ISSN 1063-7745, Crystallography Reports, 2019, Vol. 64, No. 1, pp. 24–29. © Pleiades Publishing, Inc., 2019.
Russian Text © V.G. Kohn, P.A. Prosekov, A.Yu. Seregin, A.G. Kulikov, Yu.V. Pisarevsky, A.E. Blagov, M.V. Kovalchuk, 2019, published in Kristallografiya, 2019, Vol. 64, No. 1, pp. 29–34.

Experimental Study of Two-Beam X-Ray Diffractometry Using Synchrotron Radiation

V. G. Kohn[a,b], P. A. Prosekov[a,b,*], A. Yu. Seregin[a,b], A. G. Kulikov[a,b,], Yu. V. Pisarevsky[a,b], A. E. Blagov[a,b], and M. V. Kovalchuk[a,b]**

[a] *National Research Centre "Kurchatov Institute," Moscow, 123182 Russia*

[b] *Shubnikov Institute of Crystallography, Federal Scientific Research Centre "Crystallography and Photonics," Russian Academy of Sciences, Moscow, 119333 Russia*

**e-mail: p.prosekov@gmail.com*

***e-mail: ontonic@gmail.com*

Received September 27, 2017; revised September 27, 2017; accepted November 23, 2017

Abstract—A new scheme of two-beam X-ray diffractometry on the "X-Ray Crystallography and Physical Materials Science" (XCPM) beamline at the Kurchatov Synchrotron Radiation Source (KSRS) has been experimentally investigated. The scheme includes a standard double-crystal monochromator and a narrow slit installed in front of the sample. Measurements have been performed for the Si 111 and 311 reflections in the monochromator and the Si 111 and 220 reflections in the sample crystal. It is shown that this scheme allows one to obtain a near-proper diffraction reflection curve even in the case of symmetric diffraction if the Bragg angle for the monochromator exceeds the Bragg angle for the crystal sample by a factor of 2 or more. The experimental results coincide well with the theory.

DOI: 10.1134/S1063774519010139

INTRODUCTION

The "X-Ray Crystallography and Physical Materials Science" (XCPM) beamline at the Kurchatov Synchrotron Radiation Source (KSRS) [1] includes (in the standard configuration) a double-crystal monochromator, which does not change the incident beam direction, and a two-dimensional slit, which is installed after the monochromator and limits the beam in the horizontal and vertical planes. An X-ray beam is incident on a sample crystal, and the beam reflected from the sample crystal arrives at a detector (Fig. 1). In the general case, the Bragg angles for the beam reflected from the monochromator and sample crystals do not coincide, i.e., one deals with a dispersive scheme.

As follows from the theory of double-crystal X-ray diffractometry [2], to obtain a near-proper diffraction reflection curve (DRC) for a sample crystal in the dispersive scheme, the X-ray beam should to be monochromized, i.e., have a very narrow frequency spectrum. The spectrum of laboratory sources of characteristic radiation (X-ray tubes) is not such; therefore, the nondispersive scheme is always used in laboratory experiments to this end. If the dispersive scheme is used, for example, when studying the coplanar three-beam (or quasi-multibeam) diffraction in paratellurite

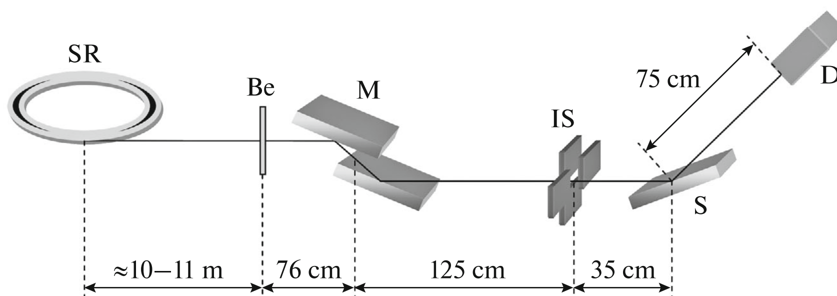

Fig. 1. Schematic of the experiment: (SR) synchrotron radiation source, (Be) beryllium window, (M) monochromator, (IS) two-dimensional slit, (S) crystal sample, and (D) detector.

Table 1. Main parameters of the XCPM KSRS beamline

Radiation source	Bending magnet
Monochromator	Double-crystal, two pairs of crystals. A pair of Si(111) or Si(311) can be installed
Energy range	5–40 keV
Minimal energy step	≈0.25 eV
Energy resolution $\Delta E/E$	10^{-4}–10^{-3}
Angular divergence	Vertical ~10^{-4} rad, horizontal ~10^{-3} rad
Goniometer	Five-circle, equipped exact position sensors, minimum step 0.7 arcsec; three linear axes for sample table motion; two-circle analyzer crystal unit
Intensity	10^8–10^9 per 1 mm^2 of beam cross section
Automated experiment control system	SPEC

(TeO_2) [3, 4], the sample crystal has a significantly broadened DRC.

Synchrotron radiation (SR) has a very wide spectrum, which can be considered as infinite from the point of view of X-ray diffraction. A slit is used to limit the spectrum. However, the results of the first SR experiment on the three-beam coplanar diffraction in TeO_2 [5] showed that the DRC FWHM (full width at half maximum) for a weak reflection is nevertheless much larger than the theoretical value.

It was experimentally found that, replacing the monochromator (in order to increase the Bragg angle for the beam reflected from its crystals) and using a narrower slit (~50 μm in size, which is several times smaller than that applied in [5]), one can significantly reduce the DRC FWHM for the sample crystal. This finding stimulated the development of an accurate theory for this version of double-crystal X-ray diffractometry [6].

As follows from the theory, when using a symmetric reflection from the monochromator, one can obtain a near-proper DRC for the sample crystal only provided that the Bragg angle for the beam reflected from the monochromator crystals exceeds greatly (by a factor of 2 or more) the Bragg angle for the reflection from the sample crystal and that the slit has optimal sizes.

In the opposite case, the experimental DRC FWHM may be many times larger than the proper (theoretical) DRC FWHM for the sample crystal. This circumstance is in no way related to the crystal quality but is determined by the characteristics of the optical scheme.

To verify the new theory [6], we performed a detailed experimental study of two-beam X-ray diffractometry using the optical scheme of the XCPM KSRS beamline. To exclude possible rise in the DRC FWHM due to the presence of defects in the sample structure, a silicon crystal of high structural quality was used as a sample. Silicon crystals are conventionally applied to fabricate a monochromator; however, reflections with low (111) Miller indices are generally chosen. In this study, we used symmetric reflections 111 and 311 for two monochromators and reflections 111 and 220 for the sample crystal.

XCPM EXPERIMENTAL BEAMLINE AT THE KSRS

The XCPM beamline is located at the output of the bending magnet (channel 4.6) of the large storage ring KSRS at the National Research Centre "Kurchatov Institute" (NRC KI). The XCPM is an experimental setup, designed to study the structure of materials by different methods: X-ray diffractometry, reflectometry, reciprocal space mapping, technique of X-ray standing waves, X-ray fluorescence analysis, and absorption spectroscopy. An important specific feature of the beamline is the possibility of studying samples under external impacts: electric field and ultrasonic load.

A large-scale upgrade of the XCPM equipment has been performed in the last years, which extended the experimental possibilities of the beamline (see parameters in Table 1). Currently, the XCPM includes several functional modules (Fig. 2): input-slit unit *1*, monochromator unit *2*, and goniometer unit *5*.

Input-slit unit *1* consists of a beam-position sensor in the input channel and water-cooled vacuum slits. Monochromator unit *2* includes the equipment of double-crystal monochromator M with a feedback system (FMB Oxford). Using a pair of Si(111) or Si(311) crystals, one can change the beam energy with a step of 0.25 eV in the range from 5 to 40 keV, retaining constant the spatial beam position. The feedback system, based on measuring the intensities at the input and output of the monochromator unit, makes it possible to correct the change in the inclination angle of

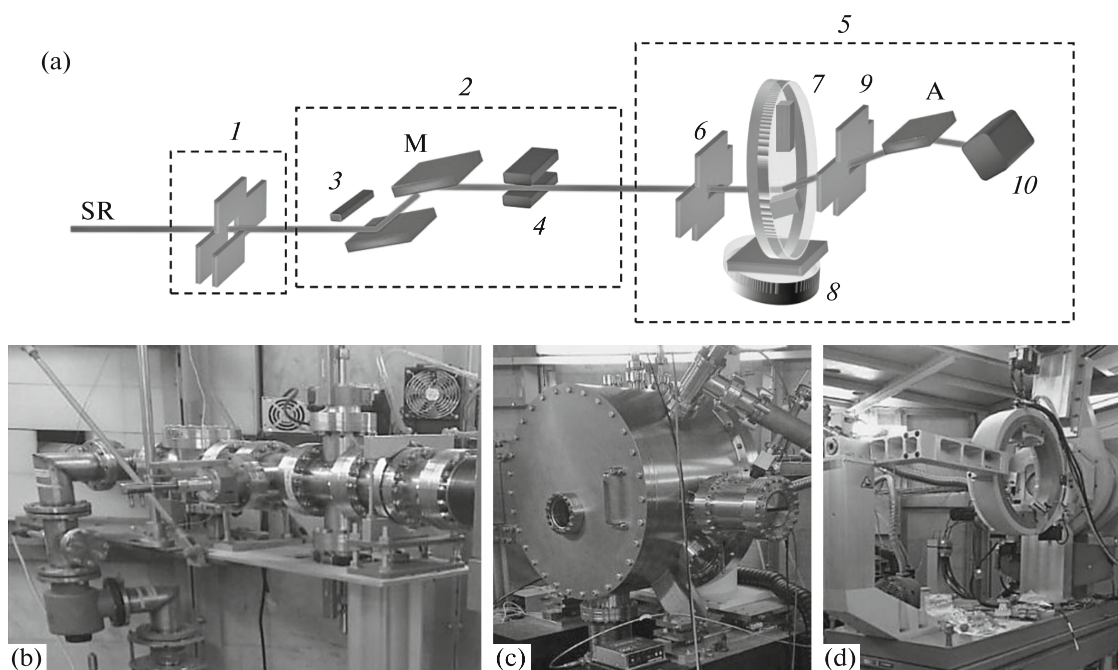

Fig. 2. (a) Optical scheme of the XCPM beamline at the KSRS and (b–d) its main units (input-slit unit (b), monochromator unit (c), and goniometer unit (d)): (SR) synchrotron radiation source, (*1*) 2D-input-slit unit, (*2*) monochromator unit, (*3*) beam sensor, (*4*) ionization chamber, (*5*) goniometer unit, (*6*) 2D slit before sample, (*7*) energy-dispersive detector, (*8*) goniometer, (*9*) 2D receiving slit, (*10*) NaI detector, (M) double-crystal monochromator Si(111) or Si(311), and (A) analyzer crystal.

the second monochromator crystal with respect to the first one.

Goniometer unit *5* includes collimating slits *6*, beam attenuators, multicircle goniometer *8*, and detection system. A multicircle Huber goniometer is installed on the XCPM, with a possibility of mounting an analyzer crystal A, which makes it possible to perform precise X-ray studies in a wide angular range. The detection system includes a NaI detector, an energy-dispersive detector Amptek X-123, and an avalanche photodiode FMB Oxford APD0005.

THEORY

A schematic of the experiment is shown in Fig. 1. Before arriving at the sample crystal, the SR beam is reflected by the monochromator crystals and passes through the slit. Under the conditions of two-beam diffraction, crystals are known to change the beam in the reciprocal space of angles and frequencies and form a rainbow (like a prism). In other words, an angular direction satisfying the Bragg condition is selected for each frequency in the emission spectrum. At the same time, the slit in no way affects the radiation frequency and only limits the wavefront in real space.

This circumstance causes certain difficulties when developing the theory of X-ray diffractometry in this experimental scheme, because one must explicitly take into account both the source transverse size and the slit size, as well as the source–slit distance. Two approximations concerning the slit size (specifically, the small- and large-size approximations) were considered in [6] to derive a relatively simple calculation formula.

The calculation formula is the Fourier integral of the product of four functions in both cases; the difference is only in the slit function, whereas the other three functions are the same in both approximations. In particular, in the approximation of small slit size, the calculation formula has the form

$$S(\theta_r) \propto \int dx G'_B([1-M]x) G'_M(Mx) \times G'_C(x) G'_S(x) \exp(-iq_r x), \quad (1)$$

where $q_r = K\theta_r$, θ_r is the rocking angle of the sample crystal relative to the incident beam direction, $K = \omega/c$ is the wave number (ω is the middle frequency in the emission spectrum and c is the speed of light), $M = \tan\theta_{B2}/\tan\theta_{B1}$ (θ_{B1} is the Bragg angle for the monochromator crystals and θ_{B2} is the Bragg angle for the sample crystal), and

$$G'_{B,M,C,S}(x) = \int \frac{dq}{2\pi} G_{B,M,C,S}(q) \exp(iqx). \quad (2)$$

Here, the three functions in the momentum space have a simple physical meaning:

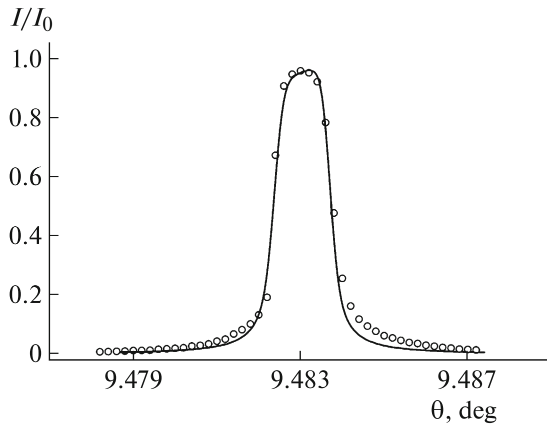

Fig. 3. Experimental (circles) and theoretical (solid line) DRCs for the first case (reflections 311 and 111 for the monochromator and sample, respectively). The vertical slit size is 100 μm. The experimental values are normalized so as to obtain the best coincidence with the calculation results.

$$G_M(q) = \left|P_M^2(q)\right|^2, \quad G_C(q) = \left|P_C(q)\right|^2, \quad G_S(q) = \left|F(q)\right|^2, \tag{3}$$

where $P_M(q)$ is the diffraction reflection amplitude (DRA) for one monochromator crystal, $P_C(q)$ is the DRA for the sample crystal, and $F(q) = (2/q)\sin(qx_0)$; x_0 is the slit half-width in the vertical diffraction plane. Note that the function $G_C(q)$, equal to the squared modulus of DRA, is the "proper" DRC of the sample crystal.

Concerning the source function, it can be calculated in the analytical form:

$$G'_B(x) = \exp\left(-\frac{1}{2}\sigma_s^2 x^2\right), \quad \sigma_s = \frac{K\sigma_x}{l_0}, \tag{4}$$

where $\sigma_x = 54$ μm is a parameter of the Gaussian that models the transverse size of the XCPM beamline source in real space and l_0 is the source–slit distance (13 m for the XCPM). Note that the function $G'_S(x)$ can also be calculated analytically:

$$G'_S(x) = 2x_0\left(1 - \frac{|x|}{2x_0}\right)\theta(2x_0 - |x|), \tag{5}$$

where the function $\theta(x)$ is equal to unity and zero at positive and negative arguments, respectively.

According to formula (1), when calculating an experimental curve, the slit may distort the proper DRC of the sample crystal only being very small. In the case of a large slit, function (4) has a large FWHM and affects in no way the result. However, the fact is that this formula is not applicable to a large slit, and one must use the other approximation, in which the slit distorts the proper DRC specifically being large rather than small. However, the calculation formula in the approximation of small slit size is quite sufficient for simulating the experimental results.

EXPERIMENTAL RESULTS AND COMPARISON WITH THEORY

The DRCs were experimentally studied for three cases: Si monochromator (311), Si sample (111); Si monochromator (111), Si sample (111); and Si monochromator (111), Si sample (220). In each case, the slit vertical size was varied as follows: 20, 50, 100, 200, and 500 μm. The horizontal slit size, according to the theory, does not affect the result; however, it was sometimes varied to correct the number of photons recorded by the detector (a large number of photons may cause detection errors). The X-ray photon energy was chosen to be 12 keV. Below we present the experimental results and their comparison with theory for all three cases.

Case of Si Monochromator (311) and Si Sample (111)

From both theoretical and practical points of view, the most interesting is the first case, i.e., reflections 311 and 111 for the monochromator and sample, respectively. Here, $M = 0.502$, and one can obtain a near-proper DRC of the sample crystal. According to the theory, the results of simulating an experimental DRC vary very little for the aforementioned slit sizes, because the curve distortion is mainly caused by the source function $G'_B(x)$. The slit of minimum size distorts the curve most strongly, but this distortion is nevertheless smaller than that made by the source function.

Experimental data were obtained by rotating the sample crystal at a fixed angle with a relatively large step (0.0002°). The result was a set of numbers of photons for different crystal rotation angles. It turned out that, at different slit sizes, the numbers of photons slightly differ at the same points in the DRC, but this difference does not change the averaged curve parameters. It is caused mainly by the insufficient stability of the experimental scheme, i.e., the relatively low accuracy of sample crystal rotation at very small angles. To compare the experimental results with the theory, we chose the version with a slit size of 100 μm. The curve calculated for this case and the corresponding experimental points are shown in Fig. 3.

A computer program for calculating theoretical curves was written in the ACL language [7], which contains a standard module for determining DRAs from formulas reported in [8]. Fourier integrals were calculated by the fast Fourier transform (FFT) method on a point grid with a constant step and number of points $2^{16} = 65536$. The range of variation in the argument x was $X = 512$ μm. In correspondence with the conditions imposed by the FFT method, the grid step for the argument q was $2\pi/X$, with the same number of points. In reality, the functions change signifi-

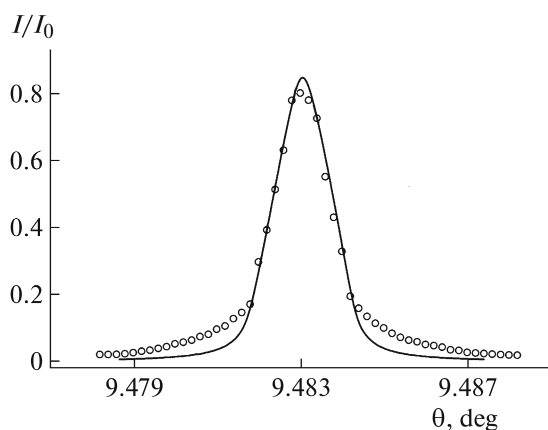

Fig. 4. Experimental (circles) and theoretical (solid line) DRCs for the second case (reflections 111 for the monochromator and sample). The vertical slit size is 20 μm. The experimental values are normalized so as to obtain the best coincidence with the calculation results.

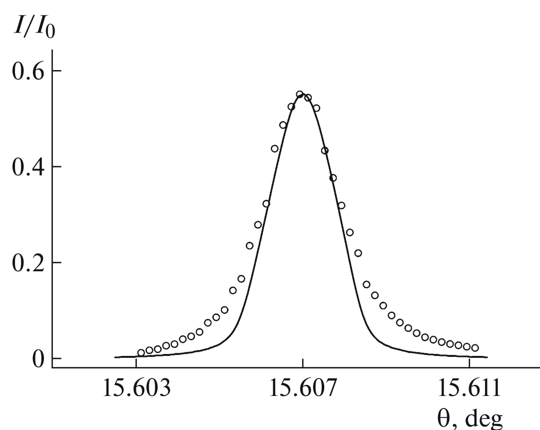

Fig. 5. Experimental (circles) and theoretical (solid line) DRCs for the third case (reflections 111 and 220 for the monochromator and sample, respectively). The vertical slit size is 20 μm. The experimental values are normalized so as to obtain the best coincidence with the calculation results.

cantly within smaller intervals; hence, only the central part of the grid was used to plot the curves.

As can be seen in Fig. 3, the theory describes the experimental data with high accuracy. In this case, we obtained a near-proper DRC with a minimum influence of instrumental function, which results in only smoothed vertex of the Borrmann fan and increased inclination angle of vertical walls. The FWHM of experimental DRC practically coincides with the calculated value.

Case of Si Monochromator (111) and Si Sample (111)

The results for the case of reflections 111 for both monochromator and sample are shown in Fig. 4. To compare the experimental results with theoretical predictions, we chose a slit with a size of 20 μm. In this case, the scheme is nondispersive, and, according to the theory, the instrumental function for this scheme is independent of the slit size when the latter is large and depends only slightly at average slit sizes of more than 10 μm.

The curve has a standard form of a convolution of two identical functions resembling a rectangular function. It is formula (5) that corresponds to purely rectangular functions. Its distinctive feature is a triangular shape in the central part. However, there is difference from the triangular function in the curve tails, because the tails of the proper DRC of crystal are more extended and fall off proportionally to the function θ^{-2}.

Experimental points fit well with the calculated curve in the central part; however, the tails turned out to be somewhat higher; the difference, although small, can yet be seen. The theory fails to describe this feature. It may be related to some additional features of the experimental scheme, disregarded by the theory.

Case of Si Monochromator (111) and Si Sample (220)

The results for the case of reflections 111 and 220 for the monochromator and sample, respectively, are shown in Fig. 5. A 20-μm slit was chosen to compare the experimental results with theoretical values. Under these conditions, the scheme is dispersive and M = 1.672. In this case, according to the theory, the monochromator increases even more the FWHM of experimental DRC in comparison with the proper DRC of sample crystal and changes its shape as well.

According to the theory developed in [8], the angular FWHM W of proper DRC is given by the formula

$$W = \frac{2|\chi_h|}{\sin(2\theta_B)}, \quad (6)$$

where χ_h is the Fourier component of the crystal polarizability. For the reflection 220 in silicon, W = 13.8 μrad = 0.00079°. The FWHM of the theoretical curve in Fig. 5 is 32.5 μrad = 0.00186°, i.e., exceeds the FWHM of proper DRC by more than a factor of 2. The maximum reflection intensity decreases simultaneously, because the theoretical curve is plotted on the assumption that the area is preserved when calculating the convolution.

Note that the experimental curve also passes above the theoretical curve in the region of DRC tails; the difference between the experiment and theory is accumulated monotonically. Therefore, the theory is in good agreement with the experiment in this case as well.

DISCUSSION OF RESULTS AND CONCLUSIONS

The main result of the study is the experimental confirmation of the theoretical conclusion stating

that, even in the case of infinite SR spectrum, one can obtain a near-proper DRC of crystal sample in the dispersive scheme with a symmetric monochromator and optimal slit sizes. It is of interest that, despite the fact that laboratory experiments with double-crystal X-ray diffractometry have been performed for many decades, this scheme has never been used by anyone.

To obtain a proper DRC, laboratory experiments were conventionally performed using a nondispersive scheme with an asymmetric reflection in the monochromator and without a slit (more exactly, with a slit of very large size). This is related, in particular, to the small intensity of X-ray tubes. The nondispersive scheme provides detection of higher intensity reflections, while a narrow slit reduces intensity.

It was shown that the nondispersive scheme can also be used with an SR source. However, in the symmetric case it distorts the shape and changes the width of the proper DRC of sample crystal. At the same time, the use of an asymmetric monochromator is not always convenient, because it cannot operate with the entire SR spectrum.

The possibility of obtaining a near-proper DRC in the dispersive scheme is useful for studying, e.g., the three-beam coplanar diffraction in different crystals. Within this approach one can obtain directly two curves of two-beam diffraction for different reflections and investigate the dynamic interaction between two reflected beams. To study reflections with high Miller indices, one must use reflections from the monochromator with even higher indices.

The scheme investigated here can also successfully be used to analyze the structure of multilayer crystals (crystal structures) and crystals with a deformed surface layer. In this case, to solve the inverse problem, it is of key importance to have a near-proper DRC, whose shape is distorted due to the deformations or complex structure.

ACKNOWLEDGMENTS

The study was supported by the Federal Agency for Scientific Organizations (agreement no. 007-ГЗ/Ч3363/26) in the part concerning the preparation of samples and computer simulation and by the Russian Foundation for Basic Research, project nos. 16-29-14057 ofi_m and 16-32-60120 mol_a_dk, in the part of concerning the development of X-ray diffraction schemes and analytical techniques involving synchrotron radiation. Experiments were performed using the unique research facility Kurchatov Synchrotron Radiation Source are the NRC KI (agreement no. 14.619.21.0007, project RFMEFI61917X0007).

REFERENCES

1. http://kcsni.nrcki.ru/pages/main/12016/12076/12083/index.shtml.
2. Z. G. Pinsker, *Dynamical Scattering of X-Rays in Crystals* (Springer, Berlin, 1978).
3. A. E. Blagov, M. V. Koval'chuk, V. G. Kohn, et al., Crystallogr. Rep. **55** (1), 10 (2010).
4. A. E. Blagov, M. V. Dekapol'tsev, M. V. Koval'chuk, et al., Crystallogr. Rep. **55** (6), 1074 (2010).
5. A. E. Blagov, M. V. Koval'chuk, V. G. Kohn, et al., J. Surf. Invest. **5**, 822 (2011).
6. V. G. Kohn, Crystallogr. Rep. **64** (1), 16 (2019).
7. http://kohnvict.ucoz.ru/acl/acl.htm.
8. V. G. Kohn, Phys. Status Solidi B **231**, 132 (2002).

Translated by Yu. Sin'kov