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$A_x^{III}B_{2-x}^{V}C_3^{VI}$ Crystals of Tetradymite Structure

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The concentration of holes in $In_xBi_{2-x}Te_3$ crystals for x = 0.0–01 has been determined using simplified assumptions on the basis of experimental values of the transport coefficients. These data and the calculated changes of bonding parameters were used to formulate more precisely the idea of the variation of the concentration of antisite defects in mixed crystals with increasing indium concentration. The obtained results have been employed in proposing a model that makes possible a generalization on the relations among structure, bonding, and concentration of antisite defects in $A_x^{III}B_{2-x}^{V}C_3^{VI}$ crystals. In agreement with the model it has been shown that the increasing content of In or Tl atoms results in an increase in the ratio c/a of the lattice parameters, in a decrease of the unit cell volume, in an increase of the electron density in the outer atomic planes of the layer, and in a decrease of the concentration of both the antisite defects and the free carriers. © 1991 Academic Press, Inc.

1. Introduction

Typical representatives of the crystals of tetradymite structure (space group D_{3d}^5–$R3m$) are Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. It is characteristic of these crystals that they form mixed crystals with corresponding chalcogenides of IIIb group elements of the periodic table. The highest solubility of the group IIIb chalcogenides has been observed in the Sb_2Te_3–In_2Te_3 system, as well as in the Bi_2Se_3–In_2Se_3 and Bi_2Te_3–In_2Te_3 systems (*1–4*).

The solubility of thallium chalcogenides is markedly lower in the chalcogenides with a tetradymite lattice. Nevertheless, $Tl_xSb_{2-x}Te_3$ crystals with relatively high thallium content in the cation sublattice have been prepared (*5*). The lower ability to form $A_x^{III}B_{2-x}^{V}C_3^{VI}$ mixed crystals, with A being thallium, is due to the higher stability of thallium in the +1 oxidation state. This view is supported by the existence of $TlBiTe_2$ and $TlBiSe_2$ crystals. The lowest solubility has been found in systems containing gallium chalcogenides. It seems that the Ga atom, owing to its smaller covalent radius, does not enter the cation sublattice as a substitutional atom, but enters the interstitial sites (*6, 7*), opposing thus the formation of mixed crystals.

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In our earlier papers (*5*, *8–15*) we studied the relations between the concentration of IIIb group atoms built in the tetradymite lattice, the changes of the lattice parameters, and the physical properties of the crystals that characterize these ternary crystals as semiconductors. A comparison of the results reported in (*8–15*), complemented by the ideas on the nature of the chemical bonding in these crystals as well as by further findings about the Bi_2Te_3–In_2Te_3 system, allows to formulate general relations among the structure, the character of the chemical bonding, the concentration of point defects in the lattice, the concentration of free carriers, and the corresponding physical properties. These regularities represent the objective of the present paper.

2. Experimental

2.1. Crystal Growth

Bi_2Te_3 crystals and $Bi_{2-x}In_xTe_3$ mixed crystals were prepared from elemental Bi, In, and Te of 5 N purity using the method described in our earlier papers (*12*, *14*). The crystals were pulled from the melt of corresponding stoichiometry by means of a modified Bridgman technique. After growth the crystals were annealed at 550°C for 24 hr. The concentration of In in the single crystal samples prepared in this way was determined using an electron microprobe. The In content in the mixed crystals varied in the interval $0 \leq x \leq 0.05$.

The orientation of the cleavage planes was checked by means of the Laue back-reflection technique. The cleavage planes have been identified as (0001) planes.

The lattice parameters of the crystals studied were determined from X-ray powder data obtained using an HZG-4B X-ray diffractometer (Freiberger Präzisionsmechanik, GDR). The diffraction maxima were measured using a stepwise procedure with steps of 0.01°. The measurements were carried out with Cu$K\alpha$ radiation in the range $2\Theta = 5°$ to $45°$ and with Cu$K\alpha_1$ radiation in the range $2\Theta = 45°$ to $100°$, using a nickel filter to reduce the $K\beta$ radiation. Calibration of the equipment was carried out on polycrystalline Si. The data published by Dönges (*16*) were used for indexing the maxima of the powder patterns and the lattice parameters a and c (Table I) were calculated from the diffraction patterns by means of a least-squares method.

TABLE I

LATTICE PARAMETERS OF $In_xBi_{2-x}Te_3$ CRYSTALS

Composition	Lattice parameters		
x	a (10^{-1} nm)	c (10^{-1} nm)	Δ^a
0.000	4.379_2	30.481	0.014
0.015	4.379_0	30.482	0.017
0.028	4.378_4	30.478	0.015
0.040	4.377_3	30.471	0.012
0.045	4.376_5	30.467	0.011

[a] $\Delta = \Sigma_1^N (2\Theta_{exp} - 2\Theta_{calc})/N$, where $2\Theta_{exp}$ is the experimental diffraction angle, $2\Theta_{calc}$ the angle calculated from the lattice parameters and N the number of investigated diffraction lines.

2.2. Determination of the Transport Coefficients

In order to determine the electrical conductivity and the Hall constant, samples of dimensions $8 \times 3 \times (0.05$ to $0.10)$ mm^3 were prepared; platinum wires 0.05 mm in diameter were used for the Hall contacts that were realized by capacitor discharge. The Hall coefficient was measured at room temperature using the ac technique at a frequency of 170 Hz in the $B \| c$ orientation (B is the magnetic induction vector), with B equal to 1.1 T. At the same time, the electrical conductivity perpendicular to the trigonal axis c, $\sigma_{\perp c}$, was also measured. The ratio $\sigma_{\perp c}/\sigma_{\| c}$ was determined using the Tredgold–Clark method (*17*).

TABLE II

TRANSPORT COEFFICIENTS (ELECTRICAL CONDUCTIVITY $\sigma_\perp$, $\sigma_\parallel$, HALL CONSTANT ρ_{123}, SEEBECK COEFFICIENT $S_{\perp c}$) AND PLASMA RESONANCE FREQUENCY ω_p OF THE $Bi_{2-x}In_xTe_3$ CRYSTALS

Composition x	$\sigma_{\perp c}$ [Ω^{-1} cm^{-1}]	$\sigma_\perp/\sigma_\parallel$	ρ_{123} (cm^3 A^{-1} sec^{-1})	$\omega_p(\bar{E} \perp \bar{c}) \times 10^{-23}$ (sec^{-1})	$S_{\perp c}$ (μV K^{-1})	$\rho_{123}\sigma_\perp$ (cm^2 V^{-1} sec^{-1})
0.000	660	2.5_6	0.44	5.34	223	290
0.015	537	2.6	0.54	4.74	230	290
0.028	414	—	0.64_5	4.33	—	267
0.040	335	2.6–2.7	0.77	—	—	258
0.045	286	—	0.81	—	—	232

The electrical conductivity and the Hall coefficient values for individual crystal samples with different values of x are given in Table II. In order to determine the free carrier concentration in the undoped Bi_2Te_3 crystal, the Seebeck coefficient and the reflectivity spectrum in the plasma resonance frequency region were measured. The value of the Seebeck coefficient measured at room temperature (294 K) is 223 μV/K, the plasma resonance frequency $\omega_p = 5.34 \times 10^{13}$ sec^{-1}, the high-frequency permittivity is 83. The concentration of holes in the undoped Bi_2Te_3 crystals was determined using a method similar to that reported in (*18*, *19*); the model used assumes the validity of the following assumptions:

(a) The valence band can be described by means of a nonparabolic six-valley one-valence band model.

(b) Scattering of the free carriers by the acoustic branch of the lattice vibrations is the dominant scattering mechanism in Bi_2Te_3 crystals.

(c) The relaxation times in the directions perpendicular and parallel to the trigonal axis c are identical (isotropic).

Under these assumptions we obtained for the free carrier concentration a value of $p = 7.5 \times 10^{18}$ cm^3, for the structure factor $\gamma = 0.53$ and for the effective mass $m_\perp = 0.11$ m$_0$. Since the band structure of the mixed crystals is not yet known and since the value of the product $R_H\sigma_{\perp c}$ varies only slightly in the series of $In_xBi_{2-x}Te_3$ crystals ($x = 0.000$–0.045), in order to estimate the concentration of the free carriers we have made an assumption that the effective mass of holes would not vary too much in the investigated range of concentrations x and therefore we assumed the value of the structure factor $\gamma = 0.53$ to apply to all the investigated mixed crystals. In this way we determined from the Hall coefficients the concentration of holes in $In_xBi_{2-x}Te_3$ mixed crystals; its values are given in Fig. 1.

2.3. Calculation of Bonding Conditions in the Crystals

The quantum chemical procedure used in this paper is merely a version of the HMO method (*20*) extended on the basis of all valence orbitals. Unlike the Del Re method (*21*), the calculation is performed on the basis of equivalent orbitals and the interaction of all equivalent orbitals between the nearest neighbors is taken into account. Coulomb integrals were identified with scaled orbital electronegativities and the resonance integrals were calibrated on a set of homonuclear diatomics. The Coulomb integrals are presented in (*21*). The details of the method and the calibration can be found in (*22*, *23*).

The calculation was carried out for a sec-

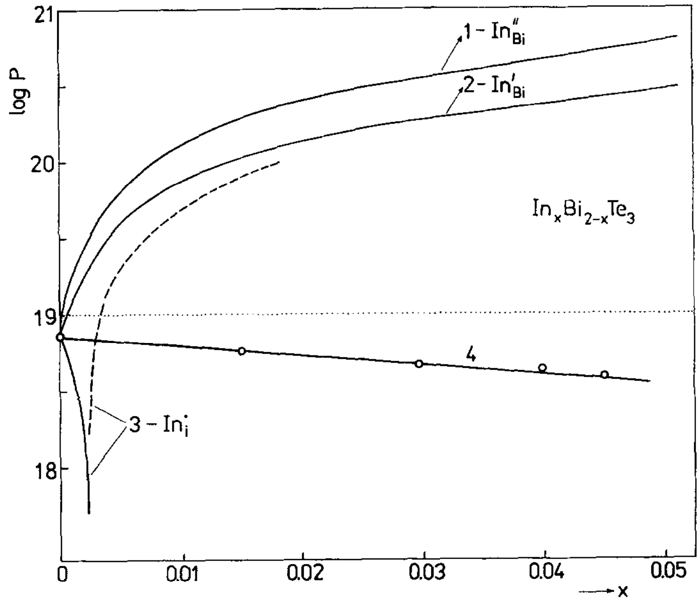

FIG. 1. Hole concentration in $Bi_{2-x}In_xTe_3$ mixed crystals (1, 2, 3, theoretical values for given point defects; 4, experimental values).

tion of the crystal layer between the van der Waals gaps. This section was formed by 31 atoms that had together 174 valence orbitals. The arrangement of the crystal section submitted to calculation is represented in (*10, 13*).

Definition of notions:

(a) Polarity of the bond b between the atoms *A* and *B* ($A \overset{b}{—} B$) is defined as the difference in the electron density on the orbitals in the direction of the bond b on atoms *A* and *B*. Its numerical value is averaged over all bonds of the same kind existing in the crystal model. It is given in units of elementary charge and denoted with *p*.

(b) Bond order is the average order of bonds of the same kind. It describes the multiplicity of a bond, i.e., it corresponds to the electron density in the space occupied by a bond). It is a dimensionless quantity.

(c) Electron density is given in units of elementary charge and related to one atom. (The valences electrons are considered.)

3. Model of a Tetradymite Structure Crystal

The results of the lattice dynamical studies of the Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3 crystals suggest that it is possible to replace the tetradymite structure crystal by a five-membered atomic chain (*24–26*), as shown in Fig. 2. This model has been used by us to shed light on the variations in the structure and nature of bonds in $A_x^{III}B_{2-x}^{V}C_3^{VI}$ mixed crystals due to gradual occupation of the sites in the cation sublattice of the tetradymite structure by group IIIb atoms. The variations of the structure and bonding parameters connected with the substitution within the cation sublattice have been explained by applying the fundamental regu-

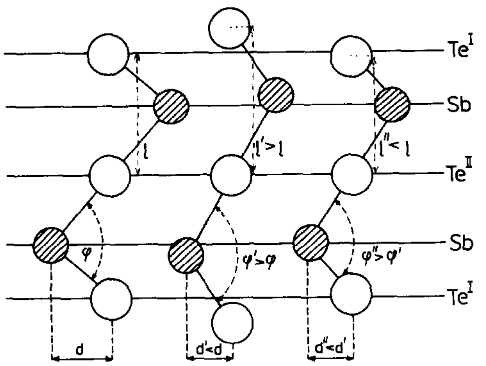

FIG. 2. Changes in five-membered atomic chain.

larities of the chemical bonding in molecules to the model of a five-membered chain.

Due to the fact that the mentioned model idea is also used for an estimate of the changes in the concentration of point defects, it has to be noted that real crystals of tetradymite structure always exhibit a certain concentration of antisite (AS) defects; i.e., Sb or Bi atoms occupy sites on the anion sublattice, thus giving rise to the formation of AS defects of the $\mathrm{Sb}'_{\mathrm{Te}}$ or $\mathrm{Bi}'_{\mathrm{Te}}$ type probably situated in Te^2 sites. Since the concentration of superstoichiometric Sb, Bi atoms in the tellurides $\mathrm{Sb_2Te_3}$ and $\mathrm{Bi_2Te_3}$ corresponds approximately to the concentration of holes, we adopt the assumption that the dominating point defects in $A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ crystals for $x = 0$ are the AS defects whose charge is compensated by holes.

Analyzing the variations in the concentration of free carriers due to the gradual introduction of In or Tl atoms into the $\mathrm{Bi_2Se_3}$, $\mathrm{Sb_2Te_3}$, and $\mathrm{Bi_2Te_3}$ crystals we proved that In or Tl atoms are incorporated into the cation sublattice of the tetradymite structure lattice (*4, 5, 10, 12, 13*). The incorporation of the mentioned group IIIb elements into the Bi or Sb sublattice gives rise to uncharged point defects, e.g., $\mathrm{In}_{\mathrm{Bi}}^{x}$, which are, however, polarized positively—with respect to lower electronegativity of the group IIIb elements. In agreement with the views put forward by Krebs (*27*), one can assume that the group IIIb elements show a formal valency of +3, which is connected with the notion of the existence of antibonding 5*s* or 6*s* orbitals of In or Tl atoms in a tetradymite lattice. Formally, we can describe such an effect—e.g., occurring at the incorporation of an In atom into the crystal—by the equation

$$\mathrm{In}\ (6s^2 6p^1) \rightarrow \mathrm{In}_{\mathrm{Bi}}^{x(\delta+)}\ (6s^0 6p^3).$$

The bond polarity increases with increasing concentration of group IIIb elements and one has to take into account the following effects:

(a) A shift of the electron density toward $C^{\mathrm{VI(1)}}$ atoms and also to $C^{\mathrm{VI(2)}}$ atom, which signifies that the angle of the bonds $C^{\mathrm{VI(1)}}$–$A_{\mathrm{B}}^{\mathrm{III}}$–$C^{\mathrm{VI(2)}}$ increases, implying an increase of the lattice parameter *c* as well.

(b) The group IIIb atoms in the tetradymite lattice show smaller radii than Sb or Bi atoms; this will result in a decrease of the lattice parameters *a* and *c*.

(c) An increase of the concentration of more electropositive group IIIb elements in the cation sublattice leads to an increase of the bond order in $A_{\mathrm{B}}^{(\delta+)}$–$C^{\mathrm{VI(1)}}$ as well as in $A_{\mathrm{B}}^{(\delta+)}$–$C^{\mathrm{VI(2)}}$ bonds; therefore one can expect a shortening of the bonds, hence also a shortening of the lattice parameters *a* and *c*.

(d) Since the increasing content of the group IIIb elements corresponds with two opposing influences on the magnitude of the lattice parameter *c*, one can expect that the dependence of the parameter *c* on the concentration of the built-in group IIIb atoms will pass through an extremum.

(e) The mentioned simple model based on the ideas of the changes in bond polarities in the five-membered chain makes possible an explanation of the variations in the concentration of antisite defects in $A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ mixed crystals with the value of *x*, the AS defects being the dominant point defects in chalcogenide crystals of tetradymite structure. For this purpose it is sufficient to adopt the assumption that the increasing bond polarity in mixed crystals of the tetradymite structure leads to a decrease of the probability of forming antisite defects, as discussed in our earlier papers (*9–15*).

4. Comparison of the Experimental Results with the Model

4.1. Structure Parameters of $A_x^{III}B_{2-x}^{V}C_3^{VI}$ Crystals

The structure parameters a and c of $In_xSb_{2-x}Te_3$ and $In_xBi_{2-x}Se_3$ mixed crystals, given in our earlier papers (*9–15*), as well as those of $In_xBi_{2-x}Te_3$ crystals, the parameters of which correspond to the data of Table I, are compared in Figs. 3–5. The lattice parameter a decreases with increasing indium content for all the investigated mixed crystals. The dependence of the lattice parameter c on the parameter x shows a pronounced maximum in the systems $In_xSb_{2-x}Te_3$ and $In_xBi_{2-x}Se_3$; in the $In_xBi_{2-x}Te_3$ system a maximum in the $c = f(x)$ dependence was also observed, though smaller and shifted toward lower indium concentrations in comparison with the preceding mixed crystals. This result is in agreement with the model mentioned under (a) above. As is mentioned below, the position of the maximum of the lattice parameter $c = f(x)$ depends also on the concentration of antisite defects. Since increasing value of x increases the bond polarity, one has to expect that the c/a ratio will grow with increasing x in the whole concentration range of mixed crystal formation. This assumption holds for all the investigated systems. The plots of the c/a ratio vs x for $In_xSb_{2-x}Te_3$ and $In_xBi_{2-x}Se_3$ are shown in Figs. 3, 4. Thus, one can claim that the variations of the lattice parameters due to the incorporation of group IIIb atoms into the tetradymite lattice are in agreement with the model.

4.2. Bonding Parameters

Figure 6 shows the variations of the electron density in the lattice sites of the Te^1, Sb, Bi, and Te^2 atomic layers relative to the concentration of In atoms built into the cation sublattice, i.e., to the concentration of substitution defects in In_{Sb}^x of In_{Bi}^x. In accordance with the ideas on the changes in bond

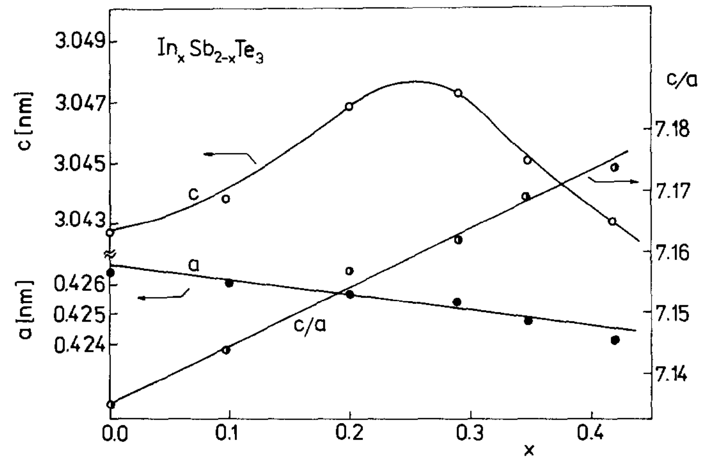

FIG. 3. Lattice parameters for $In_xSb_{2-x}Te_3$.

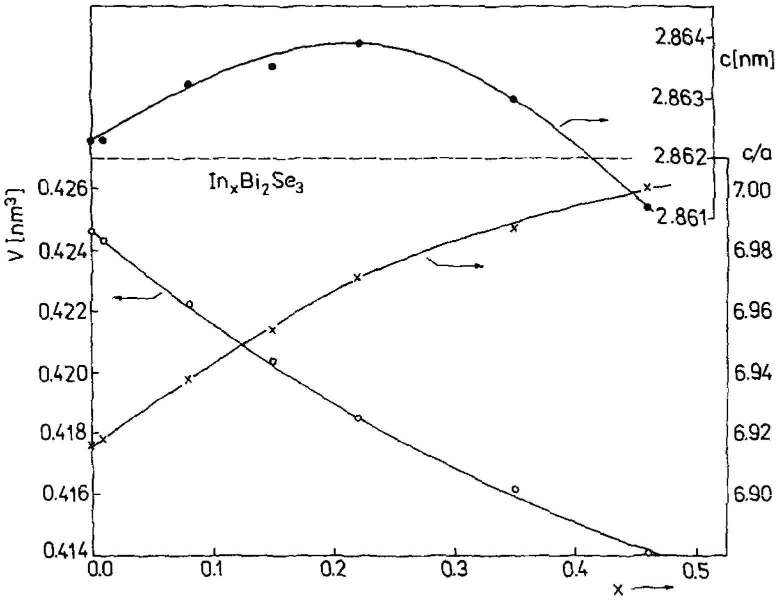

FIG. 4. Lattice parameters for $In_xBi_{2-x}Se_3$.

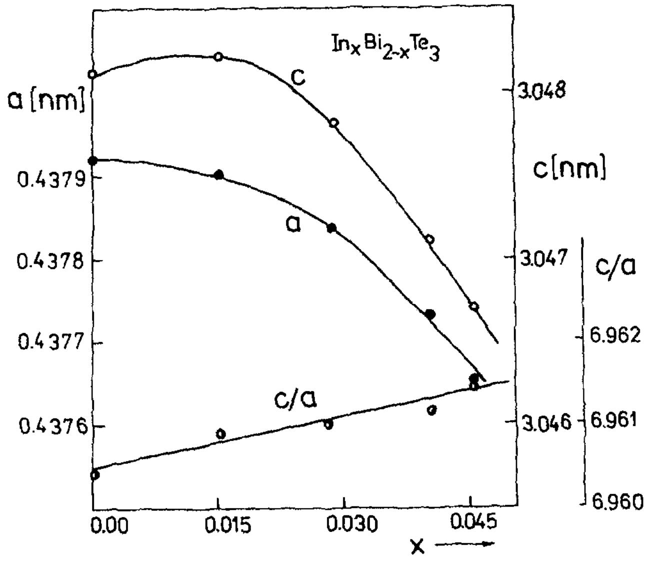

FIG. 5. Lattice parameters for $In_xBi_{2-x}Te_3$.

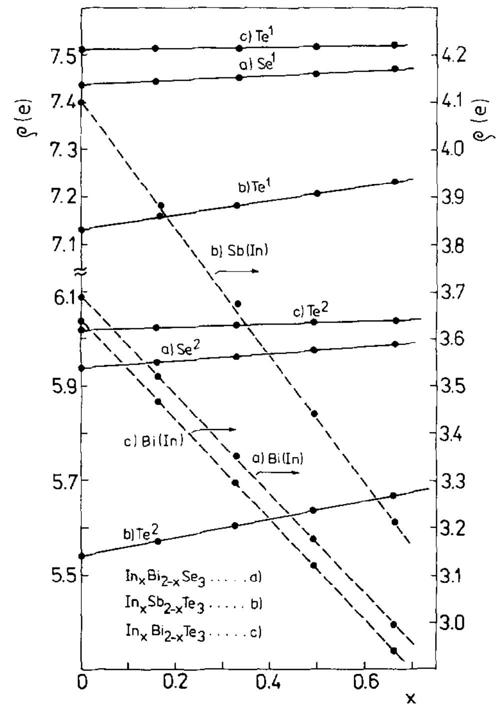

FIG. 6. Electron density in atomic planes.

polarity due to the substitution of the group IIIb elements of the periodic system for Sb or Bi atoms, the bond polarity increases with increasing content of In or Tl atoms (see Fig. 7), and that as a consequence of a more positive charge in the cation sublattice, which is connected both with the lowering of the number of valence electrons compared to Sb or Bi and with the lower electronegativity of group III elements. This leads to a shift of the electron density toward outer atomic planes of the Se^1, Te^1 layers. An increase of the electron density in the outer atomic planes of the layers brings about an increase of the electron density in the van der Waals gap as well. In view of the charge of identical polarity in the outer atomic planes of two neighboring layers one can expect an increase in the distance of the Te^1–Te^1 or Se^1–Se^1 atomic planes, i.e., an increase of the van der Waals gap in the mixed crystals with higher content of In or Tl. The calulated values of the electron density and bond polarity using a quantum chemical program TOPOLOGY confirm the qualitative ideas formulated in our model.

The increase of the bond polarity in the $A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ crystal lattice corresponds to higher ionicity of the crystal. In agreement with this assumption, the $A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ crystals show an observable shift of the short-wavelength absorption edge toward higher energies with increasing content of A^{III} atoms; this effect has been observed in the system $\mathrm{In}_x\mathrm{Sb}_{2-x}\mathrm{Te}_3$ (*28*). The value of the energy gap thus increases with increasing ionicity of the ternary crystal; we take this fact as proof of the correctness of our ideas.

4.3. Relations between Bonding Parameters and the Concentration of AS Defects

$A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ mixed crystals are formed by gradual occupation of the cation sublattice

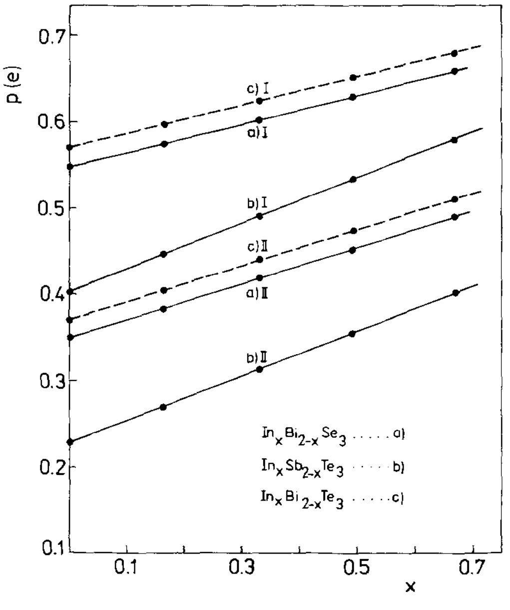

FIG. 7. Bond polarity $(A\,^{\mathrm{I}}B\,^{\mathrm{II}}A\,^{\mathrm{II}}B\,^{\mathrm{I}}A)$.

by group III elements, In or Tl. With the aim to clarify the connection between the variations of the bonding parameters and the concentration of AS defects we adopted the view that, in the whole interval of In or Tl concentrations up to the limiting solubility value of these elements, the group IIIb atoms are incorporated into the cation sublattice and that it is improbable for these atoms to enter other lattice sites (*1, 4, 5, 9–14*).

This view is supported by the following experimental result: gradual increase of the concentration of In or Tl atoms in the range of small concentrations gives rise only to monotonous variations in the transport and optical properties. In Fig. 1 is shown the dependence of the concentration of holes on the quantity of In atoms built in the lattice in the range of low indium concentrations. If In atoms would occupy the cation sublattice and form substitution In_{Bi}'' or In_{Bi}' defects, the P(x) dependence would be given by curve 1 or 2. The formation of interstitials would correspond to curve 3. However, the measured P(x) dependence is given by curve 4. This effect, i.e., slight decrease in the concentration of holes with increasing concentration of In or Tl atoms in the cation sublattice, was observed in all the investigated systems—In–Bi–Se, In–Bi–Te, In–Sb–Te, and Tl–Sb–Te. The effect can be explained in the following way: the incorporation of a group III atom into the cation sublattice of the tetradymite structure gives rise to uncharged defects, which are, however, positively polarized in view of the lower electronegativity value of group IIIb elements, as compared to antimony or bismuth.

As was shown in our earlier studies (*10, 12–14*), the increase of the bond polarity in the crystals of tetradymite structure brings about a decrease of the probability of formation of AS defects. The variations of the concentration of AS defects in undoped crystals can be described by the equation:

$$[\text{AS}] = N_0 A_1 \exp\left(-\frac{E_0}{k_B T_m}\right), \qquad (1)$$

where [AS] is the concentration of antisite defects, E_0 is the energy required for the formation of a single AS defect, k_B is the Boltzmann constant, T_m is the melting temperature of the crystal, the product N_0A_1 stands for the maximum possible concentration of AS defects in the given crystal. N_0 is the quantity of A_2B_3 stoichiometric units contained in 1 cm^3, the coefficient A_1 denotes the mean number of AS defects in one A_2B_3 unit, irrespective of any energy limitations. Adopting the validity of the assumption that the impurity enters only the cation sublattice, we can express the A_1 coefficient as

$$A_1 = \left(1 - \frac{x}{a}\right) \sum_{n=0}^{a} \frac{n \binom{a}{n}\binom{b}{n} a!b!}{(a+b)!} = \frac{(a-x)b}{a+b}, \qquad (2)$$

where x, a, b are identical with the coefficients in the formula $A_x^{III}B_{2-x}^{V}C_3^{VI}$. Provided that the change of the concentration of impurities causes a change in the bond polarity in the crystal, and thus also the tendency to form AS defects, we can rewrite Eq. (1) in a form expressing explicitly the concentration dependence:

$$[\text{AS}] = N_0 A_1(x) \exp - \frac{E + \Delta E(x)}{k_B T_m}, \qquad (3)$$

where ΔE is called the polarization energy. Its sign depends on whether the polarity of the crystal increases or decreases with increasing concentration of the impurity.

In the case of $A_x^{III}B_{2-x}^{V}C_3^{VI}$ (A = In, Tl) mixed crystals the bond polarity always increases with increasing content of In or TL atoms. Therefore, the value of ΔE and thus the energy of formation of AS defects increases.

Using Eqs. (1), (2), and (3), and the data

TABLE III

Composition x	Energy of formation of AS defect $E_0 + \Delta E$ (eV)	Polarization energy ΔE (meV)
0.000	0.500	0
0.015	0.515	15
0.028	0.530	30
0.040	0.541	41
0.045	0.545	45

of Table II, we calculated for the $In_xBi_{2-x}Te_3$ system the values of the energy of formation of AS defects and the values of the polarization energy ΔE (see Table III), which show the correctness of our ideas. Equations (1) and (3) thus allow us to account for the variations of the concentration of AS defects due to an increase or a decrease of the bond polarity caused by the introduction of foreign atoms into the cation sublattice of the tetradymite structure.

From a comparison of the superstoichiometric content of Sb or Bi (*29*) and the concentration of holes in Sb_2Te_3 and Bi_2Te_3 crystals it follows that approximately one hole corresponds with one AS defect. Therefore, we consider the antisite Sb'_{Te} or Bi'_{Te} defects as dominant and do not take into account other charged point defects in the lattice. Under these circumstances it holds that the concentration of holes is equal to the concentration of AS defects. Accepting this idea, we can describe the point defects in, e.g., Sb_2Te_3, by a symbolic eqation:

$$\begin{aligned} 2\,Sb_{Sb} + 3\,Te_{Te} &\rightleftharpoons 2\,Sb'_{Te} + V_{Te} \\ &+ 2\,V_{Sb} + 2h^{\cdot} + 3/2\,Te_2(g). \end{aligned}$$

Further it holds that

$$2\,V_{Sb} + 3\,V_{Te} \rightleftharpoons 0.$$

The building of a group IIIb atom, e.g., In, into the cation sublattice is described by

$$\begin{aligned} 2\,Sb'_{Te} + V_{Te} + 2\,V_{Sb} + (2\,V_{Sb} + 3\,V_{Te}) \\ + 2h^{\cdot} + 3\,Te_2 + 2\,In \\ \rightleftharpoons 2\,Sb_{Sb} + 2\,In_{Sb}^{x(\delta+)} + 6\,Te_{Te} \end{aligned}$$

In a similar way one can describe the incorporation of In or Tl atoms into other chalcogenides of tetradymite structure.

In view of the fact that group IIIb elements, i.e., In or Tl, are more electropositive than Sb and Bi, the concentration of AS defects in $A_x^{III}B_{2-x}^{V}C_3^{VI}$ will decrease with increasing value of x: the formation of AS defects in $A_x^{III}B_{2-x}^{V}C_3^{VI}$ is, therefore, less probable. As indicated by our preliminary results, provided that the concentration of In atoms in $In_xBi_{2-x}Te_3$ mixed crystals is equal to or larger than $x = 0.1$, electrons become the majority carriers. This means that, at a sufficiently high concentration of In or Tl atoms in the tetradymite lattice, the concentration of AS defects is suppressed to such an extent that other types of point defects can come into play. The possibility of suppressing the concentration of AS defects in the crystals of the tetradymite structure thus depends both on their concentration in undoped crystals and on the solubility of In or Tl in the cation sublattice. Whereas the description of the incorporation of In or Tl atoms into the lattice of p-Sb_2Te_3 and p-Bi_2Te_3 leading to mixed crystals is in agreement with the variations of the concentration of the free carriers in the sense of Eqs. (2, 3), the clarification of the relations between the incorporation of In atoms into the $In_xBi_{2-x}Se_3$ lattice and the variations of the concentration of the free carriers—in this case electrons—is somewhat more difficult. The In atoms occupy sites in the cation sublattice and increase the bond polarity, as shown in Fig. 2. This means that a suppression of the concentration of AS defects must ensue. In n-Bi_2Se_3 crystals, however, one has to consider that beside the AS defects there exist also positively charged $V^{\cdot}_{Se}$ defects or negatively charged V'_{Bi} defects (*30, 31*). The condition of electroneutrality then leads to

$$[e'] = [V^{\cdot}_{Se}] - [Bi'_{Se}]. \qquad (4)$$

Hence, if the concentration $[\mathrm{Bi}'_{\mathrm{Se}}]$ is lowered by gradual occupation of the cation sublattice sites with In atoms, the concentration of electrons will first increase and then, after the AS defects disappear, only start to decrease—in consequence of a decreasing departure from stoichiometry, due to increased ionicity of the $\mathrm{In}_x\mathrm{Bi}_{2-x}\mathrm{Se}_3$ crystal; the decreasing departure from stoichiometry means that a balance in the concentration of cation and anion vacancies is approached. Hence, smaller departure from stoichiometry represents a decrease in the concentration $[V^{\cdot}_{\mathrm{Se}}]$ and, consequently, a decrease of the electrical conductivity and a change in all transport coefficients, as shown in Refs. (*4, 30*). This explanation is in agreement with the ideas put forward by van Vechten (*31*), who noted that in crystal lattices of binary compounds the vacancies on sites normally occupied by atoms of smaller radius are more frequent. In a series of isostructural crystals one can thus expect an increase in the concentration of vacancies with increasing differences in the sizes of cation and anion. In $\mathrm{In}_x\mathrm{Bi}_{2-x}\mathrm{Se}_3$ crystals, smaller In atoms substitute for larger bismuth atoms, the "effective" radius in the cation sublattice decreases, which results in a decrease of the difference in size between the atoms in cation and anion sublattices. As a result, the concentration of selenium vacancies $[V^{\cdot}_{\mathrm{Se}}]$ will show a decrease.

The suppression of the concentration of AS defects due to incorporation of In or Tl atoms into the cation sublattice is also connected with changes in the structure parameters. As follows from the model of Fig. 2, the angle φ increases with increasing value of the positive charge in the cation sublattice sites. The suppression of the AS defects implies the substitution of Se or Te atoms for AS defects, an increase of the electron density in Se^2 or Te^2 lattice sites. This results in a stronger repulsion of the atoms between the Se^1 and Se^2 or Te^1 and Te^2 sites and in an increase of the angle φ and of the lattice parameter c. The higher the concentration of AS defects in the $A_x^{\mathrm{III}}B_{2-x}^{\mathrm{V}}C_3^{\mathrm{VI}}$ crystal for $x = 0$, the larger number of In or Tl atoms required to remove the AS defects. An increase of the content of In or Tl atoms will manifest itself in an increase of the parameter c provided that AS defects are present in the lattice; after disappearance of the latter, the parameter c will tend to decrease as a consequence of the smaller radius of In atoms compared to Sb or Bi atoms. In the crystals containing a larger number of AS defects, therefore, the maximum in the dependence of the lattice parameter $c = f(x)$ will be shifted toward higher x values and vice versa. This deduction is in perfect agreement with the experiment. The highest concentration of AS defects has been found in $\mathrm{Sb}_2\mathrm{Te}_3$ crystals, where also the maximum in the $c = f(x)$ dependence is shifted toward relatively large values of x; on the other hand, $\mathrm{Bi}_2\mathrm{Te}_3$ exhibits the lowest concentration of AS defects among the investigated systems and the maximum in the $c = f(x)$ function is found at low x values. The locations of the maxima in the $c = f(x)$ dependences are closely related to the concentration of AS defects, to the energy E_0 of formation of AS defects, and to the bond polarity. The location of these maxima on the concentration scale are denoted with x_{max}. The relations among the corresponding quantities are given in Table IV.

Thus we note that the dependence of the lattice parameter c of the tetradymite lattice on the concentration of In or Tl atoms is influenced both by the increasing positive charge of the cation sublattice and by the increasing negative charge in Se^2 or Te^2 sites, appearing as a result of the suppression of the concentration of AS defects.

Concluding, we add the following remark to the problems of the structure of AS defects: according to (*32*) the superstoichiometric content of Sb or Bi in the tetra-

TABLE IV

Crystal	Bond polarity p_1	p_2	E_0 (eV)	$x_{c_{\max}}$
Sb_2Te_3	0.4040	0.2265	0.35	0.25
Bi_2Se_3	0.5477	0.3527	0.37	0.21
Bi_2Te_3	0.5735	0.3727	0.50	0.015

dymite lattice can be explained by the existence of seven- or nine-layer lamellae embedded into the van der Waals gaps. So far, however, no ideas on the relations between the formation of seven-layer or nine-layer lamellae and the concentration of free carriers have been formulated. Therefore, in the present paper we adopt the view that the structure of AS defects can be represented as Sb or Bi atoms built into the anion sublattice of Te^2 atoms. The views regarding a possible connection of the AS defects and the seven-layer or nine-layer lamellae will be reported in another communication.

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