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Nonparabolicity of the conduction band and anisotropy of the electron effective mass in n-Bi_2Se_3 single crystals

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Single crystals of n-Bi_2Se_3 were prepared with free-carrier concentration N in the range $5\times10^{18} < N < 2\times10^{20}$ cm^{-3}. Results of the measurements of infrared reflectance, Seebeck coefficient, and Hall voltage are interpreted using the nonparabolic two-band approximation under the assumption of isotropic relaxation time. Good agreement between the experimental and theoretical values of the Seebeck coefficient is obtained provided the scattering of free carriers by the optical branch of the lattice vibrations is taken into account. The values of the perpendicular component of the effective mass $m_{\perp,0} = 0.07m_0$ and the density-of-states effective mass $m_{d,0} = (0.16\pm0.01)m_0$ were obtained for the bottom of the band. Taking into account the inequality $m_{\perp,0} < m_{\parallel,0} \leq m_0$ and making use of the assumptions discussed in the paper it is concluded that, in the crystals studied, the value of the $m_\parallel/m_\perp$ ratio decreases with increasing concentration of free carriers.

I. INTRODUCTION

Considerable attention has been paid in recent years to the properties of n-Bi_2Se_3 crystals, whose space group is D^5_{3d}. Results of the study of galvanomagnetic phenomena have led to the assumption that the six-valley model should apply to the description of the conduction band.[1] Using this idea, the results of the infrared-reflectance and Hall-effect measurements on the n-Bi_2Se_3 crystals were analyzed[2] and the concentration dependence of the free-carrier effective mass has been reported. The galvanomagnetic phenomena in the n-Bi_2Se_3 were studied by Caywood and Miller[3] and some results given by Hashimoto[1] were corrected. Proceeding from the analysis of a Shubnikov–de Haas effect study,[4] the idea of the single-valley model was suggested to apply to the description of the conduction band of n-Bi_2Se_3 crystals. Making use of this idea, the nonparabolicity of the conduction band was then studied in more detail.[5-8] The interpretation was then suggested[6] using the empirical nonparabolic dispersion law or the Cohen model.[8]

The scattering mechanism of the free carriers was studied by von Middendorf *et al.*[9] and Bogatyrev *et al.*[10] In both cases, both making use of the parabolic approximation, the authors report that there is a mixed mechanism of the scattering of free carriers, i.e., by acoustical branch of lattice vibrations and by ionized impurities.

The influence of impurities on some physical properties of the n-Bi_2Se_3 crystals was investigated in recent works.[11-13] So far, however, there have appeared no discussions of the relations among the optical, electrical, and thermoelectrical properties of n-Bi_2Se_3 crystals. The present paper summarizes the results of the infrared reflectance in the plasma resonance region, Hall effect, and Seebeck coefficient of thermopower, obtained on n-Bi_2Se_3 crystals with the free-carrier concentration in the range $5\times10^{18} < N < 2\times10^{20}$ cm^{-3}.

The results are interpreted using the two-band approximation and assuming isotropic relaxation time. The paper aims at an analysis of the relations among the optical properties in the plasma resonance-frequency region, the Hall constant, and the Seebeck coefficient for the investigated crystals.

II. EXPERIMENTAL

A. Technique

The Bi_2Se_3 single crystals were grown using the technique described in our earlier work.[13] The free-carrier concentration was adjusted by doping the crystals with elemental copper, or by adding copper and selenium in the atomic ratio 2:3 to the stoichiometric charge of elemental bismuth and selenium. Elements of 99.999% purity were used. The as-prepared single crystals, approximately 40 mm long and 10 mm in diameter, were cleaved along the mirrorlike natural growth faces (0001). Their orientation was checked by means of Laue back-reflection method. The homogeneity of the crystals was checked by measuring the location of the reflectivity minimum in the infrared region, and that on the upper, intermediate, and lower part of the natural cleavage face. For a given composition (dopant concentration) the location of the reflectivity minimum was in all cases identical within the accuracy of ±0.05 μm. Samples used for the measurements of the investigated properties were cut from the central part of the single crystals with a diamond saw; their dimensions were $8\times4\times1$ mm. The infrared reflectance was

TABLE I. Values of the Hall constant, the Seebeck coefficient, and the location of the reflectivity minimum.

Sample	Dopant	R_H ($cm^3A^{-1}sec^{-1}$)	α expt. ($\mu V/K$)	λ_{min} (μm)
1	2Cu + 3Se	1.2	206	22.6
2	2Cu + 3Se	0.514	115	17.8
3	2Cu + 3Se	0.322	90.25	14.8
4	...	0.23	72.1	13.4
5	Cu	0.141	69.2	10.8
6	Cu	0.0724	42.1	8.5
7	Cu	0.032	23.8	6.4

measured at room temperature using a spectrophotometer UR-10 equipped with a special adapter.[14] The measurements were performed for $\vec{E} \perp \vec{c}$ ($\vec{E}$ is the vector of the electric-field intensity of the electromagnetic radiation). The Hall voltage was measured at room temperature, in a weak field parallel to the c axis ($\vec{H} \parallel \vec{c} \sim 1.1T$), using a conventional method. The contacts were made with indium solder. The thermoelectric voltage was measured at room temperature for $\vec{\nabla} T \perp \vec{c}$ ($\vec{\nabla} T$ is the temperature gradient). Since on exposure to air (for a duration of the order of 10^2 h) the surface quality of the Bi_2Se_3(Cu) crystals deteriorates (due to the formation of Cu oxides[15]), the measurements of the investigated quantities were carried out within 3 h from the crystal preparation and repeated after 24 h. In no case was the relative difference of the measured values larger than 5%.

B. Results

The values of the Hall constant and the Seebeck coefficient and the location of the reflectivity minimum are summarized in Table I for all crystals studied. From the dependence of the investigated properties on the character of impurities, it is evident that on doping the Bi_2Se_3 crystals with elemental Cu the free-carrier concentration increases, whereas the doping with copper and selenium mixture in the 2 : 3 atomic ratio leads to a marked decrease of the free-carrier concentration. This phenomenon was discussed[13] using the ideas of interstitial and substitutional defects in the Bi_2Se_3(Cu) and Bi_2Se_3(2Cu + 3Se), respectively.

III. INTERPRETATION OF RESULTS

A. Assumptions

In the analysis of the experimental results, let us make the following assumptions: (i) The transport properties in the n-Bi_2Se_3 crystals at room temperature are governed by one type of free current carriers only. This assumption is acceptable with respect to the results given by Hyde *et al.*[8] (ii) The relaxation time is isotropic. From the results of the reflectance study of n-Bi_2Se_3 crystals having carrier concentration $N \sim 10^{19}$ cm^{-3} one deduced the value $m_\parallel/m_\perp = 4.35$, whereas for the ratio of the electrical conductivities the value $\sigma_\perp/\sigma_\parallel = 4.4$ was obtained.[2] A value close to this quantity, $\sigma_\perp/\sigma_\parallel = 4.35$, was reported by Bogatyrev *et al.*[10] Therefore, in the first approximation, one can take the assumption of isotropic relaxation time to be acceptable also. (iii) The constant-energy surface has the shape of an ellipsoid of rotation.[4,7,10] (iv) The values of the reduced Fermi level ($\eta = E_F/K_BT$) in the investigated range of the free-carrier concentrations lie in the range $0 < \eta < 15$, and the value of the effective mass at the bottom of the band ($m_{\perp,0}$) lies in the interval $0.04 \leq m_{\perp,0} \leq 0.13$. The last mentioned assumptions are realistic with regard to the results reported by Hyde *et al.*[8]

B. Energy dispersion law

As follows from Ref. 16, in the case of a two-band interaction and nonparabolic energy bands, the $\vec{k} \cdot \vec{p}$ method leads to the following expression for the dependence of the energy ϵ on the wave vector $\vec{k}$:

$$\epsilon = \frac{\hbar^2 k^2}{2m_0} - \frac{E_g}{2} \pm \left[\frac{E_g^2}{4} - \frac{\hbar^2 k_\perp^2 E_g}{2m_{\perp,0}} \left(1 - \frac{m_{\perp,0}}{m_0}\right) + \frac{\hbar^2 k_\parallel^2 E_g}{2m_{\parallel,0}} \left(1 - \frac{m_{\parallel,0}}{m_0}\right) \right]^{1/2}. \tag{1}$$

E_g is the forbidden-gap width, the remaining symbols have their usual meaning. Expressing the components of the reciprocal effective mass tensor in the form

$$\frac{1}{m_\perp} = \frac{1}{\hbar^2 k_\perp} \frac{\partial \epsilon}{\partial k_\perp}; \quad \frac{1}{m_\parallel} = \frac{1}{\hbar^2 k_\parallel} \frac{\partial \epsilon}{\partial k_\parallel}, \tag{2}$$

then, provided that $m_{\perp,0} \ll m_{\parallel,0} \leq 1$, the approximation linear in ϵ/E_g yields

$$(m_\perp)^{-1} = (m_0)^{-1} + (m_{\perp,0})^{-1} \times \left[1 + \frac{2\epsilon}{E_g} \left(1 - \frac{m_{\parallel,0}}{m_0}\right) + \frac{\hbar^2 k_\perp^2}{m_{\perp,0} E_g} \frac{m_{\parallel,0}}{m_0} \right]^{-1}, \tag{3}$$

$$(m_\parallel)^{-1} = (m_0)^{-1} + \left(1 - \frac{m_{\parallel,0}}{m_0}\right) (m_{\parallel,0})^{-1} \times \left[1 + \frac{2\epsilon}{E_g} \left(1 - \frac{m_{\parallel,0}}{m_0}\right) - \frac{\hbar^2 k_\perp^2}{m_{\perp,0} E_g} \frac{m_{\parallel,0}}{m_0} \right]^{-1}. \tag{4}$$

If, further, the relation $\epsilon + \frac{1}{2}E_g \gg \hbar^2 k_\perp^2 / 2m_{\perp,0}$ holds,

we have

$$(m_\perp)^{-1} = (m_0)^{-1} + (m_{\perp,0})^{-1}(1 + 2\epsilon/E_g)^{-1}, \quad (5)$$

$$(m_\parallel)^{-1} = (m_0)^{-1} + (1 - m_{\parallel,0}/m_0)(m_{\parallel,0})^{-1}(1 + 2\epsilon/E_g)^{-1} \quad (6)$$

In the case when $m_{\perp,0} \ll m_0$ and $m_{\parallel,0} \ll m_0$, the relations (3) and (4) acquire the well-known form:

$$m_\perp = m_{\perp,0}(1 + 2\epsilon/E_g), \quad (7a)$$

$$m_\parallel = m_{\parallel,0}(1 + 2\epsilon/E_g). \quad (7b)$$

C. Transport coefficients

Supposing that the dependence of the relaxation time τ on energy ϵ can be expressed in the form[17]

$$\tau(\epsilon) = \tau_{0,r}\left(\frac{\epsilon}{K_B T}\right)^{r-1/2} \frac{(1 + \epsilon/E_g)^{r-1/2}}{1 + 2\epsilon/E_g}, \quad (8)$$

where $\tau_{0,r}$ is a constant dependent on the scattering mechanism only and K_B is the Boltzmann constant, the parameter r takes on different values according to the dominating mechanism of the scattering of free carriers, viz.: $r = 0$ for scattering by acoustical branch of lattice vibrations; $r = 1$ for scattering by optical branch of lattice vibrations; and $r = 2$ for scattering by ionized impurities, and the transport coefficient can be advantageously described using the two-parameter Fermi integrals ${}^nL_k^m(\eta, \beta)$,[18]

$${}^nL_k^m = \int_0^\infty \left(-\frac{\partial f_0}{\partial x}\right) x^n (x + \beta x^2)^m (1 + 2\beta x)^k \, dx, \quad x = \epsilon/K_B T; \beta = K_B T/E_g. \quad (9)$$

The relation between the concentration of free carriers and the Fermi level than takes the form

$$N = [(2m_{d,0} K_B T)^{3/2}/3\pi^2\hbar^3]\,{}^0L_0^{3/2}, \quad (10)$$

where $m_{d,0}$ is the density-of-states effective mass at the bottom of the band, for which the single-valley model in our case gives the expression $m_{d,0} = (m_{\perp,0}^2 m_{\parallel,0})^{1/3}$. The expressions for the Seebeck coefficient α and Hall constant R_H then read[17]

$$\alpha = \frac{K_B}{e}\left(\frac{{}^1L_{-2}^{r+1}}{{}^0L_{-2}^{r+1}} - \eta\right), \quad (11)$$

$$R_H = A_\gamma/Ne, \quad (12)$$

where γ is the structure factor ($\gamma = 1$ in the considered case of the single-valley model). The scattering factor is

$$A = {}^0L_0^{3/2}\,{}^0L_{-4}^{2r+1/2}({}^0L_{-2}^{r+1})^{-2}.$$

The relation between the susceptibility effective mass of the free carriers and the effective mass at the bottom of the band has the form[19]

$$m_{\chi\perp} = ({}^0L_0^{3/2}/{}^0L_{-1}^{3/2}) m_{\perp,0}. \quad (13)$$

D. Calculation

In the plasma resonance-frequency region the spectral dependence of the reflectivity can be described using the well-known relation of the Drude theory,[20]

$$n^2 - \mathcal{K}^2 = \epsilon_\infty(1 - B^{-1}), \quad (14)$$

$$2n\mathcal{K} = (\epsilon_\infty/\omega\langle\tau\rangle)B^{-1}, \quad (15)$$

$$R = [(n-1)^2 + \mathcal{K}^2]/[(n+1)^2 + \mathcal{K}^2], \quad (16)$$

where $B = [(\omega/\omega_p)^2 + (1/\omega_p\langle\tau\rangle)^2]$ and ω, n, $\mathcal{K}$, R, $\langle\tau\rangle$, and ϵ_∞ denote, respectively, the frequency, index of refraction, index of absorption, reflectance, mean relaxation time, and the high-frequency dielectric constant.

The angular frequency of the plasma vibrations ω_p is given by

$$\omega_p = (Ne^2/\epsilon_0\epsilon_\infty m_\chi)^{1/2}, \quad (17)$$

where ϵ_0 is the permitivity of vacuum. Making use of relations (14) –(16), the theoretical spectral dependences $R(\lambda)$ were calculated. The best agreement of the theoretical and experimental curves (see Fig. 1) was obtained for $\epsilon_\infty = 29$ and for the values of ω_p given in Table II, column 3. The cal-

TABLE II. Calculated values of the plasma resonance frequency, the ratio $N/m_\perp$, the Fermi level, the Seebeck coefficient, the scattering factor, the free-carrier concentration, and the components of the effective mass.

Sample	Dopant	$10^{-14}\omega_p$ ($\sec^{-1}$)	$10^{-20}(N/m_{\perp c})$ (cm^{-3})	E_F (eV)	$\alpha_{\text{theor.}}$ (μV/K)	A	N (cm^{-3})	$m_\perp^*$	$m_\perp^*$ Calc.	$m_\parallel^*$
1	2Cu + 3Se	0.77	0.539	0.025	204	1.007	6.25×10^{18}	0.116	0.084	0.859
2	2Cu + 3Se	1.02	0.956	0.07	119	1.02	1.24×10^{19}	0.129	0.109	0.888
3	2Cu + 3Se	1.26	1.438	0.083	109	1.05	1.94×10^{19}	0.135	0.116	0.894
4	···	1.37	1.74	0.132	83.7	1.01	2.72×10^{19}	0.156	0.147	0.912
5	Cu	1.70	2.627	0.163	73.5	1.01	4.46×10^{19}	0.169	0.161	0.92
6	Cu	2.14	4.182	0.238	50.0	1.01	8.64×10^{19}	0.206	0.203	0.936
7	Cu	2.85	7.429	0.332	25.0	1.018	1.9×10^{20}	0.256	0.256	0.949

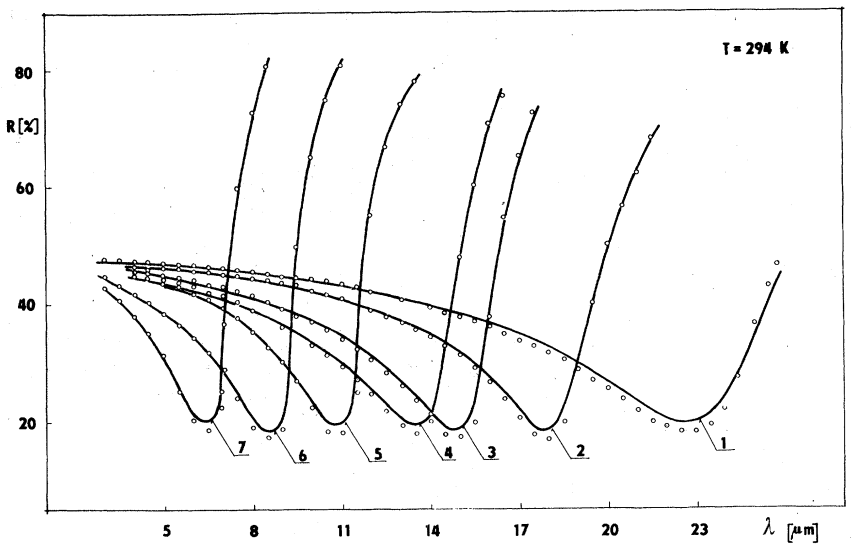

FIG. 1. Spectral dependences of reflectance $R(\lambda)$ of studied crystals. Curves 1–7 correspond to the samples 1–7. See Tables I and II.

culated values $N/m_\chi = N/m_{\chi\perp} = N/m_\perp$ (taking into account the experimental arrangement of the reflectance measurement, $m_\chi = m_{\chi\perp}$ for $\vec{E} \perp \vec{c}$) are given in Table II, column 4. Making use of relations (12) and (13) we obtain

$$eR_H \frac{N}{m_\perp} = \mathcal{R} = \frac{{}^0L_{-4}^{2r+1/2}\,{}^0L_{-2}^{3/2}}{m_{\perp,0}({}^0L_{-2}^{r+1})^2}. \tag{18}$$

The calculated $\mathcal{R}$ vs η dependences are shown in Figs. 2–4 for $r = 0, 1, 2$ and $m_{\perp,0} = 0.04m_0, 0.07m_0, 0.10m_0, 0.13m_0$. The values of η corresponding to our experimental values of the factor $\mathcal{R}$ were read off from these dependences and used in calculation of the Seebeck coefficient α_{theor} according to relation (11). Only for the case $m_{\perp,0} = 0.07m_0$ and $r = 1$ did we obtain a good agreement between the values of α_{theor} and the experimental values of α.

The calculated values of $E_F (= \eta K_B T)$ and α_{theor} are given in Table II, columns 5 and 6. For these values of the Fermi level we get $A = 1$ practically in the whole investigated range of the free carrier concentrations, see Table II, column 7. The values of the free-carrier concentrations $N = 1/R_H e$ are given in Table II, column 8. Using relation (10) and the known values of N and E_F, the value of the density-of-states effective mass, $m_{d,0} = (0.16 \pm 0.01)m_0$, was calculated, which is in very good agreement with the results given by von Middendorf.[9] The values of $m_\perp$ calculated from the $N/m_\perp$ ratio are given in Table II, column 9, to be compared with those calculated using relation (7a), which are given in column 10. In the last column of the Table II are given the values of $m_\parallel$ calculated from relation (6), where $m_{\parallel,0} = m_{d,0}^3/m_{\perp,0}^2 = 0.863m_0$.

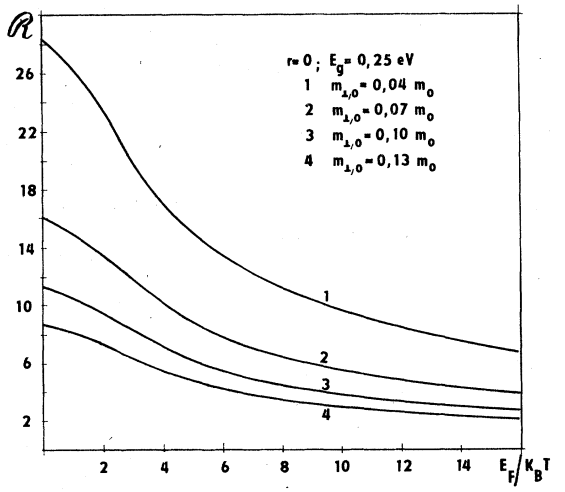

FIG. 2. Dependence of the factor $\mathcal{R}$ on the reduced Fermi level (η) for $r = 0$.

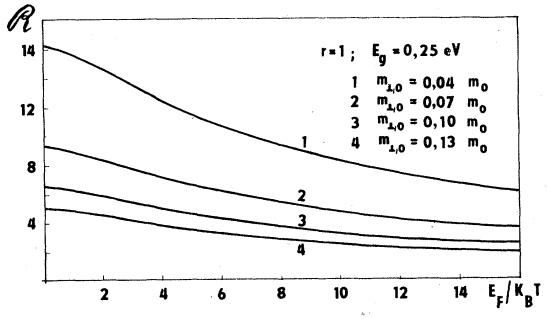

FIG. 3. Dependence of the factor $\mathcal{R}$ on the reduced Fermi level (η) for $r = 1$.

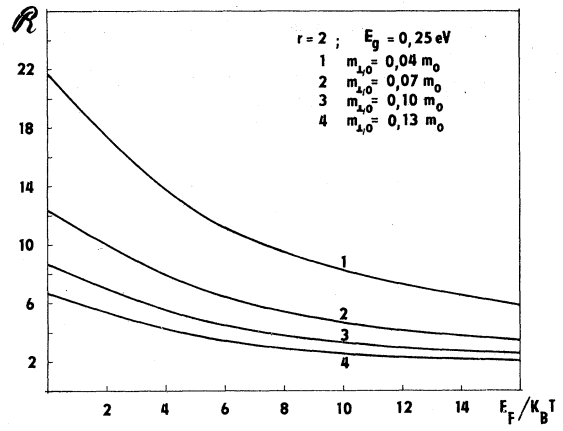

FIG. 4. Dependence of the factor $\mathcal{R}$ on the reduced Fermi level (η) for $r=2$.

IV. CONCLUSIONS

(a) The relations among the transport coefficients and the optical properties of Bi_2Se_3 have been clarified on assumptions that the transport properties are due to one type of the free carriers only, that the relaxation time is isotropic, and that the single-valley model is applicable to the description of the conduction band, i.e., the constant energy surface has the form of an ellipsoid of rotation.

(b) The agreement between the experimental values of the thermoelectric power and the theoretical values calculated using the model described in the paper leads to a conclusion that, in Bi_2Se_3, crystals having the free-carrier concentration within the range 5×10^{18}–2×10^{20} cm^{-3}, the scattering of free carriers by optical phonons dominates at room temperature.

(c) In calculating the values of the effective masses $m_\perp$, $m_\parallel$, and $m_{d,0}$, the inequality $m_{\perp,0} < m_{\parallel,0} \leq m_0$ was taken into account. On increasing the free-carrier concentration there is an increase of the effective masses $m_\perp$ as well as $m_\parallel$, hence also of the density-of-states effective mass m_d. The $m_\perp$ values, however, grow faster than $m_\parallel$. Consequently the $m_\parallel/m_\perp$ ratio decreases with increasing free-carrier concentration—from the value of 8.8 ± 1.4 for $N=6.25\times10^{18}$ cm^{-3} down to 3.7 for $N=1.9\times10^{20}$ cm^{-3}. This phenomenon, which indicates that with increasing free-carrier concentration the $m_\perp$ and $m_\parallel$ values approach each other, was taken into consideration also in the case of similar layer crystals Sb_2Te_3.[21]

(d) Comparing our results with those of other authors, it is evident that there is a fair agreement in the obtained values of the effective masses $m_\perp$ and $m_\parallel$. From the study of the Shubnikov–de Haas effect on a Bi_2Se_3 crystal with concentration $N=9.1\times10^{19}$, Hyde *et al.*[8] derived the value $(0.25\pm0.05)m_0$ for the effective mass $m_\perp$. At the same concentration of free electrons we obtained the value $m_\perp=0.21m_0$, which points to a good agreement even though different methods were used.

The values of $m_\perp$ in the concentration range 10^{18}–10^{19} cm^{-3} obtained by Gobrecht and Seeck[2] are somewhat higher than those given in the present paper. Taking into account the different methods of analyzing the experimental results, however, the observed difference, $(0.02-0.03)m_0$, is not significant. The dependence of the effective mass value $m_\perp$ on the free-carrier concentration, obtained by Hyde *et al.*,[8] is very close to our data.

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