

Free Current Carrier Concentration and Point Defects in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ Crystals

T. Plecháček, J. Navrátil, and J. Horák

Joint Laboratory of Solid State Chemistry of the Academy of Sciences of the Czech Republic and University of Pardubice, Studentská 84,
532 10 Pardubice, Czech Republic
E-mail: tomas.plechacek@upce.cz

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From IR reflectivity spectra measurement on natural (0001) cleavage planes of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals (space group $D_{3d}^5-R\bar{3}m$), values of plasma resonance frequency ω_p were determined. Using the model respecting the existence of light and heavy electrons the dependence of free current carriers concentration on Sb-atom content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals (for $x = 0.0 - 0.4$) was obtained. There is a maximum in this dependence at lower Sb concentration ($x \cong 0.024$). This effect is explained by a model of point defects, where both the concentration of negatively charged native defects in a Bi_2Se_3 lattice (anti-site defect Bi'_{Se} , “seven-layer lamellae” Bi_3Se_4) and the concentration of vacancies in a selenium sublattice (V_{Se}^{**}) decreases with Sb content. On this basis the observed rise of the Hall mobility $R_{\text{H}}\sigma$ in the range from 500 to 1200 cm^2/Vs is explained. © 2002 Elsevier Science (USA)

Key Words: crystals of tetradymite structure; Hall coefficient; electrical conductivity; reflectivity in the plasma resonance frequency region; lattice defects.

1. INTRODUCTION

Some solid solutions based on narrow-gap layered semiconductors $A_2^V B_3^{VI}$ ($A = \text{Bi}, \text{Sb}, B = \text{Se}, \text{Te}$) belong to the group having a tetradymite structure (space group $D_{3d}^5 - R\bar{3}m$). The crystal lattice consists of layers, each layer comprising five atomic planes oriented perpendicular to the trigonal c axis and alternating according to the scheme



with a van der Waals gap between the Se^1 atomic planes.

Since these materials find applications in the field of construction of thermoelectric devices (1), they are an object of both theoretical and applied research.

Despite considerable attention devoted to the research of bismuth selenide and of mixed crystals derived from the Bi_2Se_3 structure, there are few data on crystal lattice defects

and transport properties of the mixed crystals in the Bi_2Se_3 – Sb_2Se_3 system. $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ mixed crystals have the tetradymite structure up to the Sb content $x=0.66$ (according to Ref. (2)), while according to Ref. (3) it is up to $x=0.55$ under suitable cooling conditions during crystal growth. Some information on electrical conductivity and thermoelectric properties of polycrystalline Bi_2Se_3 – Sb_2Se_3 samples is presented in Ref. (4). Characterization of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ ($x=0.0 - 0.4$) single crystals by means of transport coefficients and thermoelectric properties is in (3, 5, 6); basic information on optical properties (transmissivity and reflectivity in the IR region) is in Ref. (7). In Refs. (8, 9) there is an idea on conduction band splitting of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals and information on effective masses of electrons measured by means of cyclotron resonance and Shubnikov–de Haas effect. The extreme in the dependencies of transport and Seebeck coefficients on Sb content ($x \cong 0.024$) is in Ref. (3) qualitatively explained by the existence of negatively charged defects in the crystal structure, however, this effect has not been interpreted unambiguously yet.

In the present paper we describe changes of free current carriers concentration with the content of antimony entering into the crystal structure, and we explain apparently anomalous dependencies of the Hall coefficient, electrical conductivity, and plasma resonance frequency on Sb content using the model of point defects. Using this model we also explain the rise of Hall mobility with an increase of antimony content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ mixed crystals.

2. EXPERIMENTAL

2.1. Growth of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ ($x=0.0 - 0.4$) Single Crystals

$\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals were grown using a modified Bridgman method (3). The single crystals

obtained, 50 mm in length and 10 mm in diameter, are well cleavable in the direction perpendicular to the trigonal \mathbf{c} axis, i.e., along the (0001) planes. The orientation of the cleavage faces was checked using the Laue back-diffraction technique, which confirmed that these faces were always (0001).

The samples were cut out from the central part of the single crystals. First the reflectivity was measured on the natural cleavage faces and then the measurement of the Hall coefficient and the electrical conductivity were carried out. Finally, the actual concentration of antimony in these samples was determined using an energy dispersive X-ray analyzer Kevex Delta 5 with Quantum detector.

2.2. Measurements of the Transport Coefficients

The electrical conductivity σ and the Hall coefficient R_H were measured on the bar samples of dimensions $14 \times 3.5 \times (0.1-0.3) \text{ mm}^3$ at room temperature. The measurements were realized using alternating current at a frequency of 1020 Hz. A stationary magnetic field having an induction of 0.7 T and an orientation $\mathbf{B} \parallel \mathbf{c}$ was used. The current contacts were made with the help of coated gold layer and silver paste; mechanical contacts for the Hall voltage measurement were used. The value of the electrical conductivity $\sigma_{\perp \mathbf{c}} \equiv \sigma$ has been determined from the potential drop across the sample between the voltage contacts.

2.3. Measurements of the Reflectance Spectra

Spectral dependencies of the reflectance R in the plasma resonance frequency were measured at room temperature in unpolarized light on natural (0001) cleavage planes using a Biorad FTS-45 FT-IR spectrometer with 12.5° specular reflectance accessory. The geometry of the experiment was such that the electric field vector \mathbf{E} of the electromagnetic radiation was always perpendicular to the trigonal \mathbf{c} axis, i.e., $\mathbf{E} \perp \mathbf{c}$. For the recording of the spectrum the following procedure was used. First, the background single beam spectrum was collected by using an aluminum mirror in place of the sample, then the sample single beam was recorded and the reflectivity spectrum was obtained as the ratio of the sample to background spectrum.

3. DISCUSSION

Dependencies of σ_{\perp} , $R_H(\mathbf{B} \parallel \mathbf{c})$, and $\omega_p(\mathbf{E} \perp \mathbf{c})$ on Sb content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals are illustrated in Figs. 1 and 3. They show the presence of extremes in the range of low Sb content ($x \cong 0.024$), with maxima in σ_{\perp} and $\omega_p(\mathbf{E} \perp \mathbf{c})$ and minimum in $R_H(\mathbf{B} \parallel \mathbf{c})$, respectively.

The progressive substitution of cations in Bi_2Se_3 with Sb atoms causes the changes in physical properties of the

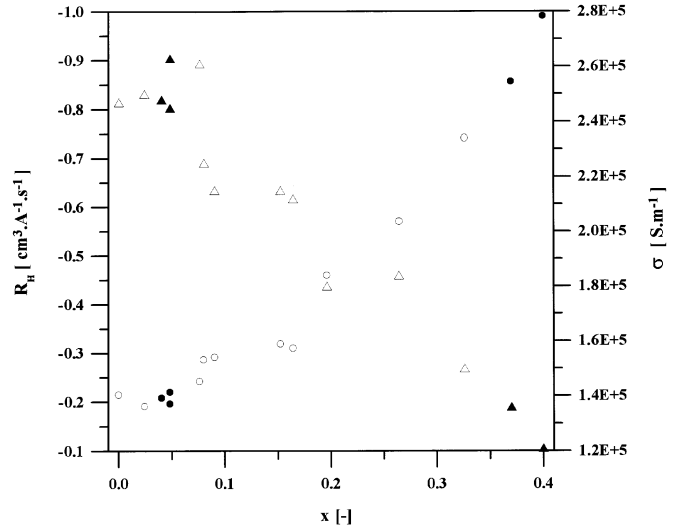


FIG. 1. Dependencies of Hall coefficient R_H (marked ●, ○) and electrical conductivity σ (marked ▲, △) on the concentration of Sb in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals. (Values denoted by ○ and △ are taken from Ref. (3).)

mixed crystals. However, the arrangement of atoms (the value of lattice parameters) in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ mixed crystals for $x=0-0.5$ does not change (3). The changes in antimony content influence the chemical bond parameters (atomic charge, bond order, interatomic distances), which bear on the changes of some optical properties. An increase in Sb content causes an absorption edge shift toward higher photon energies—the energy gap increases. One can expect that the effective mass of free carriers will increase or change. However, the cyclotron resonance measurements on $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals (8) and mainly the Shubnikov–de Haas effect measurement (9) confirm that the value of the electron effective mass perpendicular to the trigonal \mathbf{c} axis does not depend on x in the investigated range of the Sb-atom concentration, i.e., for $x=0.0-0.4$. The changes of the properties of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals due to the Sb atom incorporation could be characterized by the changes of refraction index or the high-frequency permittivity. In our paper this is respected by interpretation of reflection spectra, which we use for the calculation of free electron concentration.

With the aim to explain the above-mentioned anomalous courses the following assumptions were accepted:

(a) The incorporation of Sb atoms into the mixed crystal causes the creation of uncharged substitutional defects Sb_{Bi}^x , i.e., Sb atoms in the cation sublattice.

(b) The anomaly observed in electron concentration course is not connected with changes of free carrier effective mass.

Therefore the anomaly is caused by changes in the concentration of point defects in the Bi_2Se_3 crystal structure due to the incorporation of Sb atoms.

To encourage this statement, we have the following:

(1) The concentration of free electrons in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals in dependence on Sb content in the crystal were calculated from experimental data.

(2) The idea of changes in the concentration of point defects due to the incorporation of Sb atoms into the Bi_2Se_3 crystal structure is presented on the basis of the influence of superstoichiometric bismuth content in Bi_2Se_3 crystals.

(ad 1) According to Refs. (8, 9) the conduction band of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals is split into two subbands; heavy electrons with an effective mass $m_1 = 0.105m_0$ in the direction perpendicular to the \mathbf{c} axis and with a density-of-state effective mass $m_{d1} = 0.123m_0$ belonging to the lower subband (LCB); light electrons with an effective mass $m_2 = 0.075m_0$ and with a density-of-state effective mass $m_{d2} = 0.11m_0$ belonging to the upper subband (UCB), whose minimum is shifted 40 meV toward higher energies.

Concentrations of heavy electrons n_1 and of light electrons n_2 were calculated using the values of effective masses, the expression for electron concentration (10)

$$n_1 = 4\pi \left(\frac{2m_{d1}k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta) \quad [1]$$

$$n_2 = 4\pi \left(\frac{2m_{d2}k_B T}{h^2} \right)^{3/2} F_{1/2}(\eta - \delta) \quad [2]$$

(k_B is the Boltzmann constant, $\eta = E_F/(k_B T)$ is reduced Fermi energy; $\delta = \Delta E/(k_B T)$, where ΔE is energy separation between LCB and UCB; $F_{1/2}(\eta)$ is the Fermi integral) and the relation between the concentration of free electrons and plasma resonance frequency ω_p (obtained by fitting the reflectivity spectra shown in Fig. 2)

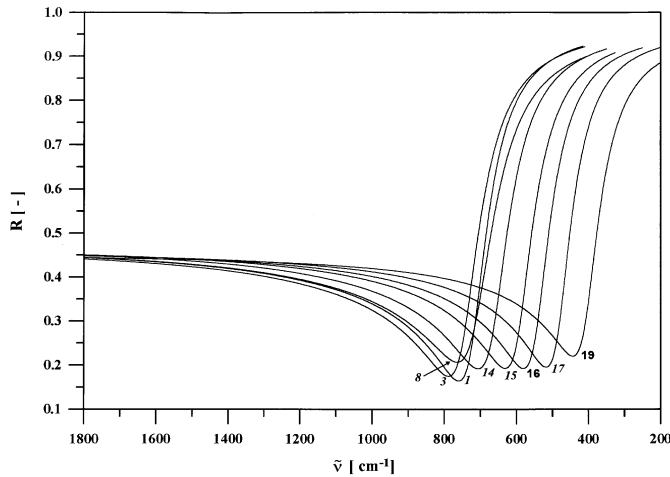


FIG. 2. Reflectance spectra of some $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ single crystals. (Samples are labeled according to Table 1. Spectra denoted by italic font are taken from Ref. (7).)

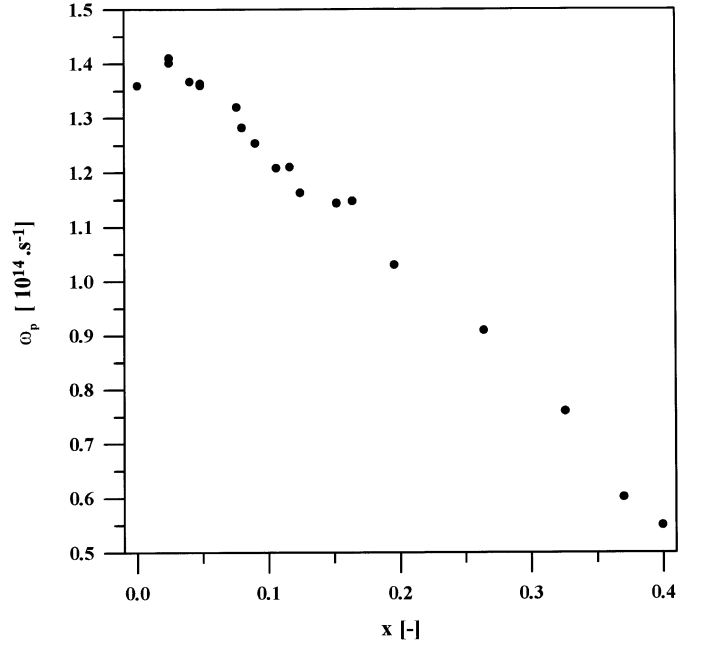


FIG. 3. Dependence of plasma resonance frequency ω_p on the concentration of Sb in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals.

following from (7) and (11),

$$\omega_p^2 = \frac{e^2}{\epsilon_0 \epsilon_\infty} \left(\frac{n_1}{m_1} + \frac{n_2}{m_2} \right) \quad [3]$$

(ϵ_0 is the permittivity of free space, ϵ_∞ is the high-frequency relative permittivity, e is the electron charge).

The results, i.e., the calculated course of $\eta = f(x)$, and the dependencies of n_1 , n_2 on Sb content are summarized in Table 1 and $n = (n_1 + n_2)$ is plotted in Fig. 4. In the region of low content of Sb ($x \cong 0.024$) a slight increase of free electron concentration is obvious; for higher Sb content the concentration of electrons decreases.

(ad 2) The creation and concentration of native defects is closely associated with the overstoichiometry of Bi atoms in Bi_2Se_3 . These bismuth atoms can induce the following defects:

(a) Selenium vacancy $V_{\text{Se}}^{\bullet\bullet}$ with 2 positive charges (defect is compensated with two electrons).

(b) Negatively charged anti-site (AS) defect Bi'_{Se} i.e., Bi atom in Se^2 plane of Se sublattice (6).

(c) Bi–Bi double layers located in the van der Waals gap (12),

(d) Structural defect of “seven-” (Bi_3Se_4^-) or “nine-layer lamellae” ($\text{Bi}_4\text{Se}_5^{2-}$) carrying one or two negative charges (13, 14).

Two types of defects, e.g., (Bi'_{Se} and $V_{\text{Se}}^{\bullet\bullet}$ or $V_{\text{Se}}^{\bullet\bullet}$ and Bi_3Se_4^-), could exist in the crystal at the same time. However, defects (b) and (d) are indistinguishable by means of electron concentration measurement.

TABLE 1
Plasma Resonance Frequency, Reduced Fermi Energy, and
Concentration of Electrons of $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ Single Crystals

Sample	x	ω_p (10^{14} s^{-1})	η	n_1 (10^{25} m^{-3})	n_2 (10^{25} m^{-3})
1	0	1.36	5.35	1.05	0.55
2	0.024	1.40	5.54	1.10	0.55
3	0.024	1.41	5.60	1.11	0.59
4	0.040	1.37	5.39	1.06	0.57
5	0.048	1.36	5.37	1.06	0.57
6	0.048	1.36	5.35	1.05	0.55
7	0.076	1.32	5.12	0.99	0.51
8	0.080	1.28	4.94	0.92	0.46
9	0.090	1.25	4.80	0.90	0.44
10	0.106	1.21	4.59	0.85	0.41
11	0.116	1.21	4.57	0.84	0.40
12	0.124	1.16	4.35	0.79	0.37
13	0.152	1.14	4.24	0.76	0.35
14	0.164	1.15	4.26	0.74	0.34
15	0.196	1.03	3.61	0.62	0.26
16	0.264	0.91	3.06	0.50	0.20
17	0.326	0.76	2.32	0.36	0.12
18	0.370	0.60	1.35	0.21	0.06
19	0.400	0.55	1.08	0.18	0.05

Further, we adopt the following principles and simplifications:

—The native defects arise during the crystal growth, i.e., on transition from the melt to the solid phase (melting point T_m).

—The interaction between Sb atoms, entering into the crystal lattice, and native defects passes at T_m . Below this temperature the concentration of point defects is unchanged.

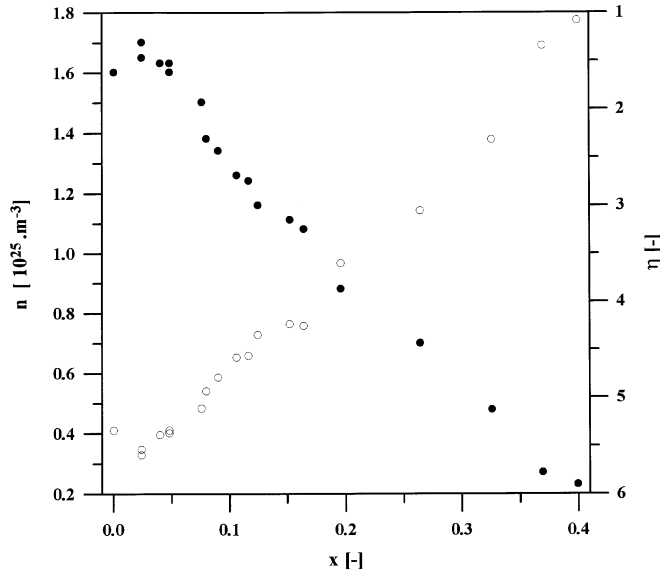
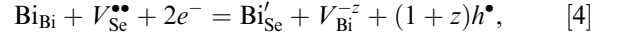


FIG. 4. Dependencies of reduced Fermi energy η and free electron concentration n (calculated from optical measurement) on antimony content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals.

—The process of the creation and interaction of the native defects approaches an equilibrium state, which can be formulated by means of



where h^{\bullet} denotes a hole, e^- an electron, V_{Bi}^{-z} is bismuth vacancy with negative charge z , Bi_{Bi} denotes a Bi atom on a regular Bi site.

As the crystal prepared from the melt of stoichiometric composition possesses superstoichiometry of Bi and a high content of AS defects, we suppose that $[V_{\text{Se}}^{\bullet\bullet}] \gg [V_{\text{Bi}}^{-z}]$ and $[\text{Bi}'_{\text{Se}}] \gg [V_{\text{Bi}}^{-z}]$.

Under given conditions, we can express the concentration of electrons

$$n = 2([V_{\text{Se}1}^{\bullet\bullet}] + [V_{\text{Se}2}^{\bullet\bullet}]) - [\text{Bi}'_{\text{Se}}] \quad [5]$$

$$[V_{\text{Se}1}^{\bullet\bullet}] = N_{\text{Se}1} \exp(-E_{V_{\text{Se}1}}/k_B T_m) \quad [6a]$$

$$[V_{\text{Se}2}^{\bullet\bullet}] = N_{\text{Se}2} \exp(-E_{V_{\text{Se}2}}/k_B T_m) \quad [6b]$$

$$[\text{Bi}'_{\text{Se}}] = N_{\text{Se}2} \exp(-E_{\text{AS}}/k_B T_m), \quad [6c]$$

where $[V_{\text{Se}1}^{\bullet\bullet}]$ is the concentration of vacancies $[V_{\text{Se}1}^{\bullet\bullet}]$ in Se^1 planes, $[V_{\text{Se}2}^{\bullet\bullet}]$ is the concentration of vacancies $V_{\text{Se}2}^{\bullet\bullet}$ in Se^2 planes, $[\text{Bi}'_{\text{Se}}]$ is the concentration of anti-site defects Bi'_{Se} in Se^2 planes, $N_{\text{Se}1}$, $N_{\text{Se}2}$ denote the number of Se^1 , Se^2 sites in an anion sublattice of unitary volume of a Bi_2Se_3 crystal, $E_{V_{\text{Se}1}}$, $E_{V_{\text{Se}2}}$, and E_{AS} are the energies of formation of vacancies $V_{\text{Se}1}^{\bullet\bullet}$, $V_{\text{Se}2}^{\bullet\bullet}$, and anti-site defects Bi'_{Se} respectively, k_B is the Boltzmann constant, and T_m is the melting point temperature.

The formation energy can be derived from the known concentration of superstoichiometric Bi atoms, a concentration of free electrons, and using

$$a \text{ Bi} + b(V_{\text{Bi}}''' + 3/2V_{\text{Se}}^{\bullet\bullet}) = (a-b)\text{Bi}'_{\text{Se}} + b\text{Bi}_{\text{Bi}} + (5/2b-a)V_{\text{Se}}^{\bullet\bullet} + (6b-3a)e^-, \quad [7]$$

which expresses the incorporation of Sb atoms into the crystal structure and the condition of charge electroneutrality.

The free energy F of the Bi_2Se_3 crystal, assuming the existence of vacancies and AS defects, is given by

$$F = F_0 + [V_{\text{Se}1}^{\bullet\bullet}] \cdot \mu_{V_{\text{Se}1}} + [V_{\text{Se}2}^{\bullet\bullet}] \cdot \mu_{V_{\text{Se}2}} + [\text{Bi}'_{\text{Se}}] \cdot \mu_{\text{AS}} + k_B T_m \cdot ([V_{\text{Se}1}^{\bullet\bullet}] \cdot \ln([V_{\text{Se}1}^{\bullet\bullet}]/N_{\text{Se}1}) + [V_{\text{Se}2}^{\bullet\bullet}] \cdot \ln([V_{\text{Se}2}^{\bullet\bullet}]/N_{\text{Se}2}) + [\text{Bi}'_{\text{Se}}] \cdot \ln([\text{Bi}'_{\text{Se}}]/N_{\text{Se}2}) + (N_{\text{Se}1} - [V_{\text{Se}1}^{\bullet\bullet}]) \cdot \ln((N_{\text{Se}1} - [V_{\text{Se}1}^{\bullet\bullet}])/N_{\text{Se}1}) + (N_{\text{Se}2} - [V_{\text{Se}2}^{\bullet\bullet}] - [\text{Bi}'_{\text{Se}}]) \cdot \ln((N_{\text{Se}2} - [V_{\text{Se}2}^{\bullet\bullet}] - [\text{Bi}'_{\text{Se}}])/N_{\text{Se}2})), \quad [8]$$

where F_0 is the free energy of the intact crystal, $\mu_{V_{\text{Se}1}}$, $\mu_{V_{\text{Se}2}}$, and μ_{AS} denote the chemical potentials of vacancies $V_{\text{Se}1}^{\bullet\bullet}$, $V_{\text{Se}2}^{\bullet\bullet}$, and AS defects, respectively. The values of these potentials can be treated as formation energy of the relevant defect.

Further, if we adopt the simplified idea that the concentration of point defects equals the steady state concentration, we obtain from a condition

$$dF/d[V_{\text{Se}1}^{\bullet\bullet}] = 0, dF/d[V_{\text{Se}2}^{\bullet\bullet}] = 0, dF/d[\text{Bi}'_{\text{Se}}] = 0 \quad [9]$$

expressions for the chemical potentials $\mu_{V_{\text{Se}1}}$, $\mu_{V_{\text{Se}2}}$, and μ_{AS} :

$$\begin{aligned} \mu_{V_{\text{Se}1}} = & -k_{\text{B}}T_{\text{m}} \cdot (\ln([V_{\text{Se}1}^{\bullet\bullet}]/N_{\text{Se}1}) - \ln((N_{\text{Se}1} \\ & - [V_{\text{Se}1}^{\bullet\bullet}])/N_{\text{Se}1})) \end{aligned} \quad [10]$$

$$\begin{aligned} \mu_{V_{\text{Se}2}} = & -k_{\text{B}}T_{\text{m}} \cdot (\ln([V_{\text{Se}2}^{\bullet\bullet}]/N_{\text{Se}2}) - \ln((N_{\text{Se}2} - [V_{\text{Se}2}^{\bullet\bullet}] \\ & - [\text{Bi}'_{\text{Se}}])/N_{\text{Se}2})) \end{aligned} \quad [11]$$

$$\begin{aligned} \mu_{\text{AS}} = & -k_{\text{B}}T_{\text{m}} \cdot (\ln([\text{Bi}'_{\text{Se}}]/N_{\text{Se}2}) - \ln((N_{\text{Se}2} - [V_{\text{Se}2}^{\bullet\bullet}] \\ & - [\text{Bi}'_{\text{Se}}])/N_{\text{Se}2})) \end{aligned} \quad [12]$$

In the calculation of chemical potentials the deviation from stoichiometry of Bi_2Se_3 published in Ref. (15) was used. According to the results in Ref. (15) there is $40.02 + 0.01$ at.% of Bi and $59.98 + 0.01$ at.% of Se in pure bismuth selenide. Furthermore the concentration of free electrons $n = 1.6 \times 10^{25} \text{ m}^{-3}$ determined from optical measurement and from Eq. [7] was used. The assumption that the concentration of $V_{\text{Se}1}^{\bullet\bullet}$ in the Se^1 plane and of $V_{\text{Se}2}^{\bullet\bullet}$ in the Se^2 plane of the unit cell is the same was accepted. Therefore, the values of chemical potential $\mu_{V_{\text{Se}1}}$ and $\mu_{V_{\text{Se}2}}$ equal. In that way listed above, the energies of formation of vacancies $E_{V_{\text{Se}1}} = E_{V_{\text{Se}2}} = E_{\text{V}} = 0.65 \text{ eV}$ and of anti-site defects $E_{\text{AS}} = 0.64 \text{ eV}$ of undoped Bi_2Se_3 crystal were determined. The incorporation of Sb atoms into the crystal causes changes in the concentration of free electrons and thus changes of the lattice defects formation energy in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ mixed crystals. This is related with changes of chemical bond parameters. Changes of E_{V} and E_{AS} can be in the first approximation estimated, accepting the assumption that energy changes ΔE_{V} , ΔE_{AS} will be linearly dependent on the content x of antimony atoms entered into the lattice, i.e., $\Delta E_{\text{V}}(x) = k_{\text{V}} \cdot x$, $\Delta E_{\text{AS}}(x) = k_{\text{AS}} \cdot x$. The equation [5] could then be expressed as

$$\begin{aligned} n(x) = & 2(N_{\text{Se}1} + N_{\text{Se}2}) \cdot \exp[-(E_{\text{V}} + \Delta E_{\text{V}}(x))/k_{\text{B}}T_{\text{m}}(x)] \\ & - N_{\text{Se}2} \cdot \exp[-(E_{\text{AS}} + \Delta E_{\text{AS}}(x))/k_{\text{B}}T_{\text{m}}(x)]. \end{aligned} \quad [13]$$

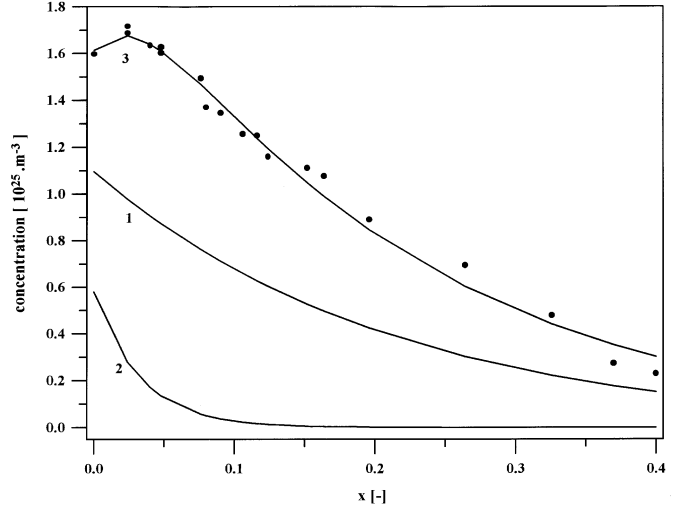
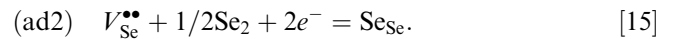
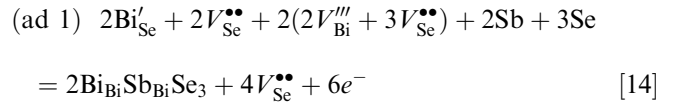


FIG. 5. Fit of the dependence of free carrier concentration on the Sb content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals: curve 1, concentration of double-charged $V_{\text{Se}}^{\bullet\bullet}$ vacancies; curve 2, concentration of the AS defects Bi'_{Se} ; curve 3, fitted concentration of free electrons using Eq. [13]. The solid circles denote electron concentration ($n_1 + n_2$) experimentally determined from optical measurement.

Experimentally determined dependence $n = f(x)$ was fitted using Eq. [13], data $T_{\text{m}}(x)$ from Ref. (2), and $E_{\text{V}} = 0.64 \text{ eV}$. It is evident from the dependence plotted in Fig. 5 that the entrance of Sb atoms into the cation sublattice rapidly reduces the concentration of negatively charged defects $[\text{Bi}'_{\text{Se}}]$ (curve 2). Electrons localized on the Bi'_{Se} defects are transferred into the conduction band and Bi atoms pass from the anion sublattice to the cation one; the concentration of electrons slightly increases. When the concentration of negatively charged defects is suppressed, the increase in antimony content tends to the occupation of $V_{\text{Se}}^{\bullet\bullet}$ vacancies by Se atoms (see Table 2) and to the creation of uncharged $\text{Sb}_{\text{Bi}}^{\times}$ defects. These two processes, i.e., (1) Bi'_{Se} defect suppression and (2) a decrease in concentration of selenium vacancies can be expressed by

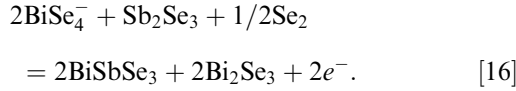


From Eqs. [14] and [15] it is evident that the increase in Sb content causes a decrease in deficit of Se atoms in the mixed crystals. This effect is not surprising since Sb_2Se_3 crystals exhibit a surplus of Se atoms. Interpretation of $n = f(x)$ dependence is evidence of the presence of negatively charged defects in crystals with low Sb content, however, it is impossible to distinguish between negatively charged

TABLE 2
Electron Concentration, Calculated Concentration of Bi'_{Se} (AS) Defects and $V_{\text{Se}}^{\bullet\bullet}$ Vacancies, and the Formation Energies E_{AS} and E_{V} in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ Single Crystals

Sample	x	$\frac{n_1+n_2}{(10^{25} \text{ m}^{-3})}$	$\frac{n_{\text{FIT}}}{(10^{25} \text{ m}^{-3})}$	$\frac{[V_{\text{Se}}^{\bullet\bullet}]}{(\text{m}^{-3})}$	$\frac{[\text{Bi}'_{\text{Se}}]}{(\text{m}^{-3})}$	E_{V} (eV)	E_{AS} (eV)
1	0	1.60	1.61	1.10×10^{25}	5.79×10^{24}	0.640	0.600
2	0.024	1.69	1.68	9.78×10^{24}	2.80×10^{24}	0.647	0.660
3	0.024	1.72	1.68	9.78×10^{24}	2.80×10^{24}	0.647	0.660
4	0.040	1.63	1.64	9.06×10^{24}	1.72×10^{24}	0.652	0.699
5	0.048	1.63	1.61	8.72×10^{24}	1.34×10^{24}	0.655	0.719
6	0.048	1.60	1.61	8.72×10^{24}	1.34×10^{24}	0.655	0.719
7	0.076	1.49	1.47	7.62×10^{24}	5.70×10^{23}	0.664	0.789
8	0.080	1.37	1.44	7.47×10^{24}	5.04×10^{23}	0.665	0.799
9	0.090	1.34	1.39	7.12×10^{24}	3.70×10^{23}	0.669	0.824
10	0.106	1.25	1.29	6.59×10^{24}	2.26×10^{23}	0.674	0.864
11	0.116	1.25	1.24	6.27×10^{24}	1.66×10^{23}	0.677	0.889
12	0.124	1.16	1.19	6.03×10^{24}	1.29×10^{23}	0.680	0.908
13	0.152	1.11	1.05	5.26×10^{24}	5.40×10^{22}	0.689	0.978
14	0.164	1.07	0.99	4.96×10^{24}	3.71×10^{22}	0.693	1.008
15	0.196	0.89	0.85	4.23×10^{24}	1.36×10^{22}	0.704	1.088
16	0.264	0.69	0.60	3.01×10^{24}	1.56×10^{21}	0.727	1.257
17	0.326	0.48	0.44	2.20×10^{24}	2.11×10^{20}	0.747	1.411
18	0.370	0.27	0.35	1.76×10^{24}	5.03×10^{19}	0.762	1.521
19	0.400	0.23	0.30	1.50×10^{24}	1.87×10^{19}	0.772	1.595

defects Bi'_{Se} and Bi_3Se_4^- by means of performed experiments. A decrease in Bi_3Se_4^- concentration is connected with a decrease in concentration of Se vacancies, too, and can be expressed as



A decrease in $V_{\text{Se}}^{\bullet\bullet}$ concentration can be schematically described as in Eq. [15].

Changes in concentration of Bi'_{Se} and $V_{\text{Se}}^{\bullet\bullet}$ defects affect the values of electrical conductivity, Hall coefficient, and Hall mobility. The dependence of Hall mobility ($R_{\text{H}} \cdot \sigma$) on x is plotted in Fig. 6.

As the band structure of these crystals has not been presented yet, the exact analysis of changes in mobility of free carriers cannot be done. However, it can be explained qualitatively:

Assuming the expression for the electrical conductivity σ and for the Hall coefficient R_{H} in the case of two types of electrons

$$\sigma = \sigma_1 + \sigma_2 \quad [17]$$

$$R_{\text{H}} = \left(\frac{\sigma_1^2}{\sigma^2} \right) \cdot \frac{1}{e \cdot n_1} + \left(\frac{\sigma_2^2}{\sigma^2} \right) \cdot \frac{\gamma}{e \cdot n_2}, \quad [18]$$

the Hall mobility can be expressed as

$$\mu_{\text{H}} \equiv R_{\text{H}} \cdot \sigma = \left(\frac{e \cdot n_1}{\sigma} \right) \cdot \mu_1^2 + \gamma \cdot \left(\frac{e \cdot n_2}{\sigma} \right) \cdot \mu_2^2 \\ \equiv A \cdot \mu_1^2 + \gamma \cdot B \cdot \mu_2^2. \quad [19]$$

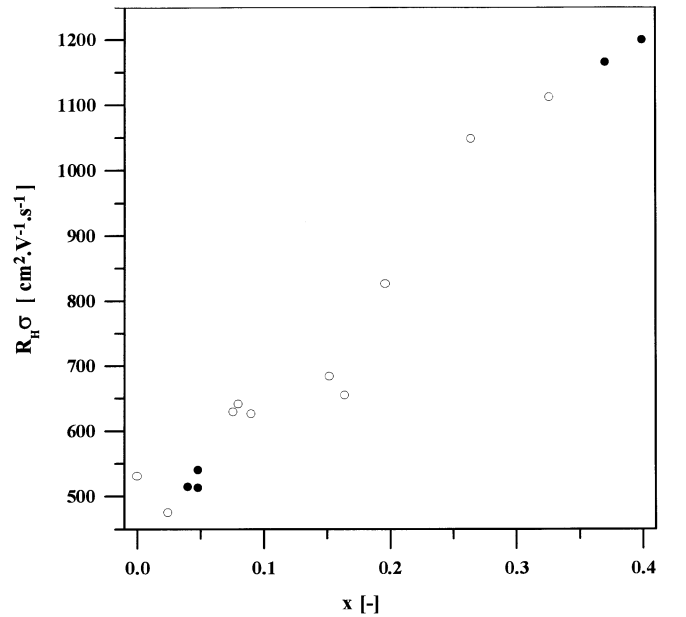


FIG. 6. Dependence of Hall mobility (product $R_{\text{H}}\sigma$) on the concentration of Sb in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ crystals. (Values denoted by \circ are taken from Ref. (3).)

As the values of quantities A and B decrease with a rise of antimony content in crystals and the value of structural factor γ is constant (according to Ref. (9)), both the mobility μ_1 of heavy electrons and the mobility μ_2 of light electrons will rise. This is due to the decrease in concentration of charged defects and free electrons and thus due to the increase in free path of electrons. The inexpressive minimum in $R_{\text{H}}\sigma$ dependence near $x = 0.024$ is caused by a simultaneous suppression of both negatively charged anti-site defects and positively charged selenium vacancies.

CONCLUSIONS

- Using the literature data on effective masses and the experimental optical data the concentration n_1 of heavy electrons and n_2 of light electrons and their dependence on antimony content in $\text{Bi}_{2-x}\text{Sb}_x\text{Se}_3$ mixed crystals were calculated.

The interpretation of reflectance spectra in the plasma resonance frequency region, which was used, can consider the changes of physical properties of mixed crystals caused by the incorporation of large amounts of Sb by means of changes of high-frequency relative permittivity.

- The existence of a maximum near $x = 0.024$ is explained using an idea of interaction of two types of point defects (anti-site defect $\text{Bi}'_{\text{Se}1}$ and selenium vacancy $V_{\text{Se}}^{\bullet\bullet}$) with Sb atoms entering into the crystal structure. The increase in concentration of uncharged substitutional defects Sb_{Bi}^x induces rapid suppression of negatively charged AS defects and the simultaneous decrease of selenium vacancy concentration. In the region of higher antimony content ($x > 0.1$) the decrease in both the concentration and the mobility of light and heavy electrons

is caused mainly by a decrease in concentration of vacancies in the selenium sublattice.

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