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X-Ray Diffraction in a Perfect Crystal with Disturbed Surface Layer

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A method of analysis of curves for diffraction reflection from crystals with a disturbed surface layer is developed. It allows to determine, directly from experimental data, the integral characteristics of the disturbed layer, such as the thickness of the disturbed layer, L_{eff}, mean change in the interplanar spacings along the layer $\overline{\Delta a}$ and so on. This method is illustrated by an example of analysis of curves of reflection from diffuse layers of silicon for different orders of reflection.

Eine Analysenmethode für Beugungsreflexion von Kristallen mit einer gestörten Oberflächenschicht wird entwickelt. Sie erlaubt eine direkte Bestimmung der integralen Charakteristiken der gestörten Schicht, wie Dicke der gestörten Schicht L_{eff}, mittlere Änderung der Abstände zwischen den Ebenen auf der Schicht $\overline{\Delta a}$ usw., direkt aus den experimentellen Daten. Diese Methode wird mit einem Beispiel von Reflexionskurven von diffusen Siliziumschichten für verschiedene Reflexionsordnungen illustriert.

1. Introduction

In the last few years much attention has been paid to the problem of disturbances of the surface structure caused by diffusion, ionic implantation, and so on. The X-ray diffraction method possesses many advantages over the existing methods for studying the structure of a disturbed layer owing to its high sensitivity to small changes of the degree of perfection in a crystal. For the perfect crystal the diffraction reflection index has a sharp peak depending on the angle of X-ray incidence on the crystal. Here, the width of the Bragg reflecting maximum is of the order of several seconds; consequently, the relative changes in the interatomic distances in the near-surface layer by 10^{-5} to 10^{-6} should manifest themselves explicitly in the shape of the reflection curve.

The development of experimental technique makes it possible to measure the change in reflection intensities with an accuracy of a few tenths of per cent of the reflection intensity for a perfect crystal.

In addition, the use of the three-crystal technique [1, 2] provides a high angular resolution. However, despite the high sensitivity, the curves measured experimentally do not yield direct information on the structure of a disturbed layer. As a consequence, there arises the problem of developing theoretical methods that would allow one to reproduce, from experimental data, the characteristic features of the real structure of a surface layer.

The present work is devoted to the solution of this problem. For disturbed layers of thickness $L \ll L_0$ (L_0 is the extinction length) from our point of view a method analogous to the Patterson method in structure analysis is very effective, which allows to obtain directly from experimental curves (from their Fourier transform, to be more precise) the whole set of integral parameters of a disturbed layer, such as the effective thickness of the disturbed layer, L_{eff}, the mean change in the crystal

lattice parameters, $\overline{\Delta a}$, and so on. The detailed description of this method is given in Section 2. The results of experimental studies of diffuse layers illustrating the possibilities of the proposed method are presented in Section 3.

2. Theoretical Analysis

Let us consider a crystal of the shape of a plane-parallel plate with a disturbed surface layer of thickness L. The local distortions in the disturbed layer will be described by two parameters: the mean displacement of the atomic planes from their positions in the undisturbed layer, $\boldsymbol{u}(z)$, as well as the parameter $W(z)$ reflecting the statical random displacements of atoms from their positions in the plane. For example, for a completely amorphous layer, $\exp\left(-W(z)\right) = 0$. In the present work we make the assumption that the mean atomic displacement $\boldsymbol{u}(z)$ depends only on one coordinate z, i.e. on the distance of the atoms from the entrance facet of the crystal, where $z = 0$ (Fig. 1).

Let the crystal be oriented in such a way that there arises Bragg-type X-ray diffraction, i.e. that the diffracted wave emerges from the entrance facet of the crystal. Let us introduce the reflection amplitude $R(\theta)$ equal to the ratio of the amplitudes of diffracted and incident waves. The experimentally measured value, i.e. the reflection intensity $P_R(\theta)$, equals the square modulus of $R(\theta)$. Let us assume that $L \ll L_0$. In the linear approximation with respect to the small parameter L/L_0 the reflection amplitude is defined by the following expression:

$$R(\theta) = R_0(\theta) + R_1(\theta) - R_0^2(\theta)\, R_1^*(\theta)\,, \tag{2.1}$$

where $R_0(\theta)$ is the amplitude of the X-ray reflection by a thick perfect crystal (reflection from a substrate) and $R_1(\theta)$ the amplitude of the reflection by the disturbed layer. The third term in (2.1) reflects the process of diffraction scattering in the following succession: The incident wave passes through the disturbed layer and is reflected from the perfect crystal; then this reflected wave is scattered by the disturbed layer, and is reflected again by the perfect substrate. This process is schematically represented in Fig. 1. In the angular range far from the centre of the Darwin curve, the third term is small as compared with the second one, but within the range of total reflection the second and third terms have the same order of magnitude.

The amplitude of reflection by the perfect crystal is determined by the known expression (see, for example, [3])

$$R_0(\theta) = \frac{2\alpha_0}{\alpha + \operatorname{sign}(\alpha)\sqrt{\alpha^2 - \alpha_0^2}}\,, \tag{2.2}$$

where

$$\alpha = -\frac{2c\pi \sin 2\theta_B}{\lambda\,|\gamma_h|}\,(\theta - \theta_0)\,; \tag{2.3}$$

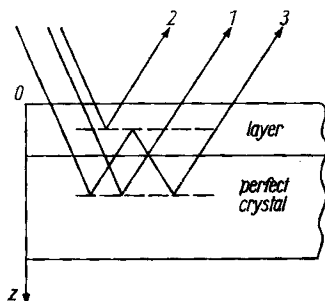

Fig. 1. Schematic representation of diffraction in the perfect layer–crystal structure

$$\theta_0 = \theta_B + \frac{|\chi_0|}{2c \sin 2\theta_B} \frac{\gamma_0 + |\gamma_h|}{\gamma_0},$$

$$\alpha_0 = \frac{1}{L_0} = \frac{\pi |\chi_h|}{\lambda \sqrt{\gamma_0 |\gamma_h|}}. \tag{2.4}$$

Here χ_0 and χ_h are the Fourier components of polarizability at scattering angles 0 and $2\theta_B$, θ_B is the Bragg angle, θ_0 the angle corresponding to the middle of the reflection maximum, λ the X-ray wavelength, γ_0 and γ_h are the cosines of the angles between the wave vectors of the incident and diffracted waves and the intrinsic normal to the entrance facet of the crystal, $c = 0.485 \times 10^{-5}$ rad/s is the conversion factor; all the angles are measured in seconds. We shall restrict the discussion to crystals with a centre of symmetry, where $\chi_{\bar{h}} = \chi_h$, in order not to make the analysis more complicated. We shall also disregard absorption and shall consider the incident radiation normally polarized. In the case $|\alpha| \gg \alpha_0$ from (2.2) we have a simple formula:

$$R_0(\alpha) = -\frac{\alpha}{\alpha_0}. \tag{2.5}$$

For the amplitude of the reflection by the disturbed layer the following expression can be obtained:

$$R_1(\alpha) = -\frac{i}{L_0} \int_0^L dz \exp\{-W(z) + i\alpha(L-z) - iu(z)\}, \tag{2.6}$$

where $u(z) = \boldsymbol{h}\boldsymbol{u}(z)$ ($\boldsymbol{h}$ is the reciprocal lattice vector). Later on, we shall take interest in such physical situations in which the presence of the disturbed layer is responsible for the appearance of a marked intensity in the angular range $|\alpha| \gg \alpha_0$. In this case, the third term in formula (2.1) can be neglected, and formula (2.5) can be used for $R_0(\alpha)$. As a result, we have

$$P_R(\alpha) = |R(\alpha)|^2 = |R_1(\alpha)|^2 + 2 \operatorname{Re}\left(R_1(\alpha) R_0^*(\alpha)\right) + |R_0(\alpha)|^2 =$$

$$= \frac{1}{L_0^2} \int_0^L dz \int_0^L dz' \exp\{-W(z) - W(z') - i\alpha(z-z') - iu(z) + iu(z')] -$$

$$- \frac{2\alpha_0}{\alpha L_0} \operatorname{Im} \int_0^L dz \exp\{-W(z) + i\alpha(L-z) - iu(z)\} + \left(\frac{\alpha_0}{\alpha}\right)^2. \tag{2.7}$$

The reflection amplitude $R_1(\alpha)$ of the disturbed layer contains information on the distortion character. In fact, the knowledge of $R_1(\alpha)$ would allow to obtain by means of a simple Fourier transformation the explicit values of both parameters: $u(z)$ and $W(z)$. However, the values measured experimentally contain the square modulus of the scattering amplitude; in other words, in this case we are in face with a problem of reconstructing the structure in the classical X-ray analysis [4]. The above-mentioned analogy points to one of the possible ways of solving the present problem, namely, to the Patterson function method [5].

Let us consider the Fourier transform of the function $P_R(\alpha)$,

$$I(x) = \frac{1}{2\pi\alpha_0^2} \int_{-\infty}^{\infty} d\alpha \, e^{-i\alpha x} P_R(\alpha) = I_1(x) + I_2(x) + I_3(x). \tag{2.8}$$

Here we have separated out three terms in accordance with the structure of formula (2.7). The first term $I_1(x)$ can be easily calculated. Actually, the integral over α is equal to $2\pi\delta(z + x - z')$. Calculating the integral over z', we obtain

$$I_1(x) = \int_0^{L-x} dz \exp\left[- W(z + x) - W(z) + iu(z + x) - iu(z)\right] . \tag{2.9}$$

Here we made use of the relationship $\alpha_0 L_0 = 1$ in accordance with (2.4). The calculation of $I_2(x)$ is carried out using the tabulated integrals

$$\int_{-\infty}^{\infty} d\alpha \frac{\cos b\alpha}{\alpha} = 0 , \qquad \int_{-\infty}^{\infty} d\alpha \frac{\sin b\alpha}{\alpha} = \pi \operatorname{sign}(b) . \tag{2.10}$$

As a result we obtain

$$I_2(x) = - \int_0^L dz\, e^{-W(z)} \cos u(z) + \int_{L-x}^{L} dz\, e^{-W(z)-iu(z)} . \tag{2.11}$$

One can easily see that the second term in (2.11) is simply an extension of the integral in (2.9) to the integration range $L - x < z < L$. Actually, in this region the argument in $u(z + x)$ and $W(z + x)$ becomes larger than L and, consequently, they are equal to zero according to the determination of the value L as the thickness of the disturbed layer.

As is seen from these expressions, the sum of two terms, $\tilde{I}(x) = I_1(x) + I_2(x)$, at a given value x gives information about the correlation of the displacements of the atomic planes in the disturbed layer at a distance x. In this case, the value of the function $\tilde{I}(x)$ and its derivatives at the point $x = 0$ is connected directly with the integral characteristics of the disturbed layer. It should be noted, however, that to solve the reverse problem we can construct, on the basis of experimental data, only the function $I(x)$, and not $\tilde{I}(x)$. In reality, we have the experimental values of the reflection intensity in a limited angular range. The upper limit is defined by the maximum resolution. On the other hand, when constructing the function $I^{\exp}(x)$ we have to exclude the range of small angles for which $|\alpha| < \alpha_1$, where α_1 is a value partitioning the central maximum of the curve. Neglecting the range of large angles leads to a specific problem which will be considered later. The error involved in ruling out small angles depends on the concrete circumstances and in each case requires a special analysis. It should also be reminded that the calculation of $I_3(x)$ makes it simple to take into account the lower limit of α_1 in its explicit form. Thus,

$$I_3(x) = \frac{\cos \alpha_1 x}{\pi\alpha_1} - \frac{x}{\pi} \int_{\alpha_1 x}^{\infty} \frac{\sin t}{t}\, dt = \frac{1}{\pi\alpha_1} - \frac{x}{2} + \frac{\alpha_1}{2\pi} x^2 + O(x^4) . \tag{2.12}$$

Let us denote the real part of the function $I(x)$ by I_c, and the imaginary part by I_s. As it follows from (2.8) to (2.12), the values of I_c and I_s as well as their derivatives at the point $x = 0$ are determined by the following relations:

$$I_c(0) - \frac{1}{\pi\alpha_1} = \int_0^L dz \left(e^{-2W(z)} - e^{-W(z)} \cos u(z)\right) = L_{\text{eff}} , \tag{2.13}$$

$$\left(\frac{\partial I_s(x)}{\partial x}\right)_{x=0} = \int_0^L dz\, e^{-W(z)} \frac{\partial u(z)}{\partial z} = \overline{\Delta a}\, L_{\text{eff}} , \tag{2.14}$$

$$\left(\frac{\partial^2 I_c(x)}{\partial x^2}\right)_{x=0} - \frac{\alpha_1}{\pi} = -\int_0^L dz\, e^{-W(z)} \left(\frac{\partial u(z)}{\partial z}\right)^2, \tag{2.15}$$

$$\left(\frac{\partial^3 I_s(x)}{\partial x^3}\right)_{x=0} = -\int_0^L dz\, e^{-W(z)} \left[\left(\frac{\partial u(z)}{\partial z}\right)^3 - \frac{\partial^3 u(z)}{\partial z^3}\right] - \left(\frac{\partial^2 u(z)}{\partial z^2}\right)_{z=L}. \tag{2.16}$$

Formulae (2.13) to (2.16) allow us to get some useful information on the structure of the disturbed layer. Equation (2.13) defines directly the effective thickness of the disturbed layer. It is of interest to note that the structure of the formula enables us to shift the upper limit automatically to infinity; since $u(z) = W(z) = 0$ at $z > L$, this region gives no contribution. One should bear in mind, however, that the slightly disturbed layers as well as the layers with a large degree of amorphization (when $e^{-W(z)}$ is close to zero) are represented with small weight.

Formula (2.14) gives information about the mean value of change in the crystal lattice parameter in the disturbed layer, since

$$-\frac{\partial u(z)}{\partial z} = |h_z| \overline{\frac{a(z) - a_0}{a_0}}, \tag{2.17}$$

where a_0 and $a(z)$ are the distances between the reflecting planes in substrate and layer in z-direction.

Similarly, formula (2.15) contains data on the mean square of the value (2.17), whereas the right-hand part of (2.16) is essentially equal to the cube of this value. Let us note that when calculating the derivatives, we disregarded the derivatives of $W(z)$ compared to those of $u(z)$, since they are, as a rule, two or three orders of magnitude smaller.

It is also easy to calculate odd derivatives of I_c and even ones of I_s, e.g., $(\partial I_c(x)/\partial x)_{x=0} = \frac{1}{2}$. These derivatives, however, are of less practical importance. One has to raise appreciably the accuracy of the experiment in order to determine them reliably.

3. Concrete Examples

In this section we shall consider some examples as illustrations to the method developed in the previous section.

We shall analyze the results of X-ray diffraction studies of diffused silicon layers on the basis of the above described method. Experimental curves are given in Fig. 2a and 3a.

The measurements were carried out on the three-crystal spectrometer [6, 7] in the $(3, -n, +n)$ position of symmetrical Bragg diffraction with CuK_α radiation. The (111) surfaces of silicon plates, about 200 µm thick, were used. After mechanical grinding and polishing the disturbed layer was removed by chemical etching. Diffusion was carried out in the prediffusion stage at 1200 °C for 120 h. The concentration of the doping element was $\approx 10^{20}$ atoms/cm³.

The diffraction reflection curves display, in addition to a smooth peak, additional maxima caused by diffraction of X-rays by the diffusion layer and by their interference with the rays diffracted on the substrate (Fig. 1). The Fourier transforms of the curves in Fig. 2a and 3a calculated within the limits $\alpha_1 \leqq |\alpha| \leqq \alpha_2$, where $\alpha_1 = 6.05\alpha_0$, $\alpha_2 = 60.5\alpha_0$ for the (111) reflection and $\alpha_1 = 32\alpha_0$, $\alpha_2 = 672\alpha_0$ for the (333) reflection, are shown in Fig. 2b and 3b, respectively. The data of Fig. 2b and 3b may be used for an estimation of the lattice parameter distortion of the layer, in accordance with formulae (2.13) to (2.15).

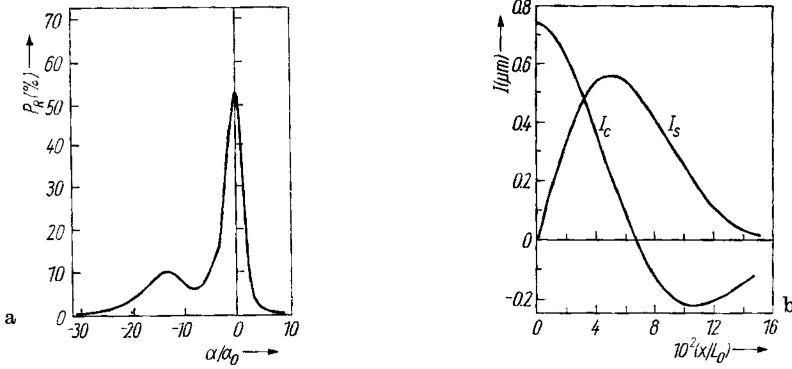

Fig. 2. a) Measured reflection intensity P_R as a function of α/α_0. b) Calculated Fourier transform, I_s and I_c, as a function of x/L_0 for the (111) reflection of a silicon layer

In this case, it is convenient to use the first Newton interpolation formulae (see, for example, [8]) for calculating the derivatives at the point $x = 0$.

The n-th order derivative of a function $f(x)$, defined by the table of values f_i at equidistant points x_i with a step h, can be determined from the formula

$$\left(\frac{\mathrm{d}^n f(x)}{\mathrm{d}x^n}\right)_{x=0} = \frac{1}{h^n} \sum_{m=n}^{\infty} C_{nm} \nabla^m f_0 , \tag{3.1}$$

where $\nabla^m f_0$ is the partitioned difference m calculated from the recurrence formulae

$$\nabla f_n = f_{n+1} - f_n , \qquad \nabla^{m+1} f_n = \nabla^m f_{n+1} - \nabla^m f_n . \tag{3.2}$$

The coefficients C_{nm} are given in Table 1. When using formula (3.1), we choose the step h not too small to enable at least the first few partitioned differences to differ from zero by a value exceeding the absolute error in the calulations. At the same time, the step h should not be too large in order to allow sufficiently rapid convergence of the series (3.1). The errors in calculations lead to the fact that the values $\nabla^m f_0$ at first decrease with increasing m, and then increase again. Therefore, the series (3.1) should be cut off at the minimum-value term analogous to what is done in the theory of asymptotic series. It is clear that the smaller the minimum term is, the more accurate is the value for a derivative. The value of the minimum term depends on the choice of the step h.

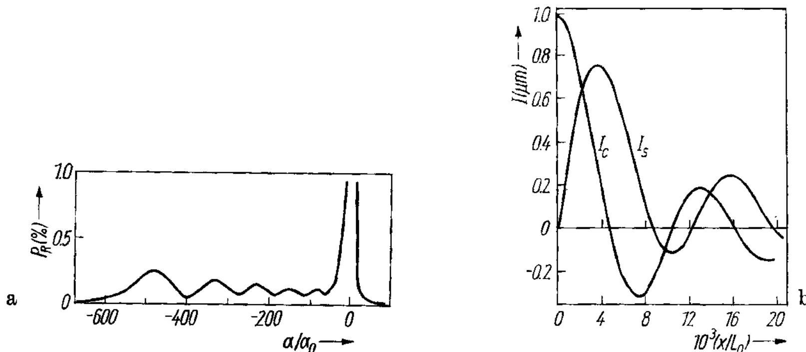

Fig. 3. a) Measured reflection intensity P_R as a function of α/α_0. b) Calculated Fourier transform, I_s and I_c, as a function of x/L_0 for the (333) reflection of a silicon layer

Table 1

m	C_{1m}	C_{2m}	C_{3m}	C_{4m}
1	1.0000	0.0000	0.0000	0.0000
2	−0.5000	1.0000	0.0000	0.0000
3	0.3333	−1.0000	1.0000	0.0000
4	−0.2500	0.9167	−1.5000	1.0000
5	0.2000	−0.8333	1.7500	−2.0000
6	−0.1667	0.7611	−1.8750	2.8333
7	0.1429	−0.7000	1.9333	−3.5000
8	−0.1250	0.6482	−1.9542	4.0292
9	0.1111	−0.6040	1.9531	−4.4500
10	−0.1000	0.5658	−1.9390	4.7862
11	0.0909	−0.5325	1.9170	−5.0562
12	−0.0833	0.5033	−1.8904	5.2739
13	0.0769	−0.4774	1.8611	−5.4498
14	−0.0714	0.4543	−1.8305	5.5923
15	0.0667	−0.4335	1.7993	−5.7076

The derivatives calculated from the data of Fig. 2b and 3b with the steps $h = 3 \times 10^{-3} L_0$ and $h = 4 \times 10^{-4} L_0$ are given in Table 2. In the calculations it was assumed that $L_0 = 1.54$ μm for the (111) reflection and $L_0 = 8.3$ μm for the (333) reflection.

It must be noted that in the case of diffusion layers, while passing from the (111) reflection to the (333) reflection, the values of the derivatives, with subtraction of 3^n arising on account of vector differences in the reciprocal lattices, do not differ very much.

However, the values of the thickness of the disturbed layer, L_{eff}, are found to change; on passing to the (333) reflection L_{eff} increases. This is accounted for by the fact that the (333) curves are more sensitive to weak distortions in a crystal than the (111) ones.

Table 2
Integral parameters characterizing the distortions in a diffused layer (Fourier analysis)

parameters		(111) reflection	(333) reflection
L_{eff}	(μm)	0.755	0.904
S_1*) $= -\dfrac{1}{\lvert h\rvert}\left(\dfrac{\partial I_s}{\partial x}\right)_0$	(10^{-4} μm)	−5.87	−6.5
C_2*) $= -\dfrac{1}{h^2}\left(\dfrac{\partial^2 I_c}{\partial x^2}\right)_0$	(10^{-7} μm)	5.87	5.44
S_3*) $= -\dfrac{1}{\lvert h\rvert^3}\left(\dfrac{\partial^3 I}{\partial x^3}\right)_0$	(10^{-10} μm)	−6.44	−5.0

*) It should be noted that

$$S_1 \approx \overline{\left(\frac{\Delta a}{a}\right)} L\,, \quad C_2 \approx \overline{\left(\frac{\Delta a}{a}\right)^2} L\,, \quad S_3 = \overline{\left(\frac{\Delta a}{a}\right)^3} L\,.$$

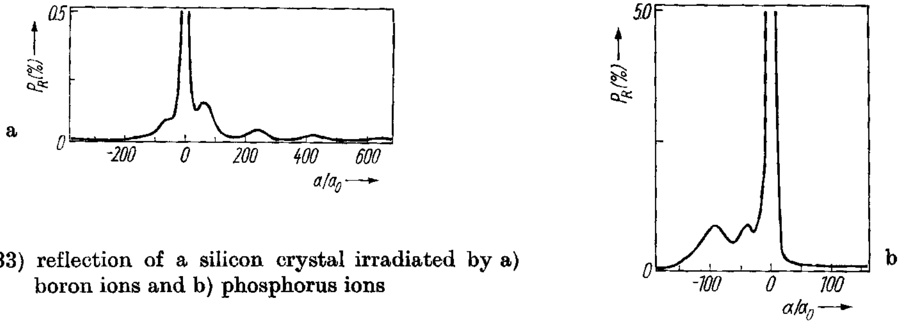

Fig. 4. (333) reflection of a silicon crystal irradiated by a) boron ions and b) phosphorus ions

We have also observed diffraction curves with oscillations analogous to the curves of Fig. 2a and 3a in the case of diffraction by a crystal in which the disturbed surface layer is formed by ion implantation of boron or phosphorus [9].

Fig. 4a shows the curve of the (333) reflection of a silicon crystal irradiated by boron ions with an ion energy of 125 keV and a dose of 6×10^{15} ions/cm^2.

Fig. 4b shows the curve of the (333) reflection of a Si crystal pre-irradiated by phosphorus ions with the energy of 40 keV and a dose of 6×10^{15} ions/cm^2. After implantation, the crystal was annealed at high temperature (1075 °C) in an oxygen atmosphere for 50 min to produce a diffusion layer of $\approx 4\,\mu$m thickness. The curves of Fig. 4a, b were measured using a three-crystal spectrometer under the same conditions as demonstrated by the curves in Fig. 2a and 3a.

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References

[1] M. Renninger, Acta cryst. 8, 597 (1955).
[2] R. Bubakova, Czech. J. Phys. B12, 776 (1962).
[3] Z. G. Pinsker, Dynamic Scattering of X-Rays in Perfect Crystals, Izd. Nauka, Moscow 1974 (in Russian).
[4] H. Lipson and W. Cochran, The Determination of Crystal Structures, G. Bell & Sons, London 1953.
[5] M. Buerger, Vector Space and Its Application in Crystal-Structure Investigation, Wiley/Chapman & Hall, New York/London 1953.
[6] M. V. Kovalchuk, E. K. Kovev, and Z. G. Pinsker, Kristallografiya 20, 192 (1975).
[7] E. K. Kovev and V. E. Baturin, Apparatura i metody rentgenovskogo analiza 16, 121 (1975).
[8] B. P. Demidovich and I. A. Maron, Computing Methods for Mathematics, Izd. Nauka, Moscow 1970 (in Russian).
[9] V. E. Barutin, M. V. Kovalchuk, E. K. Kovev, and V. E. Palapis, Kristallografiya 22, 144 (1977).

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