THE INVESTIGATION OF THE $Ga_{0,8}In_{1,2}S_3$ THIN CRYSTAL FILMS BY MEANS OF ELECTRON DIFFRACTION METHOD OF ROTATION

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It has been investigated electron diffraction patterns of $Ga_{0,8}In_{1,2}S_3$ single-crystal films obtained by rotating them on an angle φ=70° around axes lying in the plane of the film, which are perpendicular to the incident electron beam. The parameters of the new two-layer 2H polytype: a = 3.82Å, c = 24.53Å, sp. gr. $P6_3mc$ and the structural modulus … $_hT_hO_cT_hE$…, as well as the superlattice parameter: $A = \sqrt{3}\,a$ were determined. Where T and O are, respectively, two-dimensional tetrahedral and octahedral layers, E is an empty interlayer, h and c are, respectively, hexagonal and cubic packing of sulphur layers.

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INTRODUCTION

It is known from the data in the literature that layered crystals contain many polytypes (both well-justified and unproven) with a large unit-cell parameter *c*. Below are mixtures of some polytypes that can be mistaken accepted for new pure polytypes with large c parameters:
1T + 3R ≠ 3T, (2T) + 3R ≠ 6T(6H, 6R), 2H(2T) + 9R ≠ 18T(18H, 18R), 3R + 4H ≠ 12T(12H, 12R), 4H + 6H ≠ 12T(12H, 12R).

Usually, the powders or thick samples of layered crystals, which often consist of mixtures of different polytypes, are studied by various diffraction methods: X-ray, electron, neutron, etc. Thin single-crystal films less than 500Å consist only of pure polytypes [1,2].

When shooting the stationary single-crystal films (SCF), only touching or projection of the site onto the Ewald plane (EP) can take place. When the crystal rotates, the EP passes through the entire volume occupied by each site of the reciprocal lattice (RL). If the rotation is uniformly and there is no superposition of reflections, the obtained information about the intensity of reflections in the electron diffraction patterns of rotation is right. In the proposed schemes, the angles of rotation (tilt) can be more than 70°. Therefore, it is especially important to study thin SCF by various electron diffraction methods of rotation.

When the single crystals films rotates around any axes (in particular, around the axis a of atomic lattice) lying in the film plane (FP) (before rotation, the electron beams fall perpendicularly on the FP), the site rows hk (hk=const, l-changes) of the reciprocal lattice are registered on the EP along lines perpendicular to the axis of rotation. Such electron diffraction patterns are imitated as electron diffraction patterns of needle like textures.

The diffraction beams pass through the points of the Ewald sphere (in this case, the used part of the Ewald sphere is flat, and therefore we call it the Ewald plane), where during the rotation the RL sites are registered, and then continuing the own way are recorded on the plane of the photographic plate. On a photographic plate, the distances R_{hkl} correspond to the distances $R_{hkl}/L\lambda$ on the Ewald plane.

In [3], there is a crystal structure of a three-packet rhombohedral 3R polytype $(Ga,In)_2S_3$ with parameters a=3.816Å, c=36.793Å, sp. gr. R3m, $_hT_hO_cT_hE$ structural type.

EXPERIMENTAL AND DISCUSSION OF THE RESULTS

Thin SCF were obtained by peeling off a thick crystal with adhesive tape. The electron diffraction patterns were obtained on an EG-400 electron diffraction recorder at an accelerating voltage of V=350 kV. For simplicity, the multiplier $1/L\lambda$ to the vectors R_{hkl} has been removed from the rotation scheme (Fig. 1a).

The site rows *h0l* (h=const., l-varies, colored sites) of the reciprocal lattice are perpendicular to the radius-vectors R_{h00} (h=const, black lines), whose positions coincide with the EP. Therefore, R_{h00} (h is changed, black lines) is the common leg of each right-angled triangle built on the basis of this common leg and the site rows h0l (h=const, l-varying, colored sites), and R_{h0l} (colored sites) are the hypotenuses of these triangles. Lengths of vectors R_{h0l}, (h, l = const, black lines), registered on the EP of the site rows *h0l* (h=const, l-changes, black lines), remain unchanged. Therefore, despite the fact that the triangle is not rectangular (the angle is 120°) (Fig. 1a, b.), the Pythagorean theorem is applicable [2, 4].

Smooth surfaces of layered crystals were glued to the surface of a metal mesh or washer, and thin SCF were obtained from them by peeling off with an adhesive tape. The washers were placed on the surface of the crystal holder (CH) and under the electron beam, by rotating the CH, the easily decipherable electron diffraction patterns were obtained. These rotation electron diffraction patterns imitate electron diffraction patterns from needle-like textures [2,4].

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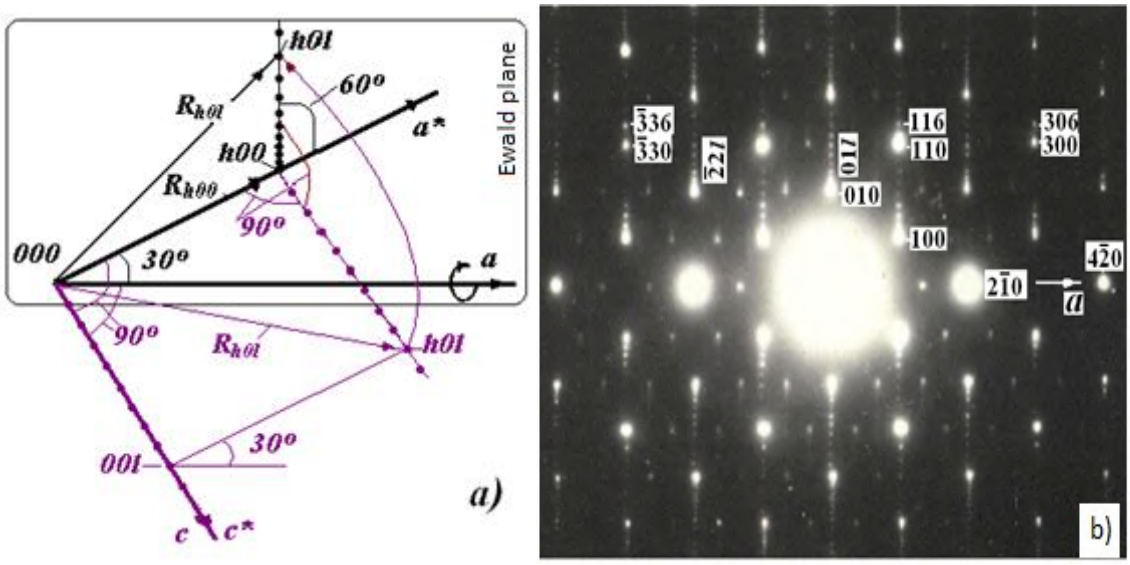

Fig. 1. a) Scheme of the site rows of the reciprocal lattice of a hexagonal crystal (colored sites) and their registration on the Ewald plane (black sites) during rotation around the axis a of the atomic lattice and b) the corresponding electron diffraction pattern from the 2H $Ga_{0,8}In_{1,2}S_3$ polytype. The electron beam is perpendicular to the axis of rotation.

Figure 1.b) shows the electron diffraction pattern obtained by rotating a $Ga_{0,8}In_{1,2}S_3$ single-crystal film around the axis *a* of a atomic lattice perpendicular to the electron beam. The registration is started from the *hk0* plane (from the SCF plane), and therefore a significant delay of this plane under the primary electron beams (EB) takes place. Different site rows (series of reflections) come out separately, but in each site row *hk* (h, k = const, l changes), sites with small values of l merge. The number of merging reflections depends on the value of c* and on the distance of the site row hk from the rotation axis (from the axis *a*).

The electron diffraction patterns were interpreted using the following formulas for oblique textures [5]:

$$d_{100} = (3/4)^{1/2}\, a = 2L\lambda h/2R_{h00}, \qquad (1)$$

$$D_{hk\,l} = (R^2_{hkl} - R^2_{hk0})^{1/2}, \qquad (2)$$

$$\Delta D = c^* L\lambda = (D_{hkl} - D_{hk(l-1)}), \qquad (3)$$

$$d_{001} = c = 1/c^* = L\lambda/\Delta D. \qquad (4)$$

On series $11\bar{2}l$, there are only reflections with l=2m (m=1,2,3…), and the second strong reflection on the second ellipse is a reflection with l = 6 = 2 x 3. Where, 2 indicates the number of packets in the elementary cell, and m = 3 on TOTE type packets [7]. The parameters of the new two-layer 2H polytype were determined: a = 3.82Å, c = 24.53Å, sp. gr. $P6_3mc$ and the structural modulus … $_hT_hO_cT_hE$…, as well as the superlattice parameter: $A = \sqrt{3}\,a$. Where T and O are, respectively, two-dimensional tetrahedral and octahedral layers, E is an empty interlayer, h and c are, respectively, hexagonal and cubic packing of sulphur layers.

CONCLUSION

In the proposed schemes, the angles of inclination can be more than 70°. Consequently, the number of registered nodes will be much greater than in the case of Precession Electron Diffraction when the inclination angle is ~3°.

Different site rows (series of reflections) come out separately, but when $a << c$ in the site rows hk (h,k=const, l-changes), reflections with small values of l are superimposed on each other, and the greater the distance of the site rows hk from the axis rotation, the more overlapping reflexes. How can these shortcomings be corrected?

By rotating the film around an axis perpendicular to the film plane (FP), it is possible to bring the studied site row hk closer to the rotation axis to such a distance that during rotation the individual reflections will take place.

When the SCF of crystals with hexagonal and higher symmetries rotates around the coordinate axes of the of the reciprocal lattice (for example, *a**), the different site rows, for example, *hkl* and h,k + 1,l (h, k = const, l - changes) with large values of l, could merge with each other. In addition, with such rotations during exposure to the EP, different RL planes are recorded in turn. Thus, secondary electron diffraction can strongly affect the intensities of all sites of an individual plane of reciprocal lattice.

When the SCF rotates around not the coordinate axes, but the axes lying in the coordinate plane of reciprocal lattice, there is no superposition of reflections with large values of l on the obtained electron diffraction patterns. In addition, during such a rotation, only a few reflections are simultaneously recorded on the EP. Obviously, the kinematic scattering dominates in this situation.

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ИССЛЕДОВАНИЯ ТОНКИХ МОНОКРИСТАЛЛИЧЕСКИХ ПЛЕНОК $Ga_{0,8}In_{1,2}S_3$ с ПОМОЩЬЮ ЭЛЕКТРОН-ДИФРАКЦИОННОГО МЕТОДА ВРАЩЕНИЯ

Изучены электронограммы монокристаллических пленок $Ga_{0,8}In_{1,2}S_3$, полученные вращением их на угол $\varphi=70^0$ вокруг осей, лежащих в плоскости пленки, которые перпендикулъярно расположены к падающему электронному лучу. Установлены параметры нового двухслойного политипа 2H: a = 3,82Å, c = 24.53Å, пр. гр. $P6_3mc$ и структурный модуль … ${}_{г}T_{г}O_{к}T_{г}П$…, а также параметр сверхрешетки: $A = \sqrt{3}\,a$. Где Т, О и П – соответственно, тетраэдр, октаэдр и пустой полиэдр, *г* и к – гексагональная и кубическая упаковки слоев серы.

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ELEKTRON DİFRAKSİYA FIRLANMA ÜSULU İLƏ $Ga_{0,8}In_{1,2}S_3$ NAZİK KRİSTAL TƏBƏQƏLƏRİNİN TƏDQİQİ

$Ga_{0,8}In_{1,2}S_3$ monokristal təbəqələrinin, onların üzərlərində yerləşən və elektron şüasına perpendikulyar olan oxlar ətrafında $\varphi=70^0$ bucağa qədər fırlanmasından alınan elektronoqrammalar öyrənilmişdir. Yeni ikilaylı 2H politipinin qəfəs parametrləri a = 3,82Å, c = 24.53Å, fəza qrupu $P6_3mc$, quruluş modulu… ${}_{h}T_{h}O_{k}T_{h}B$ … və həmçinin ifratqəfəs parametri $A = \sqrt{3}\,a$ müəyyən edilmişdir. T, O, B (uyğun olaraq dolu tetraedr, dolu oktaedr və boş kationlarla tutulmayan, poliedr). Harada ki, ***г*** və ***к*** anion laylarının heksaqonal və kubik yığılmasını göstərir.