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The Influence of Iodine Impurities on the Electrical Conductivity of Sb_2Te_3 Crystals

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A method of growing $\text{Sb}_2\text{Te}_3(\text{I})$ single crystals is described, using a modified Bridgman technique at relatively high pulling rate. The method yielded crystals with uniform iodine distribution in the lattice. Measurement of the physical properties shows that up to 2.5 at% iodine can be dissolved in the crystal, whereby the iodine atoms occupy most probably the vacant sites in the tellurium sublattice. The interpretation of the Hall constant and the infrared reflectivity measurements permitted to determine the structure factor α_1/α'_3 , the ratio N/m_{\perp}^* , and the value of the relaxation time $\langle\tau\rangle_{\perp c(\text{cond})}$ for all crystals. The concentration of free carriers in "pure" Sb_2Te_3 was estimated.

L'article décrit la préparation des monocristaux de $\text{Sb}_2\text{Te}_3(\text{J})$ employant la méthode Bridgman modifiée avec la vitesse relativement haute de tirage qui permet de préparer les cristaux aux atomes d'iode également incorporés au réseau de Sb_2Te_3 . Les résultats des mesures des propriétés physiques ont montré que les atomes d'iode étaient dissous dans les cristaux jusqu'à la concentration de 2,5 at% et que vraisemblablement les atomes d'iode occupaient des positions des atomes de tellure. Au moyen des mesures d'effet Hall et de réflectivité dans la région infrarouge la valeur du facteur structural α_1/α'_3 , plus loin la proportion N/m_{\perp}^* et la valeur moyenne du temps de relaxation $\langle\tau\rangle_{\perp c(\text{cond})}$ ont été déterminées; la concentration des porteurs libres dans les cristaux „pures“ de Sb_2Te_3 a été estimée.

1. Introduction

Antimony telluride (Sb_2Te_3) is a narrow gap semiconductor that forms layer-type crystals belonging to a class of substances with space group D_{3d}^5 . The crystals are well cleavable in the plane perpendicular to the c -axis, which is a consequence of pronounced anisotropy of the layer structure.

The properties of pure Sb_2Te_3 and those of the Bi_2Te_3 – Sb_2Se_3 mixed crystals were carefully studied in [1 to 6]; one was unable, however, to give full explanation of the transport phenomena.

The influence of the impurities on the physical properties of Sb_2Te_3 was not studied in great detail. Although the changes in the electrical conductivity and the Seebeck coefficient due to admixtures of Pb, I₂, CuBr₂, Sn, Zn, Sb, BiI₃ were investigated [7], a detailed analysis of the results has not been given and the character of individual impurities in the crystal under consideration has not been carefully examined either.

From the dependence of the Seebeck coefficient on the value of the electrical conductivity, determined for a broader range of free-carrier concentrations, the authors [7] infer that the valence band is composed of two bands separated by about 0.23 eV.

In the present paper we submit the results of an investigation of the influence of iodine atoms — incorporated in the crystals lattice — on the value of the electrical conductivity and the Seebeck coefficient, with the aim to ascertain the nature of the point defects in the Sb_2Te_3 lattice, to determine the solubility limit of iodine in the Sb_2Te_3 crystals, and to verify the ideas presented in [7].

2. Experimental Details

2.1 Growth of Sb_2Te_3 (I) crystals

For the preparation of the crystals the following starting materials were used: Sb — 99.999%, Te — 99.999%, and I — p.a. subjected to double sublimation. First, the antimony telluride was synthesized from the elements. To pull the single crystals, a modified Bridgman technique was employed; conical ampoules (10 mm diameter) were charged with Sb_2Te_3 together with the corresponding quantity of iodine in elemental form or as SbI_3 . After evacuation and sealing off, a constant temperature of 720 °C was maintained along the ampoule for 48 h. Then the ampoule was lowered — at a relatively high rate of 4.5 mm/h — to a steep temperature gradient of 400 °C/5 cm. The single crystals prepared (10 mm diameter, ≈ 35 mm long) were oriented with Laue method and their different parts were checked for iodine content. Almost in all cases the c -axis of the crystals obtained was perpendicular to the pulling direction, i.e. the (0001) plane was parallel to the axis of the conical ampoule. To determine the homogeneity of the samples, one employed a method of measuring the wavelength dependence of the reflectivity R in the plasma-resonance region on natural (0001) faces obtained by cleaving the crystals. The suitability and sensitivity of the method to determine the uniformity of the distribution of iodine atoms in the lattice, i.e. also the concentration of free carriers, consists in the fact that the reflectivity minima are unusually well developed and sharp. Each gradient of the free-carrier concentration manifests itself by broadening of the $R(\lambda)$ curve (see below). The samples used to investigate the physical properties were cut from the middle part of the single crystals; the location of the reflectivity minima was identical for samples with equal impurity concentration. One concluded that the samples of $\text{Sb}_2\text{Te}_3(\text{I})$ used for the investigation of the physical properties were homogenous.

2.2 Reflectivity measurements

The reflectivity spectrum was measured in the 2 to 20 μm wavelength range at room temperature (294 °K) with non-polarized radiation, using a Zeiss UR-10 spectrophotometer provided with special facilities for reflectivity measurements as described in [8]. The angle of incidence of the light beam on the sample was smaller than 10°. According to the quoted paper, the reflectivity was measured in two ways: both absolutely and relatively against a standard represented by a freshly prepared aluminium mirror.

Measurements of the absolute and relative (direct ratio with aluminium mirror) reflectivity gave identical results.

The measurement was performed on natural cleavage faces (0001) in such a way that the electric field vector E of the electromagnetic radiation was always perpendicular to the c -axis, i.e. $E \perp c$.

2.3 Hall measurements

The contacts for measurement of the Hall voltage were prepared by evaporating gold on the crystal. The value of the Hall constant R_H was determined for $\mathbf{H} \parallel \mathbf{c}$, $\mathbf{E}_1 \perp \mathbf{c}$. (\mathbf{H} and \mathbf{E}_1 are the intensities of the magnetic and electric fields, respectively, applied to the crystal for Hall measurement.)

The measurement was performed at room temperature ($\approx 294^\circ\text{K}$). In addition, a measurement of the electrical conductivity in the direction perpendicular to the c -axis of the crystal, i.e. $\sigma \perp \mathbf{c}$, was performed, too.

2.4 Thermopower measurements

The Seebeck coefficient S was measured on Sb_2Te_3 crystals with various iodine content in the temperature range 77 to 293°K . For all samples, the value of S for the direction perpendicular to the c -axis, i.e. $S \perp \mathbf{c}$, was determined.

3. Experimental Results

All experimental data obtained are collected in Table 1. Fig. 1 shows the plot of $R(\lambda)$ for a pure Sb_2Te_3 sample and for $\text{Sb}_2\text{Te}_3(\text{I})$ samples with different iodine

Table 1

sample	R_H ($\text{cm}^3 \text{ A}^{-1} \text{ s}^{-1}$)	$\sigma \perp \mathbf{c}$ ($\Omega^{-1} \text{ cm}^{-1}$)	λ_{\min} (μm)	$S \perp \mathbf{c}$ (293 °K) ($\mu\text{V deg}^{-1}$)
1. Sb_2Te_3 "pure"	0.050	3.78×10^3	8.7	75
2. $\text{Sb}_2\text{Te}_3 + 0.2\% \text{ I}$	0.053	3.26×10^3	9.0	77
3. $\text{Sb}_2\text{Te}_3 + 0.5\% \text{ I}$	0.058	2.99×10^3	9.5	82.5
4. $\text{Sb}_2\text{Te}_3 + 0.7\% \text{ I}$	0.063	2.69×10^3	10.0	86.0
5. $\text{Sb}_2\text{Te}_3 + 1.0\% \text{ I}$	0.069	2.42×10^3	10.5	87.0
6. $\text{Sb}_2\text{Te}_3 + 1.8\% \text{ I}$	0.079	2.38×10^3	11.1	89.0
7. $\text{Sb}_2\text{Te}_3 + 2.5\% \text{ I}$	0.102	1.98×10^3	12.8	94.0

content x , for values of x equal to: 0.2, 0.5, 0.7, 1.0, 1.8, and 2.5 at% I, respectively. The measurements reveal that a higher concentration of iodine gives rise to a shift of the reflectivity minima towards longer wavelengths. Although the $R(\lambda)$ curves of the samples 1 to 6 exhibit sharp minima, the minimum on the

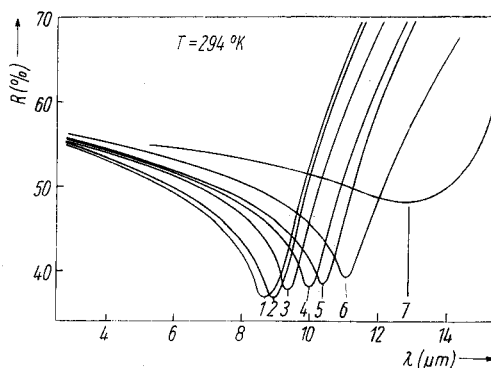


Fig. 1. Wavelength dependence of the reflectivity R measured at 294°K on Sb_2Te_3 and $\text{Sb}_2\text{Te}_3(\text{I})$ samples. Curves 1 to 7 correspond to the sample numbers 1 to 7 in Table 1 and 2

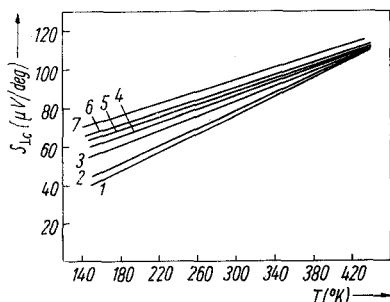


Fig. 2. Temperature dependence of the Seebeck coefficient S for some Sb_2Te_3 and $\text{Sb}_2\text{Te}_3(\text{I})$ samples. Numbering of the curves corresponds to that of Table 1

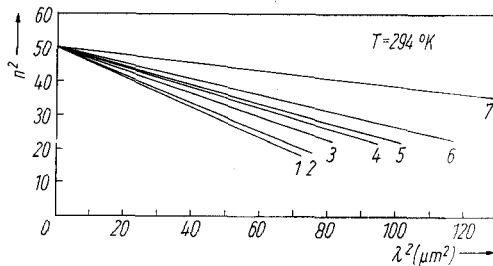


Fig. 3. Plot of $(n^2 - k^2)$ vs. λ^2 for samples 1 to 7, where $k^2 \ll n^2$. The curves correspond to 294 °K

reflectivity curve corresponding to sample 7 is poorly developed; this is due to the fact that on pulling single crystals containing a high concentration of impurities there always arises a concentration gradient of iodine atoms in the crystal bulk, which in turn gives rise to a gradient in the free-carrier concentration along the pulling direction.

The value of the Hall constant R_H , determined at room temperature of 294 °K tends to increase with increasing concentration of the incorporated iodine: from $0.05 \text{ cm}^3 \text{ A}^{-1} \text{ s}^{-1}$ for pure Sb_2Te_3 up to $0.102 \text{ cm}^3 \text{ A}^{-1} \text{ s}^{-1}$ for 2.5 at% iodine. Similarly, the value of the Seebeck coefficient $S_{\perp c}$ increases from 75 μV/deg for pure Sb_2Te_3 up to 94 μV/deg for $x = 2.5 \text{ at}\%$ iodine in Sb_2Te_3 crystals. The temperature dependence of the Seebeck coefficient for crystals with different iodine content is shown in Fig. 2.

4. Discussion of Results

Applying the theory of Drude and Zener for the interpretation of the reflectivity spectra we can express the contribution of the electrical susceptibility of the free electrons to the real part of the dielectric constant ϵ by

$$\epsilon = \epsilon_{\infty} - \frac{N e^2}{4 \pi^2 c^2 \epsilon_0 m_x} \lambda^2, \quad (1)$$

where ϵ_0 is the dielectric constant of vacuum, ϵ_{∞} that of Sb_2Te_3 in the absence of free carriers (extrapolated to $\lambda = 0$), c is the light velocity, N is the free-carrier concentration, and m_x is the effective mass of the free carriers.

From the dependence $n^2 = f(\lambda^2)$ for Sb_2Te_3 samples (n index of refraction), the value of the dielectric constant $\epsilon_{\infty} = 50 \pm 2$ has been determined (see Fig. 3). This result is in good agreement with [2], also the location of the minimum $\lambda_{\min} = 8.7 \text{ μm}$ determined for pure Sb_2Te_3 and the absolute value of the reflectivity are well comparable with the results of [2].

Thus, increasing the concentration of built-in iodine a shift of the reflectivity minimum towards the region of longer wavelengths occurs (see Fig. 1). Consequently, the quantity N/m_x^* decreases with increasing iodine content (Fig. 3). (In case of layer-type Sb_2Te_3 crystals, where the reflectivity measurements were carried out for $E \perp c$, the quantity m_x^* is equal to $m_{\perp c}^*$, i.e. to the effective mass for the direction perpendicular to the c -axis.)

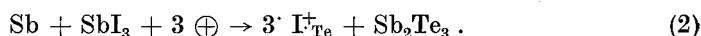
If we assume that, in the first approximation, $m_{\perp}^* e$ does not depend strongly on the hole concentration, these measurements show that the incorporated iodine gives rise to a decrease in the hole concentration in the p-type Sb_2Te_3 crystal. In full agreement with this conclusion, an increase in both the Seebeck coefficient S (see Fig. 2) and the Hall constant R_H values occurs for increasing iodine content in the lattice (cf. Table 2).

Table 2

sample	η	$N/m_{\perp}^* e \times 10^{-20}$ (cm^{-3})	α_1/α_3	$\langle \tau \rangle_{\perp} e (\text{cond}) \times$ $\times 10^{14}$ (s)	$N_{\text{I}^+_{\text{Te}}} \times 10^{-19}$ (cm^{-3})
1. Sb_2Te_3 "pure"	3.55	7.2 ₁	0.20 ₄	1.9	—
2. $\text{Sb}_2\text{Te}_3 + 0.2\%$ I	3.45	6.7 ₄	0.20 ₈	1.7	1.2
3. $\text{Sb}_2\text{Te}_3 + 0.5\%$ I	3.15	6.0 ₄	0.21 ₀	1.8	3.0
4. $\text{Sb}_2\text{Te}_3 + 0.7\%$ I	2.95	5.4 ₆	0.21 ₄	1.8	4.2
5. $\text{Sb}_2\text{Te}_3 + 1.0\%$ I	2.90	4.9 ₅	0.21 ₇	1.7	6.1
6. $\text{Sb}_2\text{Te}_3 + 1.8\%$ I	2.85	4.4 ₃	0.21 ₀	1.9	10.9
7. $\text{Sb}_2\text{Te}_3 + 2.5\%$ I	2.65	3.3 ₃	0.21 ₇	2.1	15.2

On the basis of our measurement, one can therefore explain the role of iodine in the Sb_2Te_3 lattice. The bond between Sb and Te atoms is of "covalent-metallic" character. Consequently, the forbidden gap is narrow, its width being 0.24 eV, according to [2]. Applying the concept used in [9], we can assume the existence of so-called antistructural defects which consist in the occupation of the sites in the tellurium sublattice by antimony atoms. This assumption would easily explain that a small excess of antimony gives rise to the Sb'_{Te} defect in the Sb_2Te_3 crystal lattice, thus increasing the concentration of holes. This is in accordance with the fact that perfect p- Sb_2Te_3 single crystals exhibit a departure from stoichiometry (40.8 at% Sb and 59.2 at% Te [10]).

With respect to the nearly equal atomic masses of Te and I, nearly equal covalent radii, and the observed dependence of physical properties of Sb_2Te_3 crystals on the incorporated iodine content, one can draw the following quantitative conclusions: When pulling the single crystals the iodine atoms occupy the sites in the tellurium sublattice. Using the Schottky symbols we can express this process by the equation



Equation (2) shows that the occupation of the tellurium sites with iodine atoms reduces the probability of the existence of antistructural defects Sb'_{Te} .

In Fig. 4 the dependence of the ratio $N/m_{\perp}^* e$, η , and $S_{\perp} e$ on the concentration of incorporated iodine is displayed. Owing to the fact that these plots are nearly linear up to 1 at% iodine, one can conjecture that iodine dissolves in Sb_2Te_3 giving rise to substitutional defects I^+_{Te} . Above this concentration, i.e. between 1 and 2.5 at% iodine, the function $N/m_{\perp}^* e = f(x \text{ at}\% \text{ I})$ shows a departure from linearity; further increase in iodine content of the starting material for pulling the crystals does not give rise to a change in the free-carrier concentration. Hence, we infer that the concentration of the I^+_{Te} defects does not increase with increasing iodine content in the starting material above 2.5 at%.

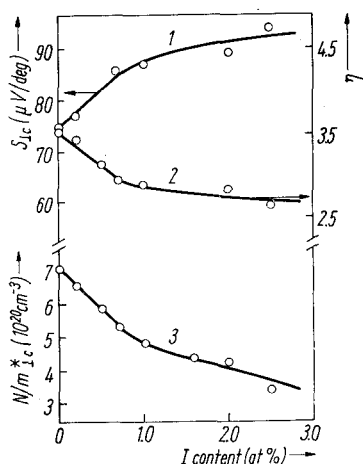


Fig. 4. Dependence of the Seebeck coefficient $S_{\perp e}$ (1), η (2), and $N/m_{\perp e}^*$ (3) on the concentration of iodine incorporated in the lattice of Sb_2Te_3 .

The measurements of the electrical conductivity and thermopower together with $R(\lambda)$ measurements performed on samples with different iodine content yield further information on the nature of the lattice defects.

It follows from [1, 2] that the acoustical vibration branch is involved in the scattering mechanism of the free carriers in the case of Sb_2Te_3 crystals. If we accept this result for the system under consideration, we are in position to explain the relations among conductivity, Fermi level, and Seebeck coefficient. Fig. 5a shows the experimentally determined dependence of the conductivity

$\sigma_{\perp e}$ on the Seebeck coefficient $S_{\perp e}$ and the dependence of $\sigma_{\perp e}$ on the value of the reduced Fermi level η obtained from the thermoelectric power using the above mentioned assumption. The $\sigma_{\perp e}(S_{\perp e})$ dependence exhibits a behaviour that is in agreement with the theory assuming the existence of a single valence band. In [7], where the existence of two bands composing the valence band is assumed, a different $\sigma_{\perp e}(S_{\perp e})$ dependence has been found. The curve 1' in Fig. 5a displays a theoretical dependence $\sigma_{\perp e}(S_{\perp e})$ assuming a single valence band only. The departure of the theoretical curve from our measurement (curve 1) is due to the assumption of constant values of the effective mass and the relaxation time, which both are not fulfilled in reality, as we shall show below.

The quoted discrepancy of the results does not imply that the conjecture of a valence band being composed of two bands would not be justified; theoretical considerations show, on the contrary, that there exists a valence band composed of two bands in the layer-type $\text{A}_2\text{B}_3^{\text{VI}}$ crystals [11]. In the investigated $\text{Sb}_2\text{Te}_3(\text{I})$ system, however, only one type of charge carriers plays a dominant role; eventually, the contribution of holes generated from the deeper band is negligible.

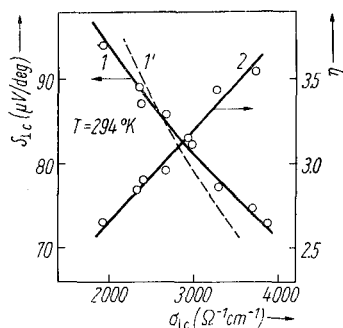


Fig. 5a. (1) Experimentally determined dependence of the electrical conductivity on the Seebeck coefficient, $\sigma_{\perp e}(S)$; (1') calculated $\sigma_{\perp e}(S)$ dependence; (2) dependence of $\sigma_{\perp e}$ on the reduced Fermi level

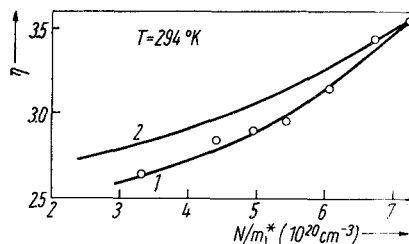


Fig. 5b. (1) Measured $N/m_{\perp e}^*$ vs. η dependence; (2) calculated $N/m_{\perp e}^*$ vs. η dependence assuming the value of the effective mass $m_{\perp e}$ to be constant

One can assume that both partners of the valence band can be separated in energy by more than 0.23 eV as given in [7]. The correctness of this argument is supported by the fact that the dependence $R(\lambda)$ is for all samples in agreement with the relevant theory and does not show a superposition of two curves, which could correspond to two types of holes.

The measurement of the Hall voltage yields a more accurate picture of the dependence of the conductivity on the incorporated iodine content. The Hall constant for hexagonal crystals, where measurements are performed for $\mathbf{H} \parallel \mathbf{c}$, can according to Austin [12] (using the concepts of the "many-valley" model) be expressed as

$$R_H = \frac{\alpha'_3 \langle \tau^2 \rangle}{\alpha_1^2 \langle \tau \rangle^2} \frac{1}{N e}. \quad (3)$$

Here α'_3/α_1 is a structure factor, α_1 is the reciprocal value of the effective mass m_{\perp}^* , and $\langle \tau \rangle_{\perp}$ is the average value of the relaxation time.

From equations (1) and (3) we obtain a numerical estimate of the value of the structure factor. As Table 2 shows the reciprocal structure factor slightly increases with increasing hole concentration. This phenomenon, however, may be explained as due to the non-parabolicity of the valence band. The quoted assumption is further supported by the η vs. N/m_{\perp}^* dependence determined for the $\text{Sb}_2\text{Te}_3(\text{I})$ system which is compared (see Fig. 5b) with the theoretical curve 2 derived for a constant value of the effective mass. To values of η lying closer to the top of the valence band (i.e. for lower hole concentration) a measured value of N/m_{\perp}^* corresponds which is higher than that on the curve 2 due to the decreasing value of m_{\perp}^* . Eventually, from the values of N/m_{\perp}^* determined from the reflectivity spectra and from the concentration of built-in iodine, one can estimate the order of magnitude of hole concentration in pure Sb_2Te_3 , with the simplifying assumption that the effective mass does not strongly depend on the hole concentration. It follows from a simple calculation that the hole concentration is of the order of 10^{20} cm^{-3} . This result, in comparison with absorption coefficient measurements [2] and the measurement of the reflectivity spectra, appears to be plausible.

5. Conclusion

In the present study we have investigated the changes in the electrical and thermoelectrical properties, and in the reflectivity spectra in the plasma-resonance region due to an increasing iodine content built in the lattice of Sb_2Te_3 crystals. Two results follow from the discussion of the measurements:

In the preparation of single crystals, I is incorporated during the pulling process of the crystal at sites of the tellurium sublattice. At room temperature which is high enough for the I_{Te} defect to be ionized, I_{Te}^+ and a free electron is created. This process leads to a decrease in the free hole concentration.

The results of the Hall effect, thermopower, and infrared reflectivity measurements on samples of the $\text{Sb}_2\text{Te}_3(\text{I})$ system show that one can interpret the observed physical properties assuming that only one type of holes takes part in the transport phenomena; the fraction of holes generated from the deep-lying band appears to be negligible for the system in question. Moreover, the relations between the measured quantities lead to the conclusion that the effective mass of free carriers increases markedly with hole concentration.

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