THE INVESTIGATION OF THIN SINGLE-CRYSTAL FILMS OF $Fe_{0,75}Ga_{0,25}InS_3$, $MnGaInS_4$ and $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ CRYSTALS BY ROTATION ELECTRON DIFFRACTION PATTERN

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The new 2H-polytypes with space group $P6_3mc$ of $Fe_{0,75}Ga_{0,25}InS_3$ crystals (with lattice parameters a=3,78 Å, c=24,44Å) and $MnGaInS_4$ crystals (with lattice parameters 3,80Å, c=24,55Å) are identified by electron diffraction patterns obtained by tilt and further rotation of crystal holder (CH) with single-crystal film (SCF). 3R-polytype of $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ crystal with parameters a=3.78Å, c=36.78Å, sp. gr. R3m is also identified. $Fe_{0,75}Ga_{0,25}InS_3$ single-crystal film evenly lies on CH surface but SCF of $MnGaInS_4$ and $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ crystals are located under some angle to CH plane. In $MnGaInS_4$ case the scheme explaining the origin of some reflections located on nonstandard positions (outside ellipse lines) is given. Such scheme can be used in further electron diffraction structural investigations of nano-objects arbitrarily oriented on CH.

Keywords: electron diffraction, new rotation methods, structure of inorganic compounds.
PACS: 61.05.-a, 61.14.-x, 61.66.Fn.

INTRODUCTION

The composition defects [1] and mixtures [2 -4] of different polytypes which strongly influence on crystal physical properties often exist in layered crystals. In many cases the mixture diffraction patterns of different polytypes with small values of crystal lattice parameters ***c*** and diffraction patterns of some polytypes with big parameter values ***c*** coincide [3]. This makes difficult the identification of diffraction patterns. The intensities of reflections from different polytypes are indistinguishable at simultaneously equal percentage of each polytype in mixture. That's why to establish the correct polytype is impossible. If the percentages of each polytype in the mixture are very different, then the intensities of reflections from different polytypes will also be very different. That's why with a more careful analysis of the electron diffraction pattern one can establish the true polytypes. If percentages of each polytype in the mixture will be more different, then reflection intensities from the one of these polytypes will be insignificant (on the background level) and this polytype will not be detected.

The electron diffraction methods are more effective ones at investigation of layered crystals especially when they consist from mixture of different polytypes. The development of modern nanotechnologies is impossible without detail structural information obtained by the different diffraction methods. The last circumstance stimulates the development of the new electron-diffraction methods having the specific advantages comparably with other diffraction methods for investigation of nanosamples [5-7].

The investigations given in [2,3] show that only one polytype modification remains in thin (less than 500Å) single-crystal films (SCF). The usage of new rotation method in electron diffraction at investigation of thin SCF significantly simplifies the study of one polytype phase is also shown in [3]. But if the one phase is known, then one can easily establish the another one.

The obtaining the thin-film preparations is the important moment of electron diffraction investigations (from this fact the accuracy and reliability of structural definition depends on). In our investigations the thin SCF are obtained by the cleaving of thin plates from thick crystal with the help of an adhesive tape. The layered crystal with plane surface is glued on metal mesh or washer and thin SCF are obtained by the cleaving from crystal by an adhesive tape. The washers in which the input hole has the diameter near 0.8–1mm and output hole has diameter near 2mm, are placed on crystal holder (CH) surface. The rotation electron diffraction patterns imitating the electron diffraction patterns from lamellar and needle-like textures [5-7] are obtained by tilting and rotating CH under electron beam in various ways due to the presence of two sample-rotation axes on the goniometer table (on electron diffractometers EG-400 and ER-102M). In order to obtain the electron diffraction patterns with necessary set of reflections the rotation of SCF round axes lying in the CH plane and perpendicular to it, is carried out [4-6].

The cases when crystal lattice parameter values of layered semiconductors lying on basal plane (*a* parameter in hexagonal case) in several and sometimes tens of times less than values of *c* parameter, are often met in practices of electron diffraction structural analysis for layered crystals. Moreover, the corresponding *c* axis can be either perpendicular or oblique with respect to basal plane. Site rows *hk* (in which *h* and *k* are constants, *l* is a variable) are much more distant from each other whereas the sites themselves are densely located on site rows *hk* lying along c* axis. This circumstance allows us to easily emphasize site rows *hk* on rotation electron-diffraction patterns of single crystal that significantly simplifies the indexation of site rows *hk* and finally the electron diffraction pattern interpretation.

Note that there is one circumstance which makes difficult the electron-diffraction pattern interpretation. There are cases when the film lies unevenly on CH surface and the main crystallographic planes are

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located under some angle to this surface. This question requires the detail consideration.

The given article is devoted to development of new schemes of electron-diffraction pattern obtaining from SCF imitating the lamellar structures and new rotation schemes of SCF and their use to investigation of crystal structure of $Fe_{0,75}Ga_{0,25}InS_3$, $MnGaInS_4$ and $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ single-crystal films

EXPERIMENTAL PART AND RESULT DISCUSSION

The two cases of single-crystal film disposition: evenly placed on the plane of CH and under some angle to it, are studied.

1. The single-crystal film is evenly placed on CH plane.

Electron-diffraction investigation of single-crystal film $Fe_{0,75}Ga_{0,25}InS_3$.

Some compositions including in Fe-Ga-In-S system are synthesized by Bridgeman method and chemical transport reaction (ChTR) with the use of I_2 as conveyer and they are studied using X-ray pattern in [8,9].

It is established that in particular, $Ga_{0,75}Fe_{0,25}InS_3$, $Ga_{0,25}Fe_{0,25}In_{1,5}S_3$ and $Ga_{0,5}Fe_{0,5}InS_3$ crystals consist of pure one-packet tetragonal polytypes (1T), $Ga_{0,5}Fe_{0,25}In_{1,25}S_3$ crystals consists of *3R* mixtures (three-packet rhombohedral-main phase) and partly one-packet phase, $Ga_{0,25}Fe_{0,75}InS_3$ crystals consist of *3R* mixtures (main phase) and partly consist of two-packet phase. These polytypes belong to structural types of TOTE. Here T and O indicate two-dimensional layers consisting of tetrahedra and octahedra respectively, E corresponds to an empty interlayer gap. The second phases were in small quantity and from them not more than 2-3 weak reflections were observed.

The qualitative electron-diffraction patterns from textures shown in [10] show that $Fe_{0,5}Ga_{0,5}InS_3$ sample is pure 1T-polytype and $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ and $Fe_{0,75}Ga_{0,25}InS_3$ samples are pure 3R- polytypes. In this part our work refers to precise definition of second phase in $Fe_{0,75}Ga_{0,25}InS_3$ crystals.

The single-crystal film of $Fe_{0,75}Ga_{0,25}InS_3$ composition is obtained by above mentioned method. It evenly lies in CH plane. That's why the sites on *hk0* plane of reciprocal lattice (RL) are registered on the electron-diffraction pattern plane along ellipse minor axis and other nodes relating to one and the same Laue zone (LZ) are registered on layer lines parallel to ellipse minor axis at CH rotation round axis perpendicular to its plane which is tilted beforehand on φ angle from perpendicular position to incident electron beam (EB).

The 6 samples of thin single-crystal films $Fe_{0,75}Ga_{0,25}InS_3$ are obtained. The electron-diffraction patterns are obtained using the developed earlier rotation method. As the films by thickness less 50nm are studied so one can separate one phase from another. From all samples only one is new two-packet hexagonal (*2H*) polytype (Fig.1). The rest samples are three-packet rhombohedral (*3R*) polytypes.

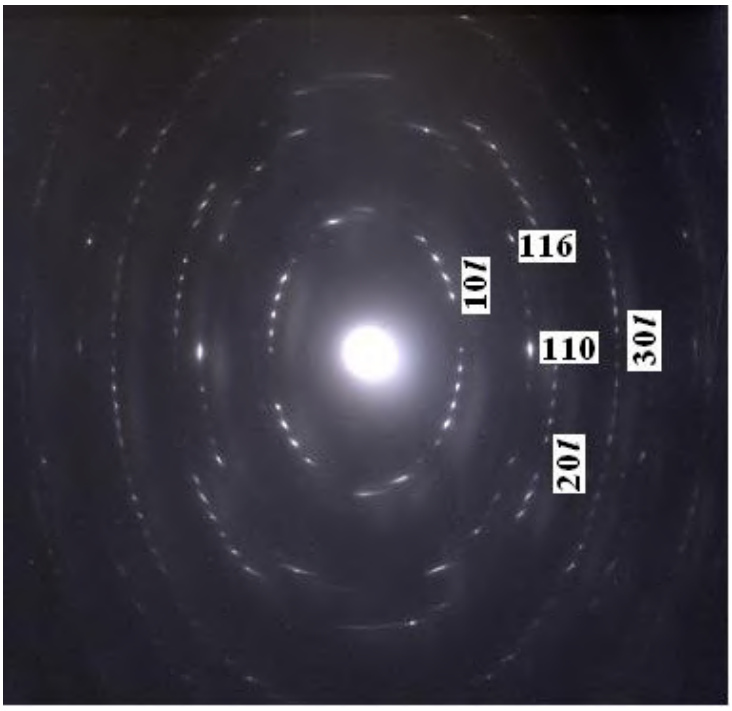

Fig.1. The rotation electron-diffraction pattern of $Fe_{0,75}Ga_{0,25}InS_3$(φ=40°, ω=45°) single crystal of 2H- polytype. The single-crystal film is evenly placed on CH plane.

The electron-diffraction pattern obtained by rotation on ω=45° angle of thin SCF round axis perpendicular to film plane which is tilted beforehand on φ=40° angle from perpendicular position to incident electron beam is shown in fig.1. In contrast to electron-diffraction patterns of oblique textures where the different series

of reflections overlap on each other, in the given case the electron-diffraction pattern doesn't cover symmetrically independent structure part and that's why there are no reflections overlapped on each other. The interpretation of electron-diffraction pattern is carried out with the help of known formulas for electron-diffraction patterns of oblique textures [11]:

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

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

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

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

Here L is the distance from diffraction point (sample) up to electron-diffraction pattern, λ is wavelength of incident electrons, h, k, l are Miller indexes, $2R$ are distances between reflections on electron-diffraction pattern, R_{hk0} are ellipse minor axes, d_{hkl} is interplanar space, D_{hkl} - in scale $L\lambda$ and at h,k=const., the distances between sites hkl and plane $hk0$ of reciprocal lattice, ΔD is distance between neighbor sites along c^* axis in scale $L\lambda$, $c^*$is reprocical lattice (RL) parameter. For simplicity in figure Miller indexes i are not shown. In given figure l index is emphasized by cursive for the difference from 1.

The hexagonal type of crystal lattice: $1:\sqrt{3}:2:\sqrt{7}=R_{100}:R_{110}:R_{200}:R_{210}$ is defined by relations of R_{hk0} reflections being on ellipse minor axis. The lattice parameters: a=3,78Å, c=24,44Å are found by distances of R_{10l} reflections placed on first ellipse (series $10\bar{1}l$). Space group $P6_3mc$ is identified by reflection extinction. The absence of reflections on second ellipse (series $11\bar{2}l$) with l uneven values shows on the fact that the structure of the given sample consists of two packets. The packet thickness (12,22Å) is found by R_{11l} reflection distances located on second ellipse (series $11\bar{2}l$), the structural type of TOTE (12) is identified by value l=6 of second strong reflection ($11\bar{2}6$). The structure of the given polytype is the iso-structural analogue of 2H-polytype $ZnIn_2S_4$(II)a [13] and 2H-polytype $CdInGaS_4$ [2,3].

2. Single-crystal films are located under some angle to CH plane.

2. Electron-diffraction investigation of $MnGaInS_4$ single-crystal film.

The crystal structure of three-packet rhombohedral polytype *(3R)* $MnGa_xIn_{2-x}S_4$ (0,4≤x≤1,6) with lattice parameters a=3,749Å-3,850Å, c=36,579Å–37,097Å and sp.gr. R3m is shown in [14]. In this structure the unit cell consists of twelve layers and unit packet consists of four layers of sulfur atoms. The tetrahedral grids are joined to central octahedral one in both sides in packets. The inter-packet octahedra and tetrahedra are empty.

The investigation of $MnGaInS_4$ crystal structure with the help of new electron-diffraction rotation methods with the aim of the identification of new polytypes which are typical in the case of layered semiconductors, is the task of our work.

The crystals for the experiment are taken from different ampoules and from different parts of the one and the same ampoule. The definite rectangular parts of $MnGaInS_4$ crystals are used to obtain thin single-crystal films suitable for electron-diffraction investigation. They are obtained by cleaving of thin plates from thick crystal with the help of adhesive tape.

The electron-diffraction pattern obtained by rotation of single-crystal film round axis (on angle ω=70°) perpendicular to film plane which is tilted beforehand on angle φ=40° from perpendicular position to incident electron beam is shown in fig.3. For the simplicity Miller indexes i are not shown in figure.

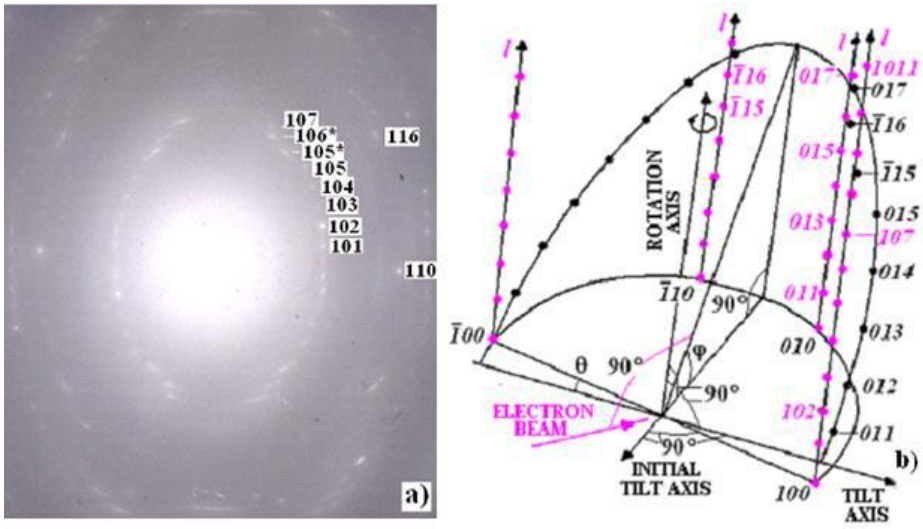

Fig.2. a) The rotation electron-diffraction pattern of $MnGaInS_4$ single crystal of 2H-polytype (φ= 40°, ω=70°), the single-crystal film is located under some angle to CH plane; b) the rotation scheme and site registration (and reflections correspondingly) of reciprocal lattice on Ewald plane. The sites designated by red color are located parallel to 00l axis of reciprocal lattice and during rotation 01l and $1\bar{1}l$ sites registered on Ewald plane are emphasized by black color. θ is the angle between SCF and CH planes.

CH towards with SCF rotate round their axes perpendicular to CH plane (not to SCF) after previous (before exposition) tilt on φ angle during the diffraction patterns survey (fig.2). RL sites being in same distances from *c* axis and from SCF plane (for example: 10*l*, 01*l*,$\bar{1}$1*l*,$\bar{1}$0*l*,0$\bar{1}$*l* and 1$\bar{1}$*l*, *l*=const.) will be in different distances from rotation axis and CH plane in the contrast to case 1 (see above). That's why because of R_{hkl} are the same for the such sites, these sites will move along circles with different radiuses and different heights from CH plane at rotation round axis perpendicular to CH plane.

Sites 015 and $\bar{1}$15 (also 016 and $\bar{1}$16 nods) being in the same distances from *c* axis and from SCF plane in the contrast to case 1 where they should overlap on each other, in the given case (case 2) are in different places of EP (fig.2a,b). As it is seen from fig.2a only two site rows $\bar{1}$15 and $\bar{1}$16 will be registered at rotation from site rows $\bar{1}$1*l* on EP.

The crystal lattice parameters: *a*=3,80Å, *c*=24,55 Å are defined by electron-diffraction pattern. Value *c*=24,55Å corresponds to thickness of eight close-packed sulfur layers. Thus, unit cell consists of eight layers and unit packet consists of four layers of sulfur atoms.

Reflection 11$\bar{2}$6 is the second strong reflection on second ellipse in fig.2. As it is known [12], the second strong reflection in *11*$\bar{2}$*l* series is the reflection-indicator defining the structural type. Value (*l*=6=*2x3*) indicates the type of structure. Value 2 corresponds to packet quantity in polytype per unit cell and number 3 indicates the type of TOTE structure of polytype packets [12]. The reflections with *l*≠2n are absent in *11*$\bar{2}$*l* series. The space group of two-packet polytype $P6_3mc$ is identified by reflection extinctions. The package type of sulfur anions is *hhch (h* and *c* are hexagonal and cubic package correspondingly). The structure of the given polytype is the isostructural analogue of 2H-polytype $ZnIn_2S_4$(II)a [13] and 2H-polytype $CdInGaS_4$ [2,3].

2. Electron-diffraction investigation of single-crystal film $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$.

The electron-diffraction pattern from $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$, SCF of which makes θ angle with CH plane (initial tilt), is shown in fig.3. After CH beforehand tilt (before diffraction exposition) towards with SCF on $\varphi \approx 55°$ angle (prepared tilt), SCF is rotated by angle $\omega \approx 60°$ round axis perpendicular to CH plane (not SCF) during survey of the diffraction.

Site rows *hk* are obliquely located to CH plane. RL sites being in the same distances from c* axis and from *hk0* plane of reciprocal lattice will move along circles with different radiuses and in different heights from CH plane. Reflections *hkl* (*l* is const.) with small values of *h* and *k* are coincide with each other widening and lengthening at small angles θ ($\theta < 5°$) because of the small difference of heights and circle radiuses.

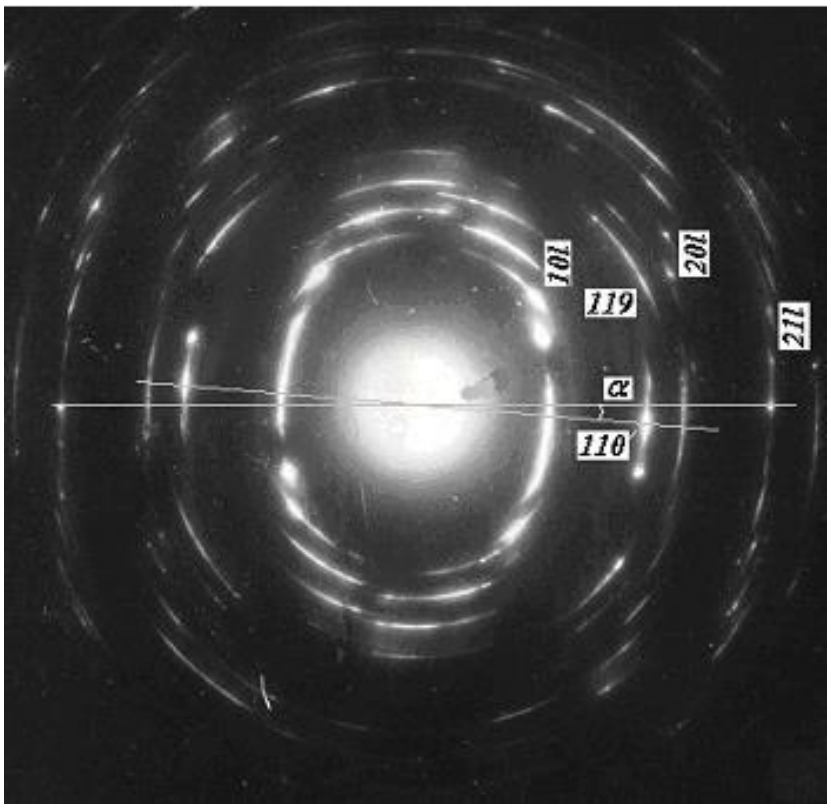

Fig.3. The rotation electron-diffraction pattern of $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ *(φ=55°, ω=60°)* single crystal of *3R* polytype. The single-crystal film is located under θ angle to CH plane. The reflection tilt 110 on α angle from direction of CH tilt axis is connected with initial tilt of film on θ angle.

The reflections located on deformed ellipses and layer lines are absent are observed on electron-diffraction pattern (fig.3). At visual estimation one can indicate incorrectly on low crystal lattice symmetry. Indeed, the reflections are more moving away from ellipse minor axis and stay outside the ellipse line at the decrease of reflection heights from ellipse minor axis (from tilt axis) because of the fact that lengths of radius-vectors of R_{hkl} sites don't change.

Knowing R_{110} value, the values of R_{hk0} other vectors are calculated. Each third reflection is extinguished in reflection series $h-k\neq 3n$ (h and k are constants, l is a variable) and, on the contrary, only each third reflection is observed in $h-k=3n$ series. This fact indicates on rhombohedral structure.

The lattice parameters are easily defined by following formulas:

$$R_{100} = R_{110}/\sqrt{3},\ d_{110} = 2L\lambda / 2R_{110},\ d_{100} = \sqrt{3}\, d_{110},$$

$$a = 2d_{100}/\sqrt{3} = 3.783\text{Å},$$

$$D_{hkl} = (R^2_{hkl} - R^2_{hk0})^{1/2},\ \Delta D = c^* L\lambda = (D_{hkl} - D_{hk(l-1)}),$$

$$c = d_{001} = 1/c^* = L\lambda/\Delta D = 36.775\text{Å}.$$

The three-packet rhombohedral 3R- polytype $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ with sp.gr. *R3m* is identified. The structure of the given polytype is the isostructural analogue of structure of 3R-polytype $ZnIn_2S_4$(III) [13] and *3R*- polytype $CdInGaS_4$ [2].

CONCLUSION

The electron-diffraction patterns from thin single-crystal films $Fe_{0,75}Ga_{0,25}InS_3$, $MnGaInS_4$ and $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$ are obtained by rotation on $\omega \leq 70°$ angle round axis perpendicular to CH plane which (before diffraction exposition) is beforehand tilted on φ<50° angle from perpendicular position to incident electron beam. The two cases are observed in the given work. In $Fe_{0,75}Ga_{0,25}InS_3$ case the single-crystal film is evenly placed on CH plane and in last two cases SCF is located under some angle θ to CH plane.

The X-ray investigation of $Fe_{0,75}Ga_{0,25}InS_3$ powders show that they consist of second unknown phase in small quantity besides the main *3R*- polytype. The new two-packet hexagonal polytype (2H) with structural module ${}_hT_hO_cT_hE$ which is the new polytype in Fe-Ga-In-S system is identified with the help of single crystal rotation method imitating the plate structures, developed by authors, where T and O are two-dimensional layers from tetrahedra and octahedra correspondingly, E corresponds to an empty interlayer gap, *h* and *c* are hexagonal and cubic package of sulfur layers.

The electron-diffraction patterns imitating the lamellar textures are obtained for thin single-crystal films of $MnGaInS_4$ compound. In this case SCF is located under some θ angle to CH plane. The electron-diffraction patterns are obtained by the way of SCF tilt on $\varphi=40^0$ angle and further rotation by $\omega=70^0$ angle round axis perpendicular to CH plane. The new two-packet hexagonal (2H) polytype with structural module ${}_hT_hO_cT_hE$ with sp.gr. $P6_3mc$ is identified by these electron-diffraction patterns. In electron-diffraction patterns the many reflections are located along ellipses and they are easily indexed. The scheme explaining the origin of additional reflexes located on not ellipse lines is given. In principle, these schemes should help in study of crystal structure of thin films with nano-meter thickness and film systems, nano-samples, nano-tubes and etc, in the case of their arbitrary orientation.

The known three-packet rhombohedral *3R*-polytype with sp.gr. *R3m* is identified by rotation electron-diffraction patterns of single crystal $Fe_{0,25}Ga_{0,5}In_{1,25}S_3$. In the given case SCF is located under some θ angle to CH plane.

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Received: 14.02.2022