

Preparation and some physical properties of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ single crystals

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$\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ ($x = 0.00$ to 0.66) single crystals were prepared using a modified Bridgmann method. Their homogeneity was studied by determining the indium content and the variations of Seebeck coefficient in the directions perpendicular and parallel to the crystal axis. X-ray structure analysis revealed that the volume of the unit cell of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystal lattice decreases with increasing value of x . Measurements of the electrical conductivity, Hall constant and Seebeck coefficient showed that incorporation of the indium atoms into the Bi_2Se_3 crystal lattice results in an increase of free electron concentration for low indium content, whereas the free electron concentration is suppressed in the range of the high indium content. This effect is explained qualitatively on the basis of our ideas on the nature of point defects in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals.

1. Introduction

Despite considerable attention devoted to the study of $\text{A}_2\text{B}_3\text{VI}$ compounds of tetradymite structure (where $\text{A} = \text{Bi, Sb}$ and $\text{B} = \text{Se, Te}$) which find applications in thermoelectric devices, there are very few data in the literature on the properties of the samples in the $\text{Bi}_2\text{Se}_3\text{-In}_2\text{Se}_3$ system.

It follows from the $\text{Bi}_2\text{Se}_3\text{-In}_2\text{Se}_3$ phase diagram [1] that both components form a continuous set of solid solutions with tetradymite structure. It was also concluded from the results of measurements of transport properties that solid solutions in this system exist over a broad range of concentrations [2, 3]. On the other hand, Rustamov and Cherstova [4] have suggested that the compound InBiSe_3 exists in the $\text{Bi}_2\text{Se}_3\text{-In}_2\text{Se}_3$ system. So far, however, nothing has been reported in the literature about the preparation and properties of single crystals of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ solid solutions, whose formation has been demonstrated previously [1-3].

In the present paper we describe a modified Bridgman method used to grow $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ single crystals ($x = 0.00$ to 0.66) and characterize the crystals obtained by measurements of their lattice parameters, Hall constant, electrical conductivity and Seebeck coefficient. Further, we suggest a view of the nature of point defects in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals with the objective to explain qualitatively the variations of the above mentioned quantities due to the substitution of indium atoms for bismuth in the crystal lattice of Bi_2Se_3 .

2. Experimental procedure

2.1. Preparation of single crystals

$\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ single crystals were prepared from elements of 99.999% purity. The compounds were synthesized in conical quartz ampoules evacuated to 10^{-4} Pa. The homogeneization of the batches and synthesis of the compounds was carried out in a horizontal furnace at 1073 K for 48 h. The crystals were grown using a vertical Bridgman method. Before pulling, the ampoules containing the melt were heat-treated at 1073 K for 24 h and when the melt filled the tip of the ampoule, the ampoules were lowered through the temperature gradient shown in Fig. 1 at a rate of 0.8 mm h^{-1} .

The single crystals obtained, 50 to 60 mm long and 9 mm diameter, could be easily cleaved. Their trigonal axis, c , was always perpendicular to the pulling direction so that the (0001) crystal plane was parallel to the ampoule axis. The orientation of the cleavage faces was carried out using the Laue back-reflection method, which confirmed that these faces were always (0001).

2.2. Microanalysis of the crystals

The prepared crystal samples were qualitatively analysed by means of a Link Systems 860 Series 2 energy dispersion analyser and a Tesla BS 300 scanning electron microscope. An electron beam at a voltage of 25 kV excited a signal of characteristic X-ray radiation from the cleavage face of the sample and the

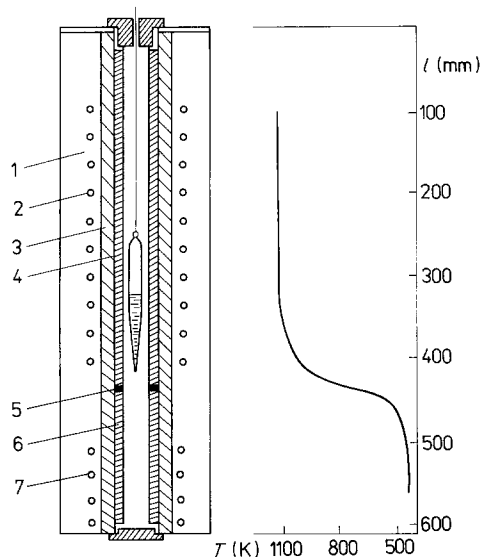


Figure 1 Schematic drawing of the furnace for the growth of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals with the temperature gradient used for the growth: 1, thermal insulation (asbestos) 2, resistance heating; 3, ceramic tube; 4, stainless-steel tube; 5, asbestos ring; 6, copper tube; 7, cooling.

signal was analysed in the 0 to 20 keV energy range. Quantitative determination of the elemental composition of the crystals was performed with the aid of pure metal standards of Link systems. The results of this analysis of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ samples, expressed as the values of x , are summarized in Table I.

With the aim of investigating the homogeneity of the crystals, in addition to quantitative analysis, the distribution of indium across the cleavage face was analysed in the directions parallel and perpendicular to the crystal axis.

2.3. Determination of lattice parameters

The lattice parameters of the prepared single crystals were determined on powder samples by X-ray diffraction analysis using an HZG-4B diffractometer (VEB Freiburger Präzisionsmechanik, East Germany). The diffraction maxima were measured by a step procedure using a step size of 0.01° . The measurement was carried out in the range of $2\theta = 5$ to 100° with $\text{CuK}\alpha$ radiation in the range to 5 to 45° and with $\text{K}\alpha_1$ radiation in the range to 45 to 100° ; the $\text{K}\beta$ radiation was removed using a nickel filter. The calibration of the diffractometer was carried out with polycrystalline silicon. The diffraction lines obtained were indexed according to Gobrecht *et al.* [5] and the values of the lattice parameters a and c of the crystals were calculated by the least squares method.

2.4 Measurement of transport coefficients

The room-temperature values of the Hall constant were determined on the samples prepared from the central parts of the crystals, rectangular slabs of $8 \times 3 \times 0.1$ to 0.3 mm^3 dimensions. The experimental geometry corresponded to $R_H(\mathbf{B} \parallel \mathbf{c})$. The samples were connected to an a.c. current supply of 170 Hz frequency, the constant magnetic field induction, B , was equal to 1.1 T.

Values of electric conductivity, $\sigma_{\perp c}$, were calculated

TABLE I Lattice parameters of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals

Sample No.	x	a (nm)	c (nm)	V (nm^3)	Δ^*
1	0	0.413 85(4)	2.8623(2)	0.4246(1)	0.008
2	0.01	0.413 74(3)	2.8623(2)	0.4243(1)	0.007
4	0.08	0.412 65(9)	2.8632(4)	0.4222(2)	0.014
5	0.15	0.411 75(4)	2.8635(2)	0.4204(1)	0.010
7	0.24	0.410 78(5)	2.8639(3)	0.4185(1)	0.011
9	0.35	0.409 73(5)	2.8630(3)	0.4162(1)	0.011
11	0.46	0.408 62(5)	2.8612(3)	0.4137(1)	0.010
12	0.66	0.406 84(7)	2.8599(5)	0.4099(2)	0.015

* $\Delta = \sum_i^N |2\theta_{\text{exp}} - 2\theta_{\text{calc}}|/N$, where $2\theta_{\text{exp}}$ is the experimental diffraction angle, $2\theta_{\text{calc}}$ is the angle calculated from lattice parameters and N is the number of investigated diffraction lines.

from the voltage drop measured across the Hall contacts. The Seebeck coefficient was determined for the direction $\Delta T \perp \bar{c}$, that is $\alpha(\Delta T \perp \bar{c})$. The temperature difference between the cold and hot junction was not higher than 10 K.

Measurement of the Seebeck coefficient by means of a special probe [6], making possible measurement of the variations or profile of α values on the cleavage faces, was used to investigate the homogeneity of the crystals. By reading the thermoelectric voltage in steps of 0.05 mm we determined the Seebeck coefficient profile in the directions parallel and perpendicular to the axis of the crystals.

3. Results and discussion

3.1. Lattice parameters of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals

The results of X-ray structure analysis of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals are given in Table I. It is evident that with increasing value of x , the lattice parameter a decreases whereas parameter c first slightly increases with maximum value corresponding to $x = 0.24$ and then, in the range of higher indium content, also decreases. The volume, V , of the unit cell monotonically decreases with increasing x . Decreasing values of V can be taken as a proof of the formation of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ mixed crystals. That is, we can adopt a plausible assumption that substitution of smaller indium atoms for bismuth atom into the Bi_2Se_3 crystal lattice would give rise to a decrease of the unit cell volume.

The diffractograms of all samples showed only the lines corresponding to the tetradymite structure; hence the prepared $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals have a structure described by the $D_{3d}^5-R\bar{3}m$ space group. This fact is in agreement with the results of Belotskii and Demyanchuk [1], according to whom there exists a continuous range of tetradymite structure crystals in the system of Bi_2Se_3 - In_2Se_3 solid solutions.

3.2. Homogeneity of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals

With respect to the chosen method of preparation of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ single crystal from the melt, considerable attention was paid to the investigations of homogeneity of these crystals. On the basis of a comparison of melting points of both components of the Bi_2Se_3 - In_2Se_3 system (according to Abrikosov *et al.* [7] the melting point of Bi_2Se_3 is equal to 706°C , according to Slavnova *et al.* [8] the melting point of In_2Se_3 is $900 \pm 10^\circ\text{C}$) one can expect a strong gradient of indium

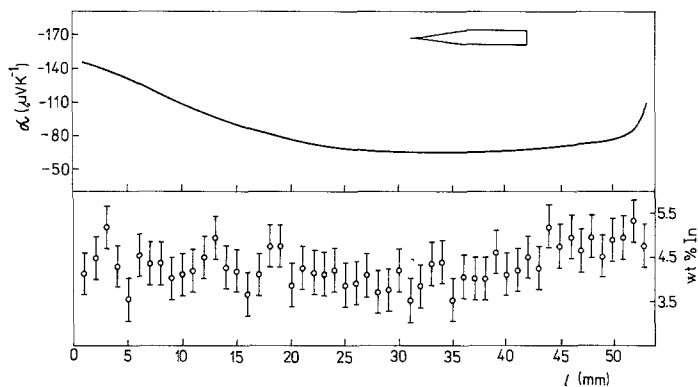


Figure 2 Comparison of the variations of the Seebeck coefficient measured on the cleavage face of a $\text{Bi}_{1.78}\text{In}_{0.22}\text{Se}_3$ crystal in the direction of crystal axis with the results of indium content determination.

concentration along the crystal axis, from the bottom tip to the upper end. It is reasonable to assume that, during growth of crystals by the Bridgman method, the tip of the crystals would contain an excess concentration of the component with higher melting point - In_2Se_3 ; towards the upper end of the crystal one can expect a gradual increase of the concentration of the component whose melting point is lower - Bi_2Se_3 .

If we suppose that the incorporation of indium atoms into the Bi_2Se_3 crystal lattice results in a change of the free carrier concentration N , the expected gradient of indium content should manifest itself in the values of all the properties that depend on N . For this reason, the homogeneity was tested using the measurements of the variations of the Seebeck coefficient by means of the probe described by Priemuth *et al.* [6].

Fig. 2 shows the variation of the Seebeck coefficient measured along the crystal axis on sample 6 ($\text{Bi}_{1.78}\text{In}_{0.22}\text{Se}_3$) compared with the results of indium content measurements by means of an energy dispersion analyser. It is evident from the $\alpha = f(l)$ plots that the value of α abruptly increases at the upper end of the crystal, being virtually constant in the middle part. A gradual increase of α towards the lower end of the crystal is observed in the tip region. The results shown of the determination of indium content, however, do not allow any unambiguous conclusion to be drawn on the gradient of indium content along the crystal axis; on the contrary, it seems that the results of the analysis exhibit only a scatter about a nearly constant value. Hence, there is no expected gradient of indium content along the crystal axis (i.e. it cannot be determined by the analytical method used). Therefore, it seems that the course of the $\alpha = f(l)$ dependence is not connected with the variation of indium concentration along the sample.

Fig. 3 shows the variations of Seebeck coefficient on a cleavage face in the direction perpendicular to the crystal axis (across the crystal) of a $\text{Bi}_{1.78}\text{In}_{0.22}\text{Se}_3$ sample, measured at distances of 2, 9 and 16 mm from the upper end of the crystal. It is seen that irrespective of the distance from the crystal end, the character of the $\alpha = f(l)$ dependence is the same - exhibiting practically constant values in the middle part, with a noticeable, relatively steep rise of α close to the margin (surface) of the crystal. It is evident from the results of the analysis of indium content, shown in Fig. 3, that these dependences are also not related to the gradient of indium content; in fact, no concentration gradient

of indium is expected in this direction, i.e. perpendicular to the pulling direction. This fact corroborates the conclusion mentioned above, that the variations of α determined along the crystal axis, are also not connected with concentration gradient of indium.

The observed variations of the Seebeck coefficient, hence also of the free carrier concentration, in the vicinity of the crystal surface and in its tip can be, in our opinion, accounted for as follows. As is known, in growing the Bi_2Se_3 crystals from a melt of stoichiometric composition, the crystals obtained always exhibit a superstoichiometry of bismuth [9], with some fraction of selenium segregating on the crystal surface. During the passage of the grown crystal through the temperature gradient in the Bridgman furnace at tem-

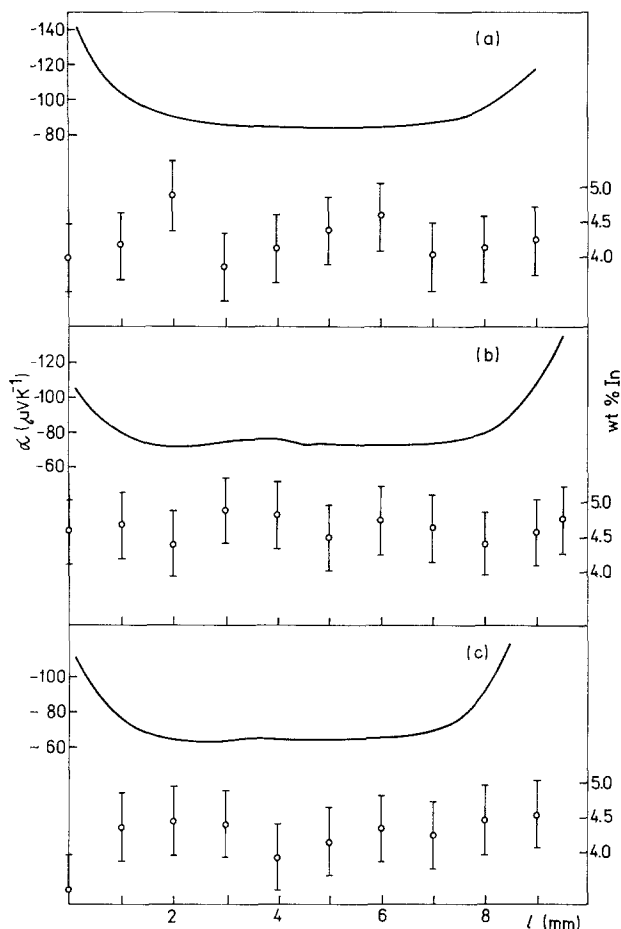


Figure 3 Comparison of the variations of the Seebeck coefficient measured on the cleavage face of a $\text{Bi}_{1.78}\text{In}_{0.22}\text{Se}_3$ crystal in the direction perpendicular to crystal axis with the results of indium content determination: measured (a) 2 mm, (b) 9 mm, (c) 16 mm from the upper end of the crystal.

peratures close to the melting point, one cannot prevent selenium segregation on the surface from diffusing into the crystal. Taking into account the view that selenium substoichiometry in the crystal lattice of Bi_2Se_3 results in the formation of positively charged selenium vacancies, V_{Se}^+ , whose charge is compensated by free electrons [10], the idea of selenium diffusing into surface layers of the crystal and occupying the V_{Se}^+ vacancies seems acceptable. The occupation of V_{Se}^+ vacancies then gives rise to a suppression of the free electron concentration. This, in turn, leads to the increase in the values of the Seebeck coefficient in the vicinity of the surface and in the narrow tip of the crystal. Owing to the fact that the prepared crystals were grown from the batches weighed up in stoichiometry corresponding to the formula $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$, segregation of selenium can be supposed to occur. That is why this view is well acceptable.

The suppression of the concentration of free carriers in Bi_2Se_3 by annealing in a selenium atmosphere, which results in a decrease of the electrical conductivity and an increase of the Hall constant and Seebeck coefficient, as reported by Gobrecht *et al.* [11], supports the interpretation given above of the experimental $\alpha = f(I)$ dependences.

It can thus be stated that the $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals prepared under the described conditions were homogeneous in their middle parts; the "inhomogeneity" observed in the surface layers and in the tip of the crystal was due to diffusion of selenium segregated on the surface. In view of this fact the samples used for the determination of transport coefficients were always cut from the middle parts of the crystals.

3.3. Transport coefficients of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals

The results of measurements of the transport coefficients of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ samples are summarized in Table II and in Figs 4 and 5. It is clearly seen that in the region of small x values, the $R_{\text{H}} = f(x)$ and $\alpha = f(x)$ dependences exhibit a noticeable decrease (with a minimum near the value $x = 0.1$), whereas at higher indium concentrations there is a marked increase of both R_{H} and α . The $\alpha = f(x)$ curve passes at first through an insignificant maximum and decreases at higher indium concentrations.

The variations of these quantities testify that the

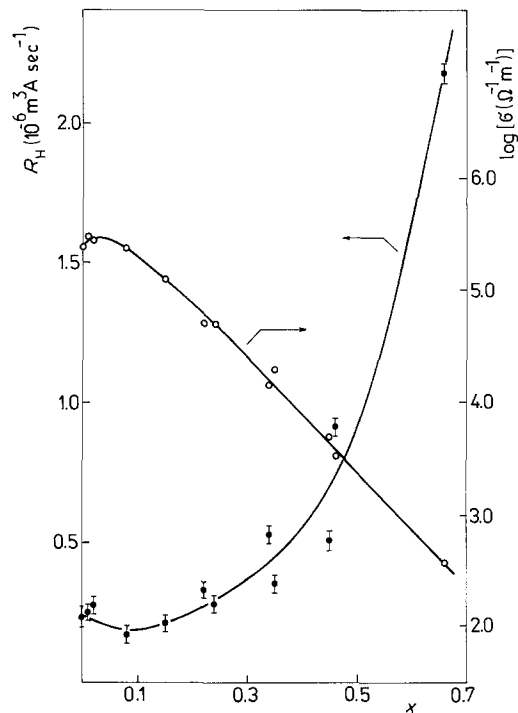


Figure 4 Plots of the Hall constant $R_{\text{H}}(\vec{B} \parallel \vec{c})$ and electrical conductivity $\sigma_{\perp c}$ of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals against indium content.

substitution of indium for bismuth atoms in the Bi_2Se_3 crystal lattice gives rise to an increase of free carrier electron concentration in the region of low indium content, whereas for higher indium content, the free electron concentration becomes suppressed.

Fig. 5 shows the dependence of the product $R_{\text{H}} \sigma$ against x , which yields information about the mobility of free carriers. The values of $R_{\text{H}} \sigma$ markedly decrease with increasing indium content; in the first approximation one can say that the mobility of free electrons in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ samples decreases with increasing x . The observed drop in the mobility is probably connected with the fact that the maximum in the $\sigma_{\perp c} = f(x)$ dependence is less significant than the minima of $R_{\text{H}} = f(x)$ and $\alpha = f(x)$ curves.

3.4. Point defects in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals

The change in free electron concentration in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ samples with increasing x value, as follows from the measurements of transport coefficients, is related to the manner in which indium atoms are

TABLE II Transport coefficients of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals at 300 K

Sample no.	x	$R_{\text{H}}(\vec{B} \parallel \vec{c})$ ($10^{-6} \text{ m}^3 \text{ A}^{-1} \text{ sec}^{-1}$)	$\sigma_{\perp c}$ ($10^3 \Omega^{-1} \text{ m}^{-1}$)	$\alpha(\Delta T \perp \vec{c})$ ($\mu\text{V K}^{-1}$)	$R_{\text{H}}(\vec{B} \parallel \vec{c}) \times \sigma_{\perp c}$ ($10^{-3} \text{ m}^2 \text{ V}^{-1} \text{ sec}^{-1}$)
1	0	-0.237	260	-61	61.6
2	0.01	-0.252	310	-59	78.1
3	0.02	-0.278	277	-51	77.0
4	0.08	-0.170	250	-48	42.5
5	0.15	-0.210	124	-43	26.0
6	0.22	-0.330	50.0	-60	16.5
7	0.24	-0.282	49.6	-53	13.9
8	0.34	-0.530	14.9	-98	7.89
9	0.35	-0.355	20.0	-70	7.10
10	0.45	-0.507	5.08	-110	2.58
11	0.46	-0.916	3.20	-135	2.93
12	0.66	-2.170	0.360	-263	0.781

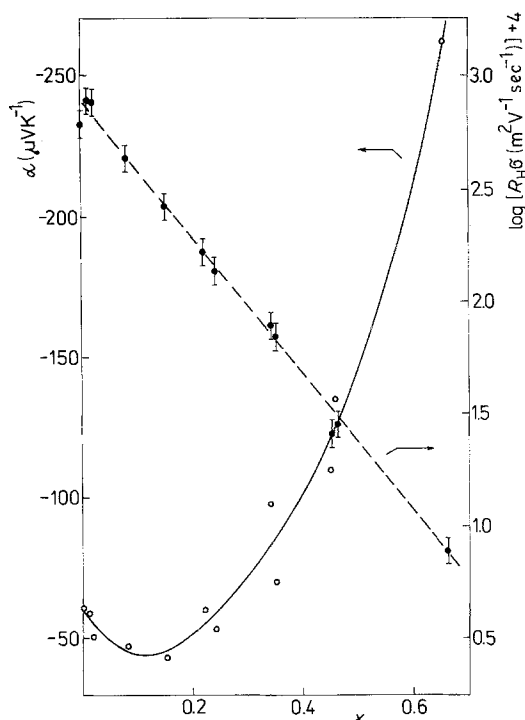


Figure 5 Plots of the Seebeck coefficient $\alpha(\Delta T \perp \bar{c})$ and the product $R_H \sigma$ of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals against indium content.

built into the Bi_2Se_3 crystal lattice, i.e. to the point defects in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals. The observed effect can be qualitatively explained as follows. The increase in the electron concentration observed in the region of low indium content is obviously connected with the fact that in the crystal lattice of "pure" Bi_2Se_3 there are not only the positively charged selenium vacancies, V_{Se}^+ , supposed by Bogatyrev *et al.* [10]. If we admit the possibility that, in addition to the dominant V_{Se}^+ defects, the crystal lattice of Bi_2Se_3 (and that in a considerably lower concentration) antisite bismuth defects, Bi_{Se}' , in a selenium sublattice, the free electron concentration is a result of compensation of charges of both types of defect. The idea of Bi_{Se}' defects existing in the lattice is an acceptable one, if we take into account that antisite Bi_{Te}' defects were found to exist in isostructural Bi_2Te_3 [12]. The substitution of indium atoms for bismuth results in the formation of uncharged substitution defects of indium atoms In_{Bi}^x in the bismuth sublattice. The mentioned type of defect, In_{Bi}^x , is in agreement with the ideas proposed by Krebs [13], according to which the bonds between bismuth and selenium are formed by electrons from the p orbitals of both elements. The configuration of the valence electrons of indium atoms forming uncharged defects is $5s^0 5p^3$. If we accept the ideas on the polarization of the lattice, due to incorporation of foreign atoms, as mentioned in our earlier papers [14–17], we can say that because of lower electronegativity of indium atoms compared to those of bismuth, in In_{Bi}^x defect carries a partial positive charge. This charge results in an increase in the polarity of bonds between the defect and the neighbouring selenium atoms ($\text{In}_{\text{Bi}}^{x(+)}\text{-Se}$) compared to the polarity of bonds in the initial Bi_2Se_3 . The higher bond polarity manifests itself by a decrease in the probability of formation of antisite defects Bi_{Se}' , whose existence is favoured by low bond polarity. The

concentration of Bi_{Se}' defects therefore decreases, their compensation effect is lowered, hence the free electron concentration increases. According to this idea, the extremes in the $R_H = f(x)$ and $\alpha = f(x)$ plots correspond to the crystals that are free from antisite defects.

The decrease in the free electron concentration, evident in the range of higher x , is probably due to a decrease in the concentration of V_{Se}^+ vacancies in $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystal lattice. The lowering V_{Se}^+ concentration with increasing indium content is undoubtedly connected with the fact that the increasing indium concentration in the mixed crystal leads to an increase of the forbidden gap width, to higher crystals ionicity; in isostructural $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals this effect shows up in a lowering of the mobility of free carriers. Increasing ionicity of $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ crystals with increasing content of indium atoms apparently leads to a lowering of the departure from stoichiometry and thus to a decrease of the concentration of V_{Se}^+ vacancies. This, in turn, results in a decrease of the free electron concentration, as proved experimentally.

This view is in a good agreement with the ideas due to van Vechten [18]; who noted that in the crystal lattice of binary compounds the more frequent vacancies are those of the atoms whose radius is smaller. In a series of isostructural crystals one can thus expect that the concentration of vacancies increases with increasing difference between the sizes of cations and anions and vice versa. In $\text{Bi}_{2-x}\text{In}_x\text{Se}_3$ smaller indium atoms are substituted for larger bismuth atoms; hence the "effective" radius of atoms in the cation sublattice decreases, which results in a smaller difference between the sizes of atoms in the cation and anion sublattice. This, in turn, manifests itself in a decrease of the concentration of selenium vacancies, V_{Se}^+ .

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