X-RAY DIFFUSIVE SCATTERING INTENSITY BY CRYSTALS WITH HETEROGENEOUS DISTRIBUTION OF COMPLEXES

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In the framework of the kinematic theory of X-ray scattering by crystals, the model that describes the asymmetry of peaks of the X-Ray reflection from strongly distorted areas of monosilicon is proposed. The case where distortions are due to a heterogeneous distribution of the high-concentration complexes of atoms of the phosphorus impurity in the surface layer is considered. The asymmetric curves that are well coordinated with experimental curves on the difractograms of $\theta - 2\theta$ scanning are theoretically obtained. The developed theory correctly describes the sign of the asymmetry of peaks and the qualitative dependence of its value on the reflection index. The divergence of theoretical and experimental values is ~20%.

1. Introduction

To use the optimal procedures and regimes of the crystal material surfaces treatment, it is necessary to have the express method of nondestructive control over a structure-impurity state of these surfaces.

The X-ray structural analysis allowing to automatize the survey process and the data processing with the help of a computer and not requiring the destruction of the manufactured products is one of the most technically simple and quite rapid methods. The attenuation, widening, and displacemen parameters measured by this method and the diffusive background analysis contain also the indirect, but detailed enough information about the type of crystal lattice defects, their density, and spatial distribution. However, the interpretation of the obtained data, i.e. the clarification of the connection between the measured peculiarities in the intensity distribution of scattered X-rays and the parameters of a material defective structure, is often a complex enough problem.

Last three decades, the statistical theory of the scattering of X-rays by crystals with different defects of the crystal lattice was developed in the kinematic approximation in the Ukraine and abroad [1—5].

In the present work in the kinematic approximation of statistical theory, we describe the diffusive scattering of X-rays by the surface of an elastoisotopic crystal with cubic symmetry containing point-like defects in the case where the distribution of defects has an exponential form with a concentration decreasing into the depth of a crystal. The high concentrations of defects which correspond to the great Debye—Waller factors for statistical distortions, ($2M \gg 1$), were studied. At the same time, the field distortion overlap of separate defects is essential. The radius of the areas, where the coherent scattering takes place, is decreased and becomes much smaller than the characteristic depth of the distribution of defects. The distribution of the diffusive scattering intensity on Debye photographs $I(q_{\mathrm{D}})$ was obtained. The curves $I(q_{\mathrm{D}})$ for different values of the parameters characterizing the distributions of defects over the depth were calculated, and the comparison with the experimental data on the scattering of X-rays by silicon monocrystals, in which a heterogeneous concentration of phosphorus atoms was created, has been carried out [6].

2. Calculation of the Diffusive Scattering Intensity of X-rays by a Crystal with a Heterogeneous Surface Distribution of Point Defects

2.1. General formulas for the intensity

The presence of crystal lattice defects changes essentially the intensity distribution of scattered X-rays. Every s-th atom in a crystal with defects may be characterized by a displacement

$$\delta\mathbf{R_s} = \sum_t c_t \mathbf{u}_{st}(\mathbf{R_t}), \qquad (1)$$

where $\mathbf{u_{st}}$ is the displacement of the s-th atom created by the defects which are at a point t, and $\mathbf{R_t}$ is the radius vector of the point t. The distribution of defects is characterized by the numbers of occupation c_t which are equal to one, if the defect is in the position t, and $c_t = 0$ if the defect is absent. The detailed location of the defects around the s-th atom is taken into account in the

summation in (1) through all possible positions of t. In the kinematic approximation, the intensity of scattered X-ray radiation $I(\mathbf{Q})$ in electron units is determined by the formula [1]

$$I(\mathbf{Q}) = \sum_{s,s'} f_s f_{s'}^* \exp\left[i\left(\mathbf{q}\mathbf{R_{ss'}}\right)\right] \exp\left[i\left(\mathbf{Q}\delta\mathbf{R_{ss'}}\right)\right], \qquad (2)$$

where $\mathbf{q} = \mathbf{Q} - \mathbf{G_{hkl}}$, $\mathbf{Q} = \mathbf{k_2} - \mathbf{k_1}$ is the diffraction vector which is equal to the difference between the wave vectors of the scattered wave and the incident one ($|\mathbf{k_1}| - |\mathbf{k_2}| = 2\pi/\lambda$, where λ is the X-ray radiation wavelength), $\mathbf{G_{hkl}}$ is the reciprocal lattice vector nearest to the end of the vector $\mathbf{Q}$, $\mathbf{R_{ss'}} = \mathbf{R_s} - \mathbf{R_{s'}}$ is the the difference of two vectors at the points s and s', and $\delta\mathbf{R_{ss'}} = \delta\mathbf{R_s} - \delta\mathbf{R_{s'}}$.

In the irradiated crystal, the observed intensity $I(\mathbf{Q})$ is self-averaging and differs slightly from the intensity $\langle I(Q)\rangle$ averaged through all possible values of c_t. Then, in the case of the chaotic distribution of defects and their small concentration, we have

$$I_1(\mathbf{Q}) = \sum_{s,s'} f_s f_{s'}^* e^{i\mathbf{Q}-\mathbf{G^0}\rho} \exp[-T(\rho,\mathbf{Q})], \qquad (3)$$

where

$$\rho = \mathbf{R_s^0} - \mathbf{R_s} \qquad (4)$$

is the difference of the radius vectors of the s- and s'-th points of the undistorted crystal lattice, and $\mathbf{G_0}$ is the reciprocal lattice vector of the perfect crystal. The complex quantity

$$T(\rho,\mathbf{Q}) = T'(\rho,\mathbf{Q}) + iT''(\rho,\mathbf{Q}), \qquad (5)$$

$$T'(\rho,\mathbf{Q}) = \int_t n[1 - \cos Q u_{ss't}(R_t)] d\mathbf{R_t}, \qquad (6)$$

$$T''(\rho,\mathbf{Q}) = \int n \sin(\mathbf{Q}\mathbf{u_{ss't}}) d\mathbf{R_t}, \qquad (7)$$

where $\mathbf{u_{ss't}}(\mathbf{R_t}) = \mathbf{u_{st}}(\mathbf{R_t}) - \mathbf{u_{s't}}(\mathbf{R_t})$, and the density of defects n in the general case depends on $\mathbf{R_t}$.

Under the condition that $2M >> 1$, the regular reflection intensity is exponentially small. Because the general integral intensity at the elastic scattering must be constant, then the total scattered radiation intensity is practically contained in the intensity distribution of the diffusive scattering $I_1(\mathbf{Q})$ described by formula (3). For the determination of $I_1(\mathbf{Q})$ by (3)—(7), it is necessary to know $\mathbf{u_{st}}(\mathbf{R_t})$.

2.2. Diffusive scattering intensity in the case of a surface heterogeneous distribution of complexes

The limited defect field in the surface layer consists of two components: the displacement component and the Coulomb one, both are connected with the influence of the boundaries. The analysis of these displacements [7] leads to the conclusion that, on the consideration of the diffusive scattering, the general regularities may be neglected.

The Coulomb fields of displacements have the form $|\mathbf{u}(\mathbf{r})| \sim cr^{-2}$. The value of the constant C has the order of the crystal volume change on the introduction of one defect. As $\mathrm{div}\mathbf{u}(\mathbf{r}) = 0$, the crystal volume change is determined only by the defect volume ΔV. The limited defects lead to the occurrence of the diffusive scattering and the attenuation of the peaks of regular reflections by the factor e^{-2M} [1]. The character of the originating intensity distribution depends essentially on the quantitative characteristics of the defects — their power C and the mean concentration $\langle C\rangle = n$ determining the mean distortion of the crystal. With increase in the concentration of defects and their power (for example, by this reason, a definite number of particles forms the cluster), the condition of smallness $2M \ll 1$ changes into the opposite one:

$$2M \gg 1, \qquad (8)$$

which leads to the qualitative change in the intensity distribution.

Since the characteristic dimensions of strongly distorted areas $(CQ)^{1/2}$ are small in comparison with the distance between the defects $r_\mathrm{D} \sim n^{-1/3}$, $2M \sim 10n(QC)^{3/2} \ll 1$ in accordance with [1]. In this case, the integral intensity of the diffusive scattering peak $I_{1i} = I_i(I - e^{-2M}) \approx 2MI_i$ is considerably less than the integral intensity of the correct reflection peak $I_{0i} = I_i e^{-2M}$. However, at large enough values of the constants C and n which characterize the power and concentration of defects, when

$$(QC)^{1/2} \gg r_\mathrm{D} \approx n^{-1/3}, \qquad (9)$$

the fields of local distortions around the separated defects are overlapped, and the crystal is very distorted not only locally, near the defects, but also generally. The value I_{0i} becomes exponentially small, and correct reflections are suppressed.

The intensity distribution $I_1(\mathbf{Q})$ is described by formula (3) and is essentially changed in comparison with the case where $2M \ll 1$. Instead of the narrow peaks of correct reflections from “a mean crystal” and the wide diffusive background which are characteristic of this case, the distribution obtains the form of a quasi-line of the bell-shaped form with the maximum displaced relative to the reciprocal lattice point.

Let's consider the defects of complex type [8], when the energy profitable defects form the clusters from impurity atoms N_0 arranged at N' points of the matrix lattice. We consider that the dimensions of complexes R_0 are smaller than the distance r_D between them,

$$R_0 \ll r_\mathrm{D}. \tag{10}$$

As the volume part of the complexes nR_0 is small in comparison with the crystal volume, it is possible to neglect the changes of the structure amplitudes and distortions at $R_{st} \sim R_0$ and to take into consideration only the defects in the main part of the volume, where $\mathbf{u}(\mathbf{r})$ is described by the Coulomb law.

In the case where the value $T(\rho, \mathbf{Q})$, which is changed with the depth of defects, depends on the s-th point location at the depth z_s, formulas (6) and (7) yield

$$T'(z_s, \rho, \mathbf{Q}) =$$

$$= \int n(z_t)\{1 - \cos(\mathbf{Q}[\mathbf{u_{st}}(\mathbf{R_{st}}) - \mathbf{u_{s't}}(\mathbf{R_{s't}})])\} d\mathbf{R_t}, \tag{11}$$

$$T''(z_s, \rho, \mathbf{Q}) =$$

$$= -\int n(z_t)\{\sin(\mathbf{Q}[\mathbf{u_{st}}(\mathbf{R_{st}}) - \mathbf{u_{s't}}(\mathbf{R_{s't}})])\} d\mathbf{R_t}. \tag{12}$$

Let's consider the most simple exponential law of the density of defects decreasing with the depth of their occurrence z_t of the form $n_t(z_t) = ne^{-\lambda z_t}$. Taking the absorption into consideration, the X-ray radiation intensity is changed with the depth according to the formula

$$I(z_s) = I_0 e^{-\mu z_s}, \tag{13}$$

where

$$\mu = \overline{\mu}\left[\frac{1}{(\mathbf{k}_{10}\mathbf{e_z})} - \frac{1}{(\mathbf{k}_{20}\mathbf{e_z})}\right]. \tag{14}$$

Here, $\overline{\mu}$ is the linear coefficient of the absorption of the X-ray radiation by a given substance, $\mathbf{k}_{10}$ and $\mathbf{k}_{20}$ are the unit vectors in the directions of the incident beam and the scattered one, and $\mathbf{e_z}$ is the unit vector of the internal normal to the surface of the crystal.

In this case, the formula for the diffusive scattering intensity takes the form

$$I_1(\mathbf{Q}) = \frac{|f|^2}{v^2} S \int_0^{R_z} e^{-\mu z} \int_\rho e^{i(\mathbf{Q}-\mathbf{G^0})\rho} e^{-T(z_s,\rho,\mathbf{Q})} d\rho dz, \tag{15}$$

where R_z is the dimension of the crystal in the direction z, the integration over $d\rho$ is performed upon all values of ρ in the crystal, and s is the irradiated part of the sample surface area.

In the displacement $\mathbf{u_{st}}$, it is possible to take into account only the Coulomb component $\mathbf{u^0_{st}}$, and the influence of the boundaries can be neglected. This and the condition $r_\mathrm{D} << \lambda^{-1}$, where λ^{-1} is the characteristic thickness of the defective layer, imply that the area $R_{st} \sim r_\mathrm{D}$ brings the main contribution to T'. As the displacement u^Γ_{st} quickly decreases with the removal from the boundary $u^\Gamma_{st} \sim (z + z_t)^{-2}$, the influence of u^Γ_{st} in u_{st} may be neglected everywhere except for the thin layer $z^* < r_\mathrm{D}$. By limiting ourselves by the second term in the decomposition in the degrees of ρ/R_{st}, the function $Qu_{ss't}$ can be represented, by analogy to what is done in [1], as

$$Qu_{ss't} = 3CQ\rho R_{st}^{-3}\psi + CQ\rho^{\mathbf{3}} R_{st}^{-5}\psi', \tag{16}$$

where

$$\psi = (1/3)\cos\gamma - \cos\theta\cos\chi, \tag{17}$$

θ, χ, and γ are, respectively, the angles between $\mathbf{R_{st}}$ and ρ, $\mathbf{Q}$ and $\mathbf{R_{st}}$, $\mathbf{Q}$ and ρ.

Neglecting the second term in (16) leads to the small corrections of $\sim M^{-4/3}$ (see [1]). So it is possible to take only the first term.

2.3. The analysis of the intensity distribution on a debye photograph

The performed simple but bulky calculations of the real and imaginary parts T' and T'' in [7] according to formulas (11) and (12) in the case of the exponential dependence $n(z_s) = n_0 \exp\{-\lambda z_s\}$ for $z^* \gg r_e \ll \lambda^{-1}$ give

$$T(z_s, \rho, Q) = (\alpha + i\beta)\rho \exp[-\alpha z_s], \tag{18}$$

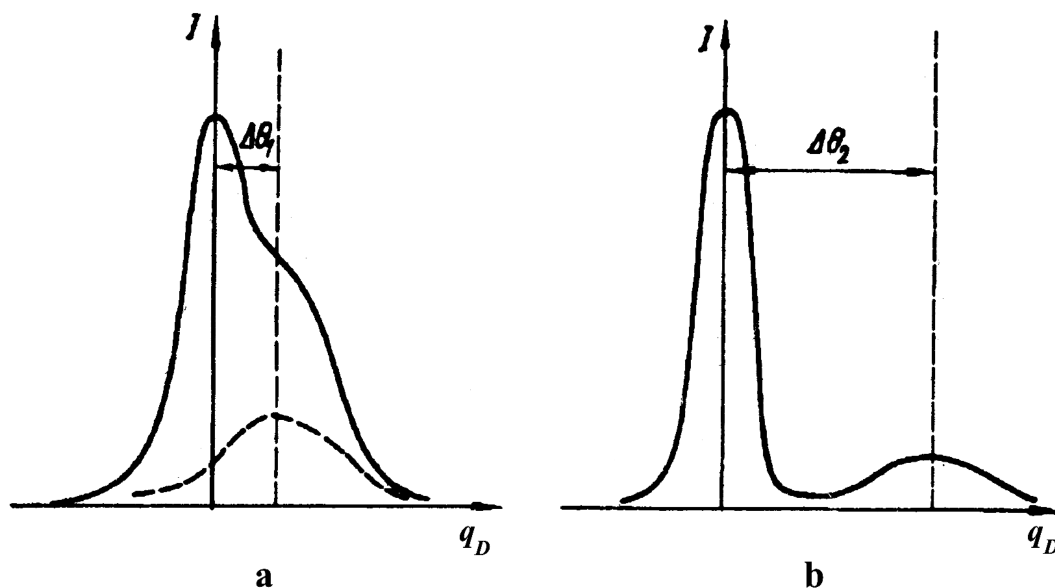

Fig. 1. X-ray patterns obtained on silicon monocrystals of different orientations after the diffusion of phosphor: *a* — Si (111), ⟨111⟩; *b* — Si (100), ⟨400⟩

where

$$\alpha = [(1+v)/(1-v)](\pi/24)n_0 Q\frac{dv}{dc}, \tag{19}$$

$$\beta = (n_0/2)(-0,669 + 4/3\pi + 4\pi\cos^2\theta)Q. \tag{20}$$

Using (15) and (18) in the case of a Debye photograph, we obtain

$$I_1(q_{\rm D}) = I_0\frac{|f|^2}{v}S\int\limits_{z^*}^{D} e^{-\mu z_s}\frac{\alpha e^{-\lambda z_s}}{(q_{\rm D}-\beta e^{-\lambda z_s})^2+\alpha^2 e^{-2\lambda z_s}}dz. \tag{21}$$

The integration in (15) over ρ reduces to the determination of the Fourier transform e^{-T}, where T has the form (18). As a result, the Lorentz-type dependence on $q_{\rm D} = |\mathbf{Q} - \mathbf{G}_0|$ is obtained for a Debye photograph. The dependence $I_1(q_{\rm D})$ has been obtained in the integral form. The component α entering (18) describes the half-width of the diffusive scattering peak, whereas the component containing β describes its displacement and asymmetry. These components are decreased with increase in the depth because of $\exp(-\lambda z_s)$ in (18). The intensity distribution parameters $I(q_{\rm D})$are obtained after the averaging over the densities of defects into layers at various depths.

3. Comparison of the Theoretical Calculations with X-ray Data Obtained on a Silicon Monocrystal Distorted by a Heterogeneous Concentration of Phosphor in the Surface Area

Work [4] presents the experiment, in which the structural changes in a monocrystal of Si caused by the diffusion of P in the surface area were investigated with the help of X-rays . Two samples of silicon with cuts (111) and (100) were investigated. The diffusive scattering intensity was measured for the reflection ⟨111⟩ in the first case and for the reflection ⟨400⟩ in the second case. The result is presented in Fig. 1,*a* and Fig. 1,*b*, where the peak asymmetry different for different reflections is clearly seen.

The reason for the asymmetry of peaks can be connected with a displacement of the reflection from the distorted surface area relatively to the reflections from undistorted deep layers of the crystal. The result of the scattering is the sum of two reflections. So the asymmetry is clearly seen in the total distribution of the X-ray scattering intensity. It can be characterized by the reflection peak displacement from different areas. This value is $\Delta\theta_1 = 3.74$ for the reflection in Fig. 1,*a*. For the reflection in Fig. 1,*b*, this value is $\Delta\theta_2 = 6.63$ (in the units of $\pi \times 10^4$ cm^{-1}).

In Fig. 2, we present the graphs which are plotted with the help of a computer according to formula (21)

describing the reflection from the distorted surface layers at different values of β. The values of β depend on the concentration of defects and the reflection index. With the growth of β, the maximum is shifted, by increasing the asymmetry of the integrated peak. To compare the theoretical distribution according to formula (21) with the experiment described in [6], it is necessary to take into account that, in the given case, the depth of the X-ray absorption is considerably larger than the distribution depth of the impurity. For comparison, the absorption depth CuK_α X-ray radiation in silicon $\mu^{-1} = 70\ \mu$m (see [9]), and the thickness of the diffusive layer of phosphor in silicon $\lambda^{-1} = 2 \div 3\ \mu$m. Consequently, $\mu \ll \lambda$, and it is possible to integrate in (21) to $z = \gamma\lambda^{-1}$, where $\gamma \sim 1$, because the conditions, under which the conclusion of this formula is true, are realized only in this layer. The obtained peak of the distribution corresponds to the reflection from surface layers, and the displacement of its maximum is equal to the asymmetry in Fig. 1,*a* and Fig. 1,*b*.

In the case where $\mu \ll \lambda$ in formula (21), the multiplier $e^{-\mu z}$ can be neglected. The relative error of the result at the integration to $z = \gamma\lambda^{-1}$ will be

$$\Delta I_1/I_1 \approx \gamma\mu\lambda^{-1} < 1. \tag{22}$$

In this case, it is easy to calculate integral (21) and obtain the expression $I_1(q_\mathrm{D})$ through elementary functions. At the same time, it was shown that some arbitrariness in the choice of the value $\gamma \sim 1$ didn't essentially influence the result. According to the condition $dI_1(q_\mathrm{D})/dq_\mathrm{D} = 0$ and knowing the value of the peak maximum displacement q_m, we can determine β from the relation

$$\frac{dI_1}{dq_\mathrm{D}} = -\frac{\beta}{\lambda\alpha q_\mathrm{D}^2}\left\{\mathrm{arctg}\left(\frac{\alpha^2+\beta^2-\beta q_\mathrm{D}}{q_\mathrm{D}\alpha}\right) - \right.$$

$$-\mathrm{arctg}\left(\frac{e^{-\lambda h}(\alpha^2+\beta^2)-\beta q_\mathrm{D}}{q_\mathrm{D}\alpha}\right) + \frac{\alpha^2+\beta^2}{q_\mathrm{D}\alpha}\times$$

$$\left.\times\left[\frac{1}{1+\left(\frac{\alpha^2+\beta^2-\beta q_\mathrm{D}}{q_\mathrm{D}\alpha}\right)^2} - \frac{e^{-\lambda h}}{1+\left(\frac{e^{-\lambda h}(\alpha^2+\beta^2)-\beta q_\mathrm{D}}{q_\mathrm{D}\alpha}\right)}\right]\right\}. \tag{23}$$

This gives the possibility to compare the theoretical and experimental results. The values of β corresponding to the displacements of the peaks in Fig. 1,*a* and 1,*b* are equal, respectively, to $\beta_1^e = 3.9$ and $\beta_2^e = 7.0$ (in the units of $\pi \times 10^4\mathrm{cm}^{-1}$). The distributions in Fig. 1,*a* and 1,*b* correspond to the different indices of reflection $\mathbf{Q}_1\langle 111\rangle$ and $\mathbf{Q}_2\langle 400\rangle$.

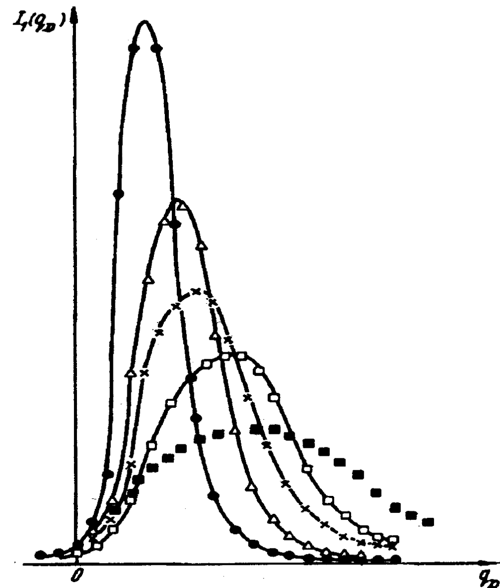

Fig. 2. Theoretical curves of the diffusive scattering intensity distribution for $\lambda = 0.1\ \mu\mathrm{m}^{-1}$, $\mu = 0.2\ \mu\mathrm{m}^{-1}$, $\alpha = 0.31\beta$. The curves (•, Δ, ×, □, ■) correspond to β =2.0; 3.0; 4.0; 5.0; 8.0

According to the theory, the following relation is valid for the given planes of the surface and the indices of reflections:

$$\beta_2^T = \beta_1^T\frac{|\mathbf{Q}_1|}{|\mathbf{Q}_2|}. \tag{24}$$

At $\beta_1^T = 3.9$, we get $\beta_2^T = 3.9(4/\sqrt{3}) = 9.0$ (in the units of $\pi \times 10^4\mathrm{cm}^{-1}$).

4. Conclusion

Thus, the theory, which is developed within the accepted model of defects of the type of complexes distributed heterogeneously in the surface layer, describes correctly the distribution asymmetry and the qualitative dependence of its value on the reflection index. The quantitative divergences β_2^T and β_2^e are $\sim$20%. Therefore, the result of the comparison of the experimental and theoretical data can be considered as satisfactory.

1. *Krivoglaz M.A.* X-rays and Neutron Diffraction in Nonideal Crystals. — Berlin: Springer, 1996.

2. *Krivoglaz M.A.* Diffusive Scattering of X-rays and Neutrons by Fluctuations. — Berlin: Springer, 1996.

3. *Likhachev V.A, Panin V.E.* Cooperative Strain Processes and Localization of Deformation. — Kyiv: Naukova Dumka, 1989 (in Russian).

4. *Ryaboshapka K.P., Bogdanov E.I., Bogdanov S.E.* // Metallofiz. Noveish. Tekhn.— 2005.— **27**, N 6. — P.705 — 720.

5. *Ryaboshapka K.P., Bogdanov E.I., Bogdanov S.E.* // Ukr. J. Phys. — 2006.— **51**, N 3. — P.265 — 268.

6. *Larikov L.N., Bogdanov E.I, Maximenko E.A.* // Cryst. Res. Technol. — 1990. — **25**, N1. — P.51 — 54.

7. *Berezovsky V.M., Bogdanov E.I., Ryaboshapka K.P.* Intensity Distribution of X-rays Scattered by Strongly Distorted Surface Layers of Crystals Containing Nonuniformly Distributed Complexes. — Dep. in VINITI, 1991 (in Russian).

8. *Krivoglaz M.A.* // Fiz. Tverd. Tela — 1970. — **12**, N8. — P.2445—2451.

9. *Pinsker Z.G.* X-ray Crystalloptics. — Moscow: Nauka, 1982 (in Russian).

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ІНТЕНСИВНІСТЬ ДИФУЗНОГО РОЗСІЯННЯ РЕНТГЕНІВСЬКИХ ПРОМЕНІВ ВІД КРИСТАЛІВ З НЕОДНОРІДНИМ РОЗПОДІЛОМ КОМПЛЕКСІЙ

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Р е з ю м е

В рамках кінематичної теорії розсіяння рентгенівських променів кристалами запропоновано модель, яка описує асиметрію піків відбиття рентгенівських променів від сильноспотворених областей монокристалічного кремнію. Розглянуто випадок, коли спотворення зумовлені неоднорідним розподілом у приповерхневому шарі високої концентрації комплексій від домішкових атомів фосфору. Теоретично отримано асиметричні криві, які добре узгоджуються з експериментальними кривими на дифрактограмах ($\theta - 2\theta$)-сканування. Показано, що розроблена теорія правильно описує знак асиметрії піків і якісну залежність її величини від індексу відбиття. Розбіжність в теоретичних і експериментальних значеннях становить приблизно 20 %.