow rate in (2) and the α value be chosen sufficiently large. Integrating (2) by parts, we arrive at

$$R(\alpha) = \frac{\chi_h}{\chi_0 - a}\exp\{i\varphi(0) - w(0)\} \tag{3a}$$

$$P_R(\alpha) = \frac{|\chi_h|^2}{|\chi_0 - a|^2}\exp\{-2w(0)\}, \tag{3b}$$

where $\varphi(0)$ and $w(0)$ are the values of these functions on the crystal surface.

For large values of angles α the main contribution to $R(\alpha)$ comes from a layer with the thickness

$$\Delta z = 2\pi|\gamma_h|/Ka = \pi/4(\omega_0 L_{ex}/\alpha), \tag{4}$$

where

$$\omega_0 = \frac{2|\chi_h|}{\sin 2\theta_B}; \qquad L_{ex} = \frac{2(\gamma_0|\gamma_h|)^{1/2}}{K|\chi_h|}.$$

Since the diffraction peaks at $\omega_0\alpha^{-1} < 10^{-2}$ can readily be measured, we arrive at the direct method of characterization of surface layers with thickness $\Delta z \simeq 10$ nm [this value was obtained using $L_{ex} = 0{\cdot}64$ μm for Ge(111) reflection and Cu $K\alpha$ radiation].

Expressions (3) and (4) are valid only if parameters $\varphi(z)$ and $w(z)$ change slowly. This means that the transitional layer between an ideal crystal and the damaged crystal layer (the latter can form as a result of ion implantation, epitaxial growth *etc.*) is not too thin. In this connection, it is interesting to consider the following hypothetical case. Suppose that the factor $e^{-w(z)}$ varies along the crystal depth according to the law

$$e^{-w(z)} = de^{-xz} + b. \tag{5}$$

Here, for simplicity, we assumed that interatomic

distances within the layer are constant. Then the integral in (2) can readily be taken and the reflection coefficient can be written in the form

$$P_R(\alpha)=\frac{(d^2+2db)}{x^2+\psi^2}+\frac{b^2}{\psi^2}. \qquad (6)$$

Here the following notation is introduced:

$$\psi=\frac{K(a-\chi_0)}{2|\gamma_h|}\simeq\frac{Ka}{2|\gamma_h|}.$$

Experimental

The surface structure of a perfect Ge crystal has been studied by the method of three-crystal diffractometry (TCD). The experimental set up is shown in Fig. 1. The first crystal, K_{I}, a plane monochromator, forms a beam with small divergence which falls on crystal K_{II} under investigation fixed at a certain position α near θ_B. The angle distribution of X-rays reflected by the second crystal – TCD spectrum – is recorded during simultaneous rotation of a crystal analyser, K_{III}.

It is evident that angular intensity distribution obtained after the reflection by the second crystal is determined by the product of the reflection curves obtained for the first ($P_{R_{\text{I}}}$) and the second ($P_{R_{\text{II}}}$) crystals taking due account of their mutual angular position.

In the general case, the TCD spectrum consists of three maxima. One of them, the so-called main peak, characterizes the tail of the reflection curve for the crystal under investigation and is formed by the rays incident on the first crystal at angle θ_B and rays reflected by the crystal under investigation beyond the reflection maximum. The rays incident on the first crystal at angle $\theta_B-\alpha$ are reflected by the second crystal in the reflection maximum and form the second peak (the so-called pseudopeak). Analyzing the TCD spectrum one can readily see that for the symmetrical Bragg diffraction the TCD pseudopeak has the angular position $\Delta\theta=\alpha$, whereas the main peak is located at $\Delta\theta=2\alpha$ with respect to the angular position of the Bragg peak at $\Delta\theta=0$.

If both crystals have the same rocking curves in the given reflection, the intensities of the pseudo and main peaks are the same and decrease proportionally to ω_0^2/α^2 with the increase of the deviation angle α. The slightest change in the crystal reflectivity results in the redistribution of peak intensities in the spectrum.

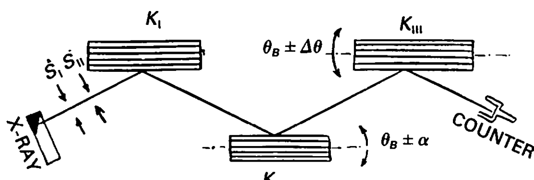

Fig. 1. Experimental arrangement of a triple-crystal diffractometer.

For the perfect crystals the TCD spectrum has only the two above-mentioned dynamical peaks (the main peak and the pseudopeak). The third diffuse maximum is observed only for imperfect crystals, its position and shape being fully determined by the defects in the crystal.

Thus, the TCD method provides a unique possibility to distinguish between the coherent and incoherent components of the total scattering. Changing the angular position of the crystal under consideration (second crystal), we can obtain a series of TCD spectra and observe the changes in the main peak intensity up to high angles.

Figs. 2 and 3 show the results obtained for two Ge crystals – a perfect crystal first polished with a diamond paste and then etched in such a way that a partially damaged layer is still preserved on the crystal surface. The presence of the damaged layer is proved by a weak diffuse maximum at $\Delta\theta=0$ (Fig. 2a). As is seen from Figs. 2 and 3, the angular dependence of intensities for the peaks obtained for both specimens are quite different. The TCD spectra shown in Figs. 2(a), (b) and obtained for deviation angles $\alpha=$ 90″ (Fig. 2a) and $\alpha=450''$ (Fig. 2b) show that at small

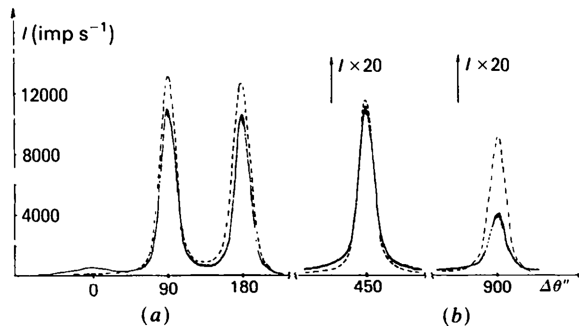

Fig. 2. TDC spectra from Ge(111) crystals, (n, $-n$, n) arrangement, symmetric Bragg diffraction for (a) $\alpha=90''$, (b) $\alpha=450''$. Dashed line for ideal crystal, solid line for crystal first polished with diamond paste and then partially etched.

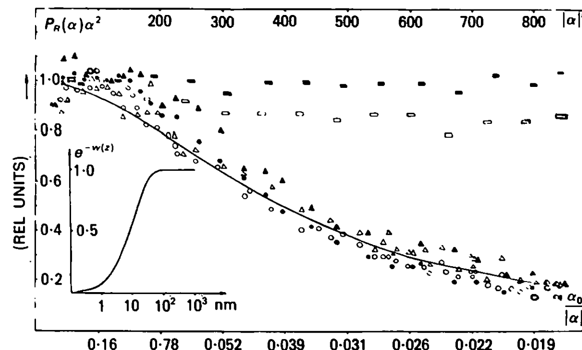

Fig. 3. Experimental results of function $P_R(\alpha)\alpha^2$ for the ideal crystal (□, ■) and specimen (○, ●, △, ▲); ■, ▲, ● $\alpha<0$; □, △, ○ $\alpha>0$. Theoretical calculation (solid line) according to equation (6) with $b=1$, $d=-1$ (inset shows a model of a damaged layer).

deviation angles the intensities of main peaks for a perfect crystal ($\Delta\theta = 180''$) and a crystal with the damaged layer are almost the same, whereas at $\alpha = 450''$ the intensity of the main peak ($\Delta\theta = 900''$) for the specimen with the damaged layer is much lower than that of the main peak for the perfect crystal. Fig. 3 shows that in the case of a perfect crystal the intensity of the main peak decreases proportionally to ω_0^2/α^2, whereas for the specimen with the damaged layer the decrease of the function $P_R(\alpha)\,\alpha^2$ is observed for deviation angles exceeding 200''. Experimental data and theoretical calculations (solid line, Fig. 3) from equation (6) with $d = -1$ and $b = 1$ are in good accordance, which gives 9 ± 3 nm as the thickness of the damaged layer.

Conclusion

The use of three-crystal diffractometry permitted us to observe directly for the first time a damaged layer with a thickness of 9 nm. It should be noted that the real potentialities of the method are even greater – the absence of a $P_R(\alpha)\alpha^2$-function decrease for a perfect crystal within the whole range of measurements (~900'') indicates that no damaged layer is formed within a depth of 3 nm. Of course, the method would give even better results if we used more powerful radiation sources or accumulate intensity.

It is worth noting that for simplicity we discussed the thickness of a distorted layer. Analysing (2), we can readily see that, in fact, we measure not the thickness of the damaged layer but rather that of a transitional layer between damaged and perfect parts of the crystal. It is evident that the addition of an amorphous layer to the crystal (if this does not result in additional stresses) does not affect the diffraction spectra. We believe that the method discussed here will be very powerful for the effective study of transitional layers between a perfect-crystal matrix and the growing film.

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The $\Delta\omega$, $\Delta 2\theta$ Two-Dimensional Nature of Bragg X-ray Reflexions from a Small Single Crystal: Its Influence on the Assessment of Structure Factors

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Abstract

By its two-dimensional nature, the $\Delta\omega$, $\Delta 2\theta$ intensity distribution of a Bragg X-ray reflexion has greater angular resolution and greater information content than the corresponding one-dimensional $\Delta\omega$ reflexion profile. It allows for the measurement of integrated intensity, exactly and equally truncated, over the full range of θ. Also, it is potentially correctable point by point for extinction and simultaneous diffraction. Consequently, it has inherent capabilities for the estimation of structure-factor values with improved accuracy. To realize this potential, it is necessary to identify and appreciate the various factors which, convoluted together, determine the 2D distribution. Among these factors, important ones are the crystal mosaic/fragment distribution, μ, the X-ray source emission distribution and the wavelength distribution. By first treating the situation for a hypothetical point source, the relation of the reflectivity (or 'level of interaction') with the μ distribution is highlighted. Extension to a real source indicates the probable need for deconvolution in practical cases to extract meaningful estimates of the μ distribution and hence the reflectivity distribution, the most significant measured quantity for accurate structure-factor evaluation. The 2D distribution is discussed in relation to single (H) scattering, multiple ($H.\bar{H}$) scattering (extinction) and simultaneous ($H.K$) scattering.

Introduction

Since the advent of the four-circle X-ray diffractometer in the late 1950's and its use for the determination of structure-factor values, much effort has been devoted to (a) clarifying the roles of the many components in the measured intensity distribution of

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