

Low- and High-Field Galvanomagnetic Properties of p -Type Bi_2Te_3 †

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Nine of the twelve low-field galvanomagnetic coefficients of a p -type sample of Bi_2Te_3 having a carrier concentration of $6.8 \times 10^{18} \text{ cm}^{-3}$ were measured at 4.2, 77, and 300 °K. These results are combined with the Fermi-surface effective-mass tensor α obtained previously by de Haas-van Alphen experiments on the same sample to yield the relaxation time τ and its anisotropy. Reasonable success is obtained with the assumption of a single populated set of valence-band ellipsoids and a tensor form of τ . It is shown that either the tensor τ or the product $\alpha\tau$ for an ellipsoid is nonsymmetrical although $\alpha\tau$ for the crystal, as required by reciprocity, is symmetrical. Hall coefficients and longitudinal and transverse magnetoresistances for several orientations were also measured at 4.2 and 77 °K in fields up to 160 kG. High-field saturation values of the longitudinal magnetoresistance were in reasonably good agreement with the results predicted from the mass and low-field-relaxation-time anisotropies. The saturation of the high-field Hall coefficient under both classical ($\hbar\omega_c < kT$) and quantum-mechanical ($\hbar\omega_c > kT$) conditions also agrees with the low-field findings and indicates, further, the absence of carriers from a second populated valence band for this sample.

I. INTRODUCTION

The study of the low-field galvanomagnetic (LFGM) behavior has often been used to obtain information on the electronic band structure. These results, however, are complicated by the anisotropy of the relaxation time τ , and for a many-valley model, it can be shown (with certain assumptions) that all static-field transport properties will not distinguish between the anisotropies of the effective mass m^* and τ .

The LFGM tensors in p -type Bi_2Te_3 have been studied in order that these results, together with de Haas-van Alphen (dHvA) data, would yield these two important anisotropies separately. Recently Ashworth, Rayne, and Ure¹ have analyzed the LFGM of n - and p -type Bi_2Te_3 in this manner and obtained the anisotropy of τ . These authors have found that the parameters obtained from a fitted single-band model were dependent upon the carrier concentration and concluded that a two-band model was applicable. Such an assumption is reasonable but it is not the only explanation of the observed behavior.

We present below some previously unpublished studies on p -type Bi_2Te_3 contained in a thesis by one of us (L. R. T.). These studies, although old, still apparently constitute one of the few cases where quantitative analysis of the anisotropy of m^* and τ in a semiconductor is obtained from de Haas-van Alphen low- and high-field galvanomagnetic studies, and optical studies of the same sample. Our treatment does assume a single populated valence band for this hole concentration ($6.8 \times 10^{18} \text{ cm}^{-3}$). A reasonably successful interpretation of both the low- and high-field galvanomagnetic behav-

ior results with this assumption. Several experimental observations relevant to the possibility of a second valence band will be noted below. From these it is concluded that such a band, if it exists, would appear of minor consequence in the analysis of the transport properties of our sample.

The dHvA experiments on this sample have been reported in a previous publication.² We summarize here the results of these studies. (i) The Fermi surface was found to consist of three or six ellipsoids centered on mirror planes or binary axes. The effective-mass components and the tilt angle of the ellipsoids relative to the crystal axes (with x =bisectrix, y =binary, and z =trigonal axes) are given in Table V. Note that the identification of the x and y axes used by Ashworth *et al.*¹ is opposite to that used here. (ii) The density-of-states-effective-mass ratio $m_{ds}^*/m_0 = 0.16$ per ellipsoid, the carrier concentration $n_e = 1.13 \times 10^{18} \text{ cm}^{-3}$ per ellipsoid, and the calculated Fermi level = $24.5 \times 10^{-3} \text{ eV}$. (iii) For $\vec{H} \parallel$ trigonal axes the cyclotron-mass ratio $m_c^*/m_0 = 0.13$, $\omega_c\tau \sim 1$ at 10 kG (estimated from the onset of dHvA oscillations), the Dingle broadening temperature $\approx 6.3^\circ\text{K}$, and the infinite-field phase factor was in agreement with that expected for a maximal area, a quadratic E -vs- k law, and a positive spin-splitting term. (If the argument of the usual spin term is restricted to the first quadrant, then $|g^*| < 4$.) (iv) No evidence of a second populated valence band in this sample was found in fields up to 200 kOe.

II. THEORY OF LFGM BEHAVIOR

The phenomenological equations for the LFGM tensors relating the current density J_i , the electric field E_i , and the magnetic field H_i are given by

$$\begin{aligned} J_i &= \sigma_{ij} E_j + \sigma_{ijk} E_j H_k + \sigma_{ijkl} E_j H_k H_l, \\ E_i &= \rho_{ij} J_j + \rho_{ijk} J_j H_k + \rho_{ijkl} J_j H_k H_l \end{aligned} \quad (1)$$

(with the summation convention), where ρ_{ij} is the resistivity, ρ_{ijk} are the Hall coefficients, ρ_{ijkl} the magnetoresistance coefficients, and the σ 's are the corresponding conductivity coefficients. The relations between the various coefficients, established from crystalline symmetry and Onsager reciprocity, have been determined by Juretschke³ for the crystal class $3m$ and Fumi⁴ has shown that these will also apply for the class $\bar{3}m$ (Bi_2Te_3). The results give 12 independent, nonvanishing components with two for the resistivity tensor ($\vec{J} \parallel$ and $\perp$ to the trigonal axis), two for the Hall tensor ($\vec{H} \parallel$ and $\perp$ to the trigonal axis) and eight magnetoresistance coefficients. These tensor components (both σ and ρ) are given by Drabble and Wolfe⁵ and by Juretschke.³ The coordinate system applied in the dHvA experiments is used here.

The first calculations of the LFGM tensor components for the many-valley model were made with the assumption of isotropic scattering.⁵⁻⁸ The most convenient results are those of Keyes⁸ who established a matrix formalism which could be applied to any crystal with an axis of symmetry. Herring and Vogt⁹ extended the analysis to allow a symmetrical relaxation-time tensor (diagonal in the Fermi-surface representation) and showed, for this case, that in all static-field transport properties m_i must be replaced by m_i/τ_i . For Bi_2Te_3 a more general analysis has been established by Korenblit¹⁰ in which the τ tensor may be nonsymmetrical but the results are in a cumbersome form for analysis. We find by direct calculation that the general case of a nonsymmetrical τ tensor can be immediately incorporated into the more tractable results of Keyes⁸ by replacing the reciprocal-mass-tensor components α_{ij} by the ij component of the matrix product $\alpha\tau$.

Before giving the general formulas for the LFGM behavior, we list the required assumptions: (i) The Fermi surface consists of a set of general ellipsoids of arbitrary orientation centered on any N -fold ($N=3, 4, 6$) equivalent points in $\vec{k}$ space. (ii) A relaxation time of the form $\tau = \tau' \varphi(\epsilon)$ exists where τ and τ' are tensors and $\varphi(\epsilon)$ is a scalar. No restriction on the symmetry of τ is made other than the requirement (from Onsager reciprocity) that $\alpha\tau$ be symmetrical. Further discussion of the symmetry of the τ tensor is given by Mackey and Sybert.¹¹ The function $\varphi(\epsilon)$ may be completely general. The justification for assuming a scalar $\varphi(\epsilon)$ is based on the observed Seebeck coefficient which we, as well as others,¹² have found to be isotropic between 78 and 300 °K. (No measurements below 78 °K have been reported.) Herring and Vogt⁹ have shown that, under assumption (i), a sufficient con-

dition for an otherwise anisotropic crystal to show an isotropic Seebeck coefficient is that the energy dependence (but not necessarily the magnitude) of τ be isotropic.

With these assumptions, we obtain the following theoretical expressions for the LFGM-conductivity-tensor components:

$$\begin{aligned} \sigma_{ij} &= (I_0 \Sigma \alpha \tau')_{ij}, \\ \sigma_{ijk} b_k &= [I_1 \Delta \Sigma (\alpha \tau')^{-1}]_{ij}, \\ \sigma_{ijkl} - \sigma_{\mu\nu} &= [NI_2 \Delta [U - (1/N) \Sigma (\alpha \tau') (\alpha \tau')^{-1}]]_{\mu\nu}, \end{aligned} \quad (2)$$

where the summation is over the N valleys, α and τ' are the reciprocal-effective-mass-ratio and relaxation-time tensors, $\Delta = |\alpha \tau'|$ (the determinantal value of $\alpha \tau'$), $(\alpha \tau')^{-1}$ is the tensor reciprocal to $\alpha \tau'$, and $\vec{b}$ is the unit vector parallel to the field. The fourth-rank magnetoresistance coefficients and the fourth-rank tensor $(\alpha \tau') (\alpha \tau')^{-1}$ have been reduced to the usual 6×6 matrix, and U is the unit 6×6 matrix. The quantities

$$I_n = \left(\frac{e}{m_0}\right)^n \frac{e^2}{3\pi^2 m_0} \left(\frac{2m_0}{\hbar^2}\right)^{3/2} \frac{1}{|\alpha|^{1/2}} \times \int [\Phi(\epsilon)]^{n+1} \epsilon^{3/2} \frac{\partial f_0}{\partial \epsilon} d\epsilon \quad (3)$$

are those given by Keyes.⁸ We define $B = I_1^2/I_0 I_2$ and for a completely degenerate electron gas $B=1$ while for arbitrary degeneracy with $\Phi(\epsilon) = \epsilon^\lambda$, the integral above can be replaced by

$$\left[\frac{3}{2} + \lambda(n+1)\right] (kT)^{3/2 + \lambda(n+1)} F_{1/2 + \lambda(n+1)}(\eta), \quad (4)$$

where F_r is the Fermi-Dirac integral of order r which has been tabulated elsewhere¹³ and $\eta = E_F/kT$ the reduced Fermi level. The function $\Phi(\epsilon) = \epsilon^{-1/2}$ corresponds to scattering by acoustic lattice modes which has been shown to occur above 78 °K in Bi_2Te_3 ¹⁴ when proper account of the degeneracy is taken.

Although the crystal class $\bar{3}m$ allows, in general, 12 independent nonvanishing LFGM-tensor components, neither the Fermi surface nor the relaxation time chosen in this model is of the most general form for the crystal symmetry so that the 12 coefficients can be expressed with only seven parameters. (These are the three diagonal and one off-diagonal components of $\alpha \tau'$ and I_0 , I_1 , and I_2 .) There exist, therefore, five constraint relations between the coefficients among which the following three (given by Efimova *et al.*¹²) will be useful:

$$\begin{aligned} K_1 &= \sigma_{33} \sigma_{231} \sigma_{1133} / \sigma_{11} \sigma_{123} \sigma_{3311} = 1, \\ K_2 &= \sigma_{1133} (4\sigma_{11} \sigma_{231} - \sigma_{123} \sigma_{33}) / \sigma_{11} \sigma_{123} (3\sigma_{1122} - \sigma_{1111}) = 1, \\ K_3 &= 2(\sigma_{11}^2 \sigma_{3311} - \sigma_{33}^2 \sigma_{1133}) / \sigma_{11} \sigma_{33} (4\sigma_{1111} - 3\sigma_{3333}) = 1. \end{aligned} \quad (5)$$

These relations serve as the best test of assumptions (i) and (ii).

III. EXPERIMENTAL ARRANGEMENT

The sample starting charge consisted of 99.9999% purity Bi and Te. The materials, weighed to stoichiometric proportions, were placed in a Vycor tube, evacuated (10^{-6} Torr) and sealed off with a minimum enclosed volume of free space. The charge was melted (585°C is the melting point of Bi_2Te_3), agitated for complete mixing, and subsequently quenched or lowered (Bridgman growth). The ingot, removed from the tubing, was placed in a horizontal Vycor boat containing a well-out-gassed graphite-powder bedding, and evacuated and sealed off in Vycor tubing. (The soft bedding was crucial for obtaining large crystals of good quality.) The final crystal growth is performed in a horizontal furnace consisting of a background heater which keeps the average temperature of the entire evacuated sample chamber at $\sim 50^{\circ}\text{C}$ below the compound melting point, and a ring heater which establishes a molten zone. The furnace is pulley driven on tracks and the molten zone traversed the length of the stationary ingot at a speed of $\frac{1}{8}$ in./h. The inhomogeneity resulting from Te segregation was minimized by "zone leveling" whereby the total number of passes in each direction is the same.

The ingot which yielded the samples for our measurements was approximately 20 cm long (1-cm^2 cross section) of which all but the first 4 cm was a single crystal of excellent quality possessing no visible twinning or low-angle boundaries.

Samples were spark cut from the ingot in the form of parallelepipeds. All 12 tensor components can be obtained from two samples (used for dHvA studies) using three orientations. The sample orientations and the formulas for the resistivity coefficients employed by Drabble and Wolfe⁵ have been followed here. Several coefficients are measured twice in these orientations and a fourth (redundant) orientation was also used to obtain additional checks on the reproducibility of the measured coefficients. The consistency of the data indicates that inhomogeneity effects were small. It was also determined from measurements on adjacent samples that gross variations in the resistivity and Hall coefficient over the sample length were less than several percent.

Current leads were soldered to the sample ends with indium-tin alloys. The 0.003-in. tantalum-wire potential leads were spot welded to the sample surfaces. The usual precautions in lead placements, sample sizing, and contact uniformity have been followed.¹⁵

Measurements of the LFGM tensor were made at 4.2, 77, and 300°K to establish the temperature dependence of the measured parameters. At helium and nitrogen temperatures, the sample was immersed in the respective liquids while at room

temperature measurements were performed in air with reduced currents. The dc measurements of the galvanomagnetic effects are affected by Seebeck voltages for slight departures from isothermal conditions at the sample and at the lead-wire junctions. To avoid this, an ac differential method which allowed good sensitivity ($0.02\text{--}0.05\text{ }\mu\text{V rms}$) was used. With the resultant elimination of effects irreversible in the current, the separation of effects irreversible in the H field was obtained by magnet rotation. The orientation of the H field could be accurately ($\frac{1}{4}^{\circ}$) determined from the vanishing of the Hall voltage.

At each temperature the field dependence of the Hall and magnetoresistance coefficients was established from 0 to 25 kOe so that the theoretical low-field region (magnetoresistance proportional to H^2) could be determined. The limiting fields for the LFGM behavior depended on the temperature as well as the individual tensor component.

IV. RESULTS

The complete description of the numerous data obtained in these experiments will not be given. The field and temperature dependences of the coefficients and the satisfaction of the required angular dependence involve a tedious but straightforward analysis. The final results in the form of the LFGM tensor coefficients at the three temperatures are given in Tables I–III. Only nine of the 12 coefficients could be determined accurately (ρ_{311} , ρ_{113} , ρ_{313} were too small) but these, fortunately, are sufficient.

The validity of the model assumptions may be checked from the three constraint relations¹⁶ in Eq. (5). The values for the various K 's are given

TABLE I. Low-field-galvanomagnetic-tensor coefficients at 4.2°K .

Coefficient ratio	Obs. ^a	Calc. ^b	Calculated from
			dHvA data (isotropic τ)
ρ_{33}/ρ_{11}	2.62	2.68	2.55
ρ_{321}/ρ_{123}	2.00	1.97	2.37
ρ_{1111}/ρ_{1133}	0.61	0.65	0.51
ρ_{1122}/ρ_{1133}	0.52	0.53	0.49
ρ_{3333}/ρ_{1111}	4.5	4.9	0.37
ρ_{3311}/ρ_{1133}	1.0	0.33	0.022
Consistency check			
$K_1 = 0.98$			
$K_2 = 1.10$			
$K_3 = 1.05$			

^a $\rho_{11} = 0.88 \times 10^{-6}$ (mks), $\rho_{123} = 0.42 \times 10^{-6}$ (mks), $\rho_{1111} = 0.20 \times 10^{-6}$ (mks).

^bFor $(\alpha\tau)_{22}/(\alpha\tau)_{11} = 6.5$, $(\alpha\tau)_{33}/(\alpha\tau)_{11} = 1.4$, $(\alpha\tau)_{13}/(\alpha\tau)_{11} = 0.96$, $B = 1.0$.

TABLE II. Low-field galvanomagnetic-tensor coefficients at 78°K.

Coefficient ratio	Observed ^a	Calculated ^b
ρ_{33}/ρ_{11}	2.7	2.5
ρ_{321}/ρ_{123}	2.0	2.0
ρ_{1111}/ρ_{1133}	0.72	0.75
ρ_{1122}/ρ_{1133}	0.76	0.73
ρ_{3333}/ρ_{1111}	3.6	3.9
ρ_{3311}/ρ_{1133}	1.44	0.67
Consistency check		
$K_1 = 0.86$		
$K_2 = 0.88$		
$K_3 = 0.80$		

^a $\rho_{11} = 2.3 \times 10^{-6}$ (mks), $\rho_{123} = 0.44 \times 10^{-6}$ (mks), $\rho_{1111} = 0.108 \times 10^{-6}$ (mks).

^bFor $(\alpha\tau)_{22}/(\alpha\tau)_{11} = 6.8$, $(\alpha\tau)_{33}/(\alpha\tau)_{11} = 1.6$, $(\alpha\tau)_{13}/(\alpha\tau)_{11} = 1.05$, $B = 0.98$.

in Tables I–III. Since each of the constraint relations involves eight measured resistivity components, the over-all agreement is generally good. At the higher temperatures this agreement becomes poorer, possibly indicating some breakdown of the model assumptions. The largest discrepancy ($K_3 = 0.7$ at 300°K) is essentially identical to that reported by Efimova *et al.*¹² which suggests that experimental errors are not the cause in this case. It is not possible to determine which of the model assumptions has been violated at the higher temperatures. Considering that only K_3 is in error, and that this 30% error occurs in a combination of eight measured quantities which is very sensitive to small differences (see below), it appears that the model, in fact, is reasonably adequate at all temperatures.

To demonstrate the anisotropy of the relaxation time, the complete calculation of the anisotropy of the LFGM tensor has been carried out using the values of α obtained from the dHvA analysis and assuming the scalar τ . These results are compared with the observed anisotropies at 4.2°K in Table I. From Eq. (2), it can be shown that the ratios ρ_{11}/ρ_{33} , ρ_{123}/ρ_{231} , and ρ_{1111}/ρ_{3333} are independent of electron degeneracy. Therefore, the calculated values will further be temperature independent if we assume $\alpha\tau'$ to be temperature independent.

From the comparison of the observed and predicted behavior, we note the following: (i) At 4.2°K the results calculated for a scalar τ give a qualitative agreement with the measured resistivity-coefficient ratios, but most of the results for the Hall and magnetoresistance coefficients, which are particularly sensitive to an anisotropic τ , show discrepancies. (ii) At the higher temperatures, the disagreement becomes somewhat larger. If the

band structure is temperature independent, this result is not in agreement with the expectation of a scalar τ at high temperatures as assumed by Efimova *et al.*¹² in their analysis.

The tensor-coefficient ratios given in Tables I–III are actually independent of the magnitude and energy dependence of τ . In this form, the values depend only on $\alpha\tau'$ and one degeneracy parameter $B = I_1^2/I_0I_2$ which is unity for a degenerate gas independently of $\Phi(\epsilon)$. For the higher temperature data, we have calculated the values for B from Seebeck coefficient data of this sample based on the experimental finding¹⁴ of acoustical scattering and find $B = 0.98$ and 0.80 at 78 and 300°K, respectively.¹⁷

From the six measured tensor ratios, and the three constraint equations [Eq. (5)], three unknowns can be obtained and these were chosen to be of the form $(\alpha\tau')_{22}/(\alpha\tau')_{11}$, $(\alpha\tau')_{33}/(\alpha\tau')_{11}$, and $(\alpha\tau')_{13}/(\alpha\tau')_{11}$. In practice, the solutions were obtained by iterative approximations. The results of the solutions are given in Tables I–III for 4.2, 77, and 300°K. (As Efimova *et al.*¹² have noted, the quadratic nature of the analytic problem actually establishes two solutions for the $\alpha\tau'$ ratios. The resultant τ anisotropies are markedly different in the two cases; however, the theoretical approximations required that the solution with the smaller anisotropy be chosen.)

The agreement obtained from the chosen sets of $\alpha\tau'$ is generally a satisfying one. At the higher temperatures, as expected, the discrepancies become larger but the results still remain sufficiently useful. In every case, only the coefficient ratio ρ_{3311}/ρ_{1133} showed large deviations. This is apparently due to its analytical form which, in our case, is given by the difference of two nearly equal quan-

TABLE III. Low-field-galvanomagnetic-tensor coefficients at 300°K.

Coefficient ratio	Observed ^a	Calculated ^b
ρ_{33}/ρ_{11}	2.85	2.75
ρ_{321}/ρ_{123}	1.67	1.58
ρ_{1111}/ρ_{1133}	0.43	0.41
ρ_{1122}/ρ_{1133}	0.68	0.54
ρ_{3333}/ρ_{1111}	4.6	4.6
ρ_{3311}/ρ_{1133}	1.6	0.78
Consistency check		
$K_1 = 0.90$		
$K_2 = 1.05$		
$K_3 = 0.70$		

^a $\rho_{11} = 21.7 \times 10^{-6}$ (mks), $\rho_{123} = 0.66 \times 10^{-6}$ (mks), $\rho_{1111} = 0.025 \times 10^{-6}$ (mks).

^bFor $(\alpha\tau)_{22}/(\alpha\tau)_{11} = 4.5$, $(\alpha\tau)_{33}/(\alpha\tau)_{11} = 1.0$, $(\alpha\tau)_{13}/(\alpha\tau)_{11} = 0.59$, $B = 0.80$.

tities and may be very sensitive to a minor breakdown of the assumptions.

The ratios of the $\alpha\tau'$ components so obtained represent the most useful information which can be obtained from the LFGM behavior. Assuming that τ is a symmetric tensor simultaneously diagonal with α we can obtain the tilt angle of the Fermi-surface ellipsoids by diagonalizing $\alpha\tau'$. These results, at the three temperatures, together with the values of m_i/τ_i in the Fermi-ellipsoid-principal-axes system are given in Table IV. It can be seen that although the m_i/τ_i are fairly temperature dependent the tilt angle is less so. Even in this approximation, a large anisotropy in τ is obtained on substituting the dHvA effective-mass data. However, the disagreement in the tilt angles obtained from diagonalizing $\alpha\tau'$ (51°) and from dHvA measurements (65°) shows that α and τ are not diagonal in the same representation.

The correct values for the relaxation-time tensor are obtained from $\tau = \alpha^{-1}\alpha\tau$, where α^{-1} can be computed from dHvA data alone. The values of τ obtained in this manner and a general summary of the LFGM results are given in Table V. Summarizing the importance of these results we find the following.

(i) τ takes the form of a nonsymmetrical tensor. The crystalline symmetry imposes no restriction on the symmetry of τ although, in the Korenblit analysis, Onsager reciprocity (required for $\alpha\tau$) establishes the relation $\tau_{13}/\tau_{31} = m_1/m_3$ in the Fermi ellipsoid system. The nonsymmetrical nature of τ essentially states that there is a rotational component in the collision term governing the rate of change of charge-carrier velocity v in the ensemble. This can be seen from the collision term $(dv_i/dt)_c = \nu_{ij}v_j$, where ν_{ij} is the frequency tensor ($\nu = \tau^{-1}$). Writing $\nu = \nu_s + \nu_{as}$ (symmetric and antisymmetric parts) we obtain $\vec{v} = -\nu_s\vec{v} + \vec{\omega} \times \vec{v}$ with $|\omega| = \frac{1}{2}(\nu_{13} - \nu_{31})$. The transitions between states of a charge carrier which arise from collisions, therefore, exhibit a rotational component

TABLE IV. Effective-mass-relaxation-time parameters for symmetric τ tensor.

Temp. Ellipsoid tilt angle ^a	4.2°K	78°K	300°K
	51°	52°	45°
$\tau_1(m_0/m_1)^b$	3.4×10^{-12} sec	1.5×10^{-12} sec	1.4×10^{-13} sec
$\tau_2(m_0/m_2)^b$	10×10^{-12} sec	4.2×10^{-12} sec	4.0×10^{-13} sec
$\tau_3(m_0/m_3)^b$	0.31×10^{-12} sec	0.135×10^{-12} sec	0.36×10^{-13} sec
τ_1/τ_2^c	1.33	1.44	1.45
τ_3/τ_2^c	0.28	0.29	0.82
τ_1/τ_3^c	4.75	5.0	1.77

^aValues referred to trigonal axis (rotation about binary axis).

^bValues referred to ellipsoid principal-axes system.

^cCalculated with effective masses obtained from dHvA data.

TABLE V. Effective masses and relaxation times for nonsymmetric τ tensor. At 78° and 300°K, τ 's have been computed using effective masses obtained at 4.2°K.

Temp. Ellipsoid tilt angle	4.2°K	78°K	300°K
	66°	...	...
(In crystal-axes system)			
α_{11}	2.80	...	...
α_{22}	20.8	...	...
α_{33}	4.65	...	...
α_{13}	-1.04	...	...
τ_{11}	4.7×10^{-13} sec	1.85×10^{-13} sec	3.0×10^{-14} sec
τ_{22}	4.85×10^{-13} sec	2.0×10^{-13} sec	1.91×10^{-14} sec
τ_{33}	3.72×10^{-13} sec	1.75×10^{-13} sec	1.62×10^{-14} sec
τ_{13}	-4.2×10^{-13} sec	-1.68×10^{-13} sec	-1.24×10^{-14} sec
τ_{31}	-2.28×10^{-13} sec	-0.98×10^{-13} sec	-0.45×10^{-14} sec
(In ellipsoid principal-axes system)			
m_1^*/m_0	0.196	...	...
m_2^*/m_0	0.048	...	...
m_3^*/m_0	0.43	...	...
τ_{11}	5.7×10^{-13} sec	2.74×10^{-13} sec	2.46×10^{-14} sec
τ_{22}	4.85×10^{-13} sec	2.00×10^{-13} sec	1.90×10^{-14} sec
τ_{33}	2.75×10^{-13} sec	0.85×10^{-13} sec	2.15×10^{-14} sec
τ_{13}	1.61×10^{-13} sec	0.59×10^{-13} sec	0.70×10^{-14} sec
τ_{31}	3.54×10^{-13} sec	1.30×10^{-13} sec	1.51×10^{-14} sec

in the mirror plane. Diagonalizing the symmetric part of our τ in Table V obtained at 4.2°K gives $\tau_{11} = 2.39$, $\tau_{22} = 4.65$, and $\tau_{33} = 3.77$ in units of 10^{-13} sec, with a tilt angle about the binary axis of -43° relative to the ellipsoid principal axis or $+23^\circ$ relative to the crystal axis. It is important to note that both ρ_{ij} and ρ_{ijk} were quite insensitive, in our case, to the existence of a nonvanishing τ_{as} . The occurrence of a nonsymmetrical τ tensor is due to the assumption, by Korenblit,¹⁰ that Onsager reciprocity applies to the conductivities of the individual ellipsoids (i.e., $\alpha_1\tau_{13} = \alpha_3\tau_{31}$) and, thereby, to the crystal as a whole. Mackey and Sybert¹¹ have recently questioned the necessity of the former constraint. They show, by example, how the reciprocity may apply to the crystal but not to the individual ellipsoids. One may attempt this approach to our results in the following way. Assume that the relaxation time is a symmetric tensor and indicate it by τ^s . Then the product $\alpha\tau^s$ will, in general, contain both symmetric $(\alpha\tau^s)_s$ and antisymmetric $(\alpha\tau^s)_{as}$ parts. The latter, for all ellipsoids, must sum to zero (crystal reciprocity). The former we associate with the symmetric tensors assumed in the analysis of Korenblit¹⁰ and others.⁵⁻⁹ Thus the experimental result gives only the symmetric part of $\alpha\tau^s$. One then readily computes the components of τ^s in terms of the τ in Table V; $\tau_{11}^s = \tau_{11}$, $\tau_{22}^s = \tau_{22}$, $\tau_{33}^s = \tau_{33}$, $\tau_{31}^s = \tau_{13}^s = [2\alpha_1/(\alpha_1 + \alpha_3)] \times \tau_{13} = 2.2 \times 10^{-13}$ sec. The values refer to the ellipsoid principal axes system. In the crystal-axes system this gives $\tau_{11}^s = 4.87$, $\tau_{22}^s = 4.85$, $\tau_{33}^s = 3.56$, and $\tau_{31}^s = \tau_{13}^s = -2.65$ in units of 10^{-13} sec. This yields the physically reasonable result that the re-

laxation time in the cleavage planes is isotropic and larger than in the perpendicular direction. However, τ is not diagonal in the crystal-axes system. It is not known whether this procedure is rigorously correct. It is safest to conclude that τ is not a tensor diagonal with α and that either τ or $\alpha\tau$ (for an ellipsoid) contains a rotational component.

(ii) At 77 and 300 °K the τ tensors have been computed assuming that α is temperature independent. If this be true, the results show that the usual expectations of a scalar τ for high-temperature acoustical scattering are not realized at room temperature in Bi_2Te_3 .

(iii) The general results allow a calculation of $\omega_c\tau$ (the cyclotron frequency $\omega_c = eH/m_c^*$, where m_c^* is the cyclotron mass) for any orientation. We find $\omega_c\tau = 1$ at $H = 13$ kOe for H parallel to the trigonal axis and a mobility of $10^4 \text{ cm}^2/\text{V sec}$ in the basal plane. The dHvA oscillations which should appear at $\omega_c\tau \sim 1$ were first observed at $H \approx 10$ kOe for this orientation. The computed values of $\omega_c\tau$ are further confirmed in the high-field galvanomagnetic behavior (Sec. VIII).

These results assume the validity of the model (single, ellipsoidal, paraboloid band, and the tensor form of τ given above). It appears unlikely that alternate models would lead to the same constraint relations [Eq. (5)] and to the (consistent) galvanomagnetic data discussed in Secs. V and VI below.

V. NUMBER OF ELLIPSOIDS IN FERMI SURFACE

The LFGM data can now be combined with the dHvA results to determine the number of ellipsoids in the band model. On inverting the Hall-conductivity tensor the total hole concentration p can be obtained from the Hall coefficients by $\rho_{ijk} = r\beta_{ijk}/pe$, where r is the usual degeneracy-field-strength relaxation time parameter¹⁸ and β is an anisotropy factor which gives the correct relation between the Hall coefficient and the carrier concentration for nonspherical energy surfaces and anisotropic relaxation times.

There is little to be uncertain in the value of r ; it is always unity for a degenerate system (our sample at 4.2 °K) and for acoustical scattering increases by only 18% in going to the nondegenerate (high-temperature) limit. At the higher temperatures, r was calculated¹⁸ from Fermi-Dirac integrals using Seebeck-coefficient data.¹⁴

The correct analytical forms for β are found to be

$$\beta_{123} = 4(\alpha\tau)_{22}(\alpha\tau)_{11}/[(\alpha\tau)_{11} + (\alpha\tau)_{22}]^2 \quad (6)$$

and

$$\beta_{321} = [(\alpha\tau)_{22}(\alpha\tau)_{33} + (\alpha\tau)_{11}(\alpha\tau)_{33} - (\alpha\tau)_{13}^2]/[(\alpha\tau)_{11} + (\alpha\tau)_{22}](\alpha\tau)_{33}, \quad (7)$$

which can be evaluated from the LFGM data.

A complete summary of the carrier concentration data is given in Table VI. These results are obtained using the $\alpha\tau$ components given in Tables I–III and do not depend on the various individual τ components which have been calculated or their symmetry. In an important confirmation of self-consistency, we find that both Hall coefficients (which differ by a factor of 2) give the same carrier concentration and that the carrier concentration is essentially independent of temperature even though the Hall coefficients vary by approximately 50%. Similar findings have been obtained by Efimova *et al.*¹²

Comparing the over-all carrier concentration at 4.2 °K $[(6.85 \pm 0.2) \times 10^{18} \text{ cm}^{-3}]$ —an independent determination of this number comes from the high-field studies—with the carrier concentration per ellipsoid from dHvA data $[(1.13 \pm 0.05) \times 10^{18} \text{ cm}^{-3}]$ we find that there are six ellipsoids in the valence-band structure of Bi_2Te_3 . The existence of six ellipsoids requires that they be centered on symmetry elements which normally lead to doubling.¹⁹ Since only the orientation of the ellipsoids is obtained in these experiments one cannot discriminate between twofold axis centering and mirror plane centering of the ellipsoids.

VI. HIGH-FIELD GALVANOMAGNETIC BEHAVIOR

The calculation of the high-field galvanomagnetic (HFGM) tensor with anisotropic α and τ for the “classical” case ($\hbar\omega_c < kT$) has been carried out by Herring and Vogt⁹ for τ diagonal with α . Hübner²⁰ has calculated the galvanomagnetic coefficients for the case of τ anisotropic but not diagonal with α and confirms our results given below. The high-field limiting values of the magnetoresistance and Hall coefficients can be computed in terms of standard parameters, and strong independent support for the band model can be obtained from the high-field behavior. We shall give below only the general features of these results which will affect our analysis.

TABLE VI. Carrier-concentration data. Low-field Hall-coefficient anisotropy factors.

Coefficient	4.2 °K	77 °K	300 °K
β_{123}	0.46	0.445	0.59
β_{321}	0.91	0.89	0.94
Carrier concentration from low-field Hall data			
ρ_{123}	$6.9 \times 10^{18} \text{ cm}^{-3}$	$6.6 \times 10^{18} \text{ cm}^{-3}$	$6.6 \times 10^{18} \text{ cm}^{-3}$
ρ_{321}	$6.8 \times 10^{18} \text{ cm}^{-3}$	$6.6 \times 10^{18} \text{ cm}^{-3}$	$6.3 \times 10^{18} \text{ cm}^{-3}$
Carrier concentration from high-field Hall data			
ρ_{123}	$6.8 \times 10^{18} \text{ cm}^{-3}$	$6.5 \times 10^{18} \text{ cm}^{-3}$	
Carrier concentration from dHvA data			
	$1.13 \times 10^{18} \text{ cm}^{-3}/\text{ellipsoid}$		

(i) The most powerful result is that in the high-field limit the Hall coefficient R_H equals $1/pe$ independently of the charge-carrier degeneracy, the form of the band structure, the relaxation time, or their anisotropies. Therefore, a determination of the carrier concentration is possible based only on the assumption of a closed Fermi surface.

(ii) The limiting value of the longitudinal magnetoresistance ρ_H/ρ_0 will depend only on the anisotropy in $\alpha\tau$ if τ can be expressed by $\tau'\phi(\epsilon)$, and this value may be computed from the LFGM data alone.

(iii) The limiting value of the transverse magnetoresistance depends, in addition, on the form of the energy dependence of τ

For the longitudinal case, the limiting value of ρ_H/ρ_0 for a single valley obtained from the calculations of Herring and Vogt⁹ is given in our notation by $\sigma_H/\sigma_0 = (\alpha\tau)_{ii}^{-1}(\alpha\tau)_{ii}$, where $(M)_{ii}$ is the ii component of the matrix M , i is the direction of the magnetic field, and $\alpha\tau$ is referred to the crystal-line axis. After summation over all equivalent valleys we find

$$\frac{\sigma_0}{\sigma_H} = \frac{\rho_H}{\rho_0} = \frac{v}{w} \quad (8)$$

for $\vec{H} \parallel$ trigonal axis, and

$$\frac{\sigma_0}{\sigma_H} = \frac{\rho_H}{\rho_0} = \frac{3v(1+u)(uv+3w)}{2w(9uv+3w)} \quad (9)$$

for $\vec{H} \parallel$ bisectrix axis. In these expressions we have used the relations

$$\begin{aligned} u &= (\alpha\tau)_{22}/(\alpha\tau)_{11}, & v &= (\alpha\tau)_{33}/(\alpha\tau)_{11}, \\ w &= (\alpha\tau)_{33}/(\alpha\tau)_{11} - [(\alpha\tau)_{13}/(\alpha\tau)_{11}]^2. \end{aligned} \quad (10)$$

The simple relation between ρ and σ in this case results from the vanishing Hall-conductivity contribution in the high-field limit.

The necessary condition for observing classical magnetoresistance saturation $\omega_c\tau \gg 1$ is already a sufficient condition for the Landau levels to be distinguished over collision broadening. However, it is generally the thermal (kT) broadening which gives rise to a discrete separation between the classical and quantum-mechanical effects. In

our samples, this distinction occurs between nitrogen and helium temperatures so that both effects should be observable. When the Landau levels are discrete, the calculation of the magnetoconductivity tensor becomes complicated but the most distinct feature of the HFGM behavior for $E_F > 3/2\hbar\omega_c$ is the existence of Schubnikov-de Haas oscillations in the conductivity tensor components which arise largely from the relaxation time through the oscillatory density of final states.²¹

The bulk of the theoretical high-field calculations applies to the "extreme" quantum limit, i.e., when all carriers occupy the ground state ($E_F < 3/2\hbar\omega_c$). Such calculations²¹⁻²⁵ have always employed the assumption of a single spherical Fermi surface and an isotropic τ but the results have not been in complete agreement. In almost every case, however, the classical saturation in ρ_H is superseded by a field-dependent expression. In Table VII, we give the field dependence of the transverse and longitudinal magnetoresistance in the extreme quantum limit for various scattering mechanisms as predicted in several theoretical treatments.

The most useful result, again, is that the Hall coefficient is still given by $1/pe$.²⁶ The saturation of the Hall coefficient, predicted in both the classical and quantum treatments, is the least ambiguous and the most important test for determining the number of valleys in the Bi_2Te_3 valence-band structure.

VII. EXPERIMENTAL ARRANGEMENT

Magnetic fields up to 160 kOe were produced using pulsed fields. A long pulse duration (~ 30 msec) was used to minimize the effects of eddy currents. The sample accommodations for this experiment were made compatible with those in the low-field case so that the LFGM experiments were often followed by the high-field measurements without disturbing the sample, its holder, or lead wires. Measurements were made using standard dc techniques. Although the sensitivity was not so good as that obtained with the ac method, the signals were larger and an over-all accuracy of 5% could be obtained.

TABLE VII. Galvanomagnetic effects in the quantum limit^a (degenerate statistics).

Scattering mechanism	Magnetoresistance		Hall coefficient
	Transverse	Longitudinal	
Low-temp. acoustical (Ref. 25)	$H^{11/2}T^0$	$H^{5/2}T^0$	$1/Ne$
Point defect (Ref. 25)	H^5T^0	H^2T^0	$1/Ne$
Low-temp. piezoelectric	$H^{9/2}T^0$	$H^{3/2}T^0$	$1/Ne$
Ionizid impurity (Ref. 25)	H^3T^0	H^3T^0	$1/Ne$
Impurity (Refs. 23 and 24)	Slowly increasing	H^{-2}	$1/Ne[1 \times O(1/H)]$
Acoustical (Refs. 23 and 24)	H^2	H^2	$1/Ne[1 \times O(H)]$
δ -function impurities (Ref. 22)	H^5 to H^1	H^2	

^aOnly low-temperature scattering mechanisms have been included.

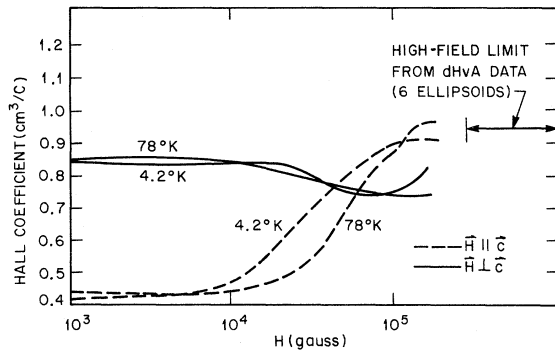


FIG. 1. Field dependence of Hall coefficients at 4.2 and 78 °K.

VIII. RESULTS

The observed Hall coefficients ρ_{123} and ρ_{321} (with $\vec{H} \parallel$ and $\perp$ to the trigonal axis, respectively) between 0 and 160 kOe at 4.2 and 78 °K are shown in Fig. 1.²⁷ At both temperatures, ρ_{123} starts from its low-field value which is field independent until $\omega_c \tau \sim 0.2$ to 0.3 and then increases rapidly until reaching a saturation value of approximately twice the low-field value. At 4.2 °K, saturation occurs at somewhat less than 100 kOe with the limiting R_H equal to 0.92 cm³/C. At 77 °K, the limiting value of R_H , equal to 0.96 cm³/C, is not reached until practically the highest fields attained. This is the result of a lower $\omega_c \tau$. The strong field dependence and the saturation values for the Hall coefficients are in good agreement with the predictions from the dHvA model assuming six valleys (see Fig. 1). The result is established without recourse to relaxation-time assumptions and is confirmed in both the classical and quantum-mechanical saturation regions. The data are also found to be in good agreement with the independent LFGM analysis since the ratio of the limiting low- and high-field Hall coefficients is given by the parameter $r\beta$ computed in Sec. V.

The remaining Hall coefficient ρ_{321} showed a low-field value of ~ 0.85 cm³/C at both temperatures, and, theoretically, is expected to rise to the same high-field limiting value as ρ_{123} . Experimentally, the low-field value was observed to decrease initially with increasing field until a minimum is reached at 80 kOe for 4.2 °K and apparently at 160 kOe for 77 °K. At the lower temperature, there is a subsequent rise toward the expected saturation value but this has not yet been reached at 160 kOe. The failure to saturate as well as the relative displacements of the minima between 4.2 and 78 °K are consistent with the differences in $\omega_c \tau$.

The origin of the minima observed in the Hall coefficient for the orientation is not known. Al-

though a similar behavior has been calculated theoretically to occur in germanium,²⁸ the effect in that case is the result of incomplete degeneracy. This argument could not be applied to Bi₂Te₃ at 4.2 °K.

Experimentally, the distinction between the classical and quantum-mechanical effects becomes most apparent in the magnetoresistance. The results in the transverse (ρ_t) and longitudinal (ρ_l) configurations at both temperatures with H parallel to the trigonal axis are shown in Figs. 2(a) and 3(a). Contrary to general behavior, ρ_t and ρ_l are approximately equal in Bi₂Te₃ at both temperatures and over a wide range in field. (As shown in Sec. V, this results from the appreciable anisotropy in $\alpha\tau$.) Up to 70 kOe the magnetoresistance curves at 4.2 and 77 °K are parallel and for $(\rho_H - \rho_0)/\rho_H$ are displaced from each other by essentially the $\omega_c \tau$ ratios between the two temperatures. At higher fields, the behavior at the two temperatures is distinctly different. The field dependence of the magnetoresistance at 77 °K decreases at the highest fields and, for the longitudinal configuration, near saturation is observed at the highest fields. This result is in fairly good agreement with the predicted classical limiting value from the LFGM analysis $\rho_H/\rho_0 \rightarrow 3.35$.

At 4.2 °K, however, where the Landau levels are well defined, the saturation is replaced with an increase in the field dependence of the magnetoresistance. This is the general behavior predicted for the quantum high-field effects; however, no

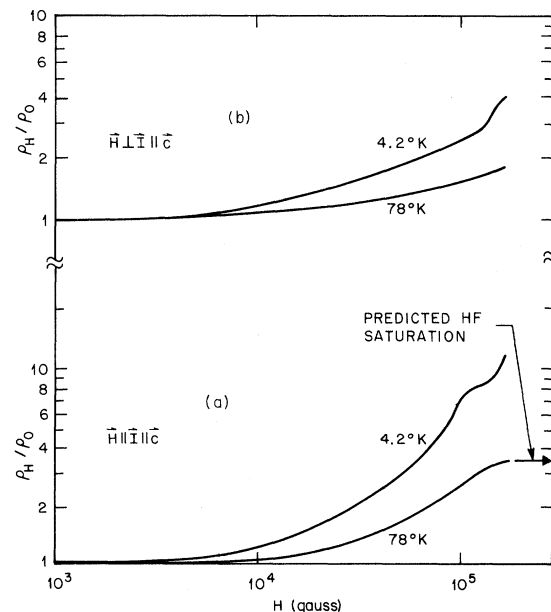


FIG. 2. Field dependence of the magnetoresistance for $\vec{H}$ parallel to the trigonal axis. Several Shubnikov-de Haas oscillations appear in the data for 4.2 °K.

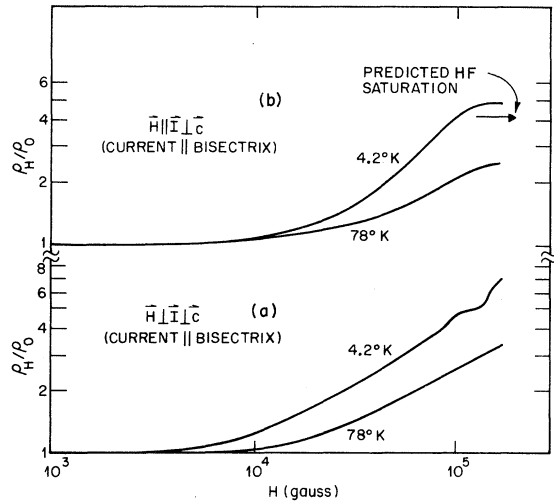


FIG. 3. Field dependence of the magnetoresistance for $\vec{I}$ perpendicular to the trigonal axis. Several Shubnikov-de Haas oscillations appear in the data for 4.2°K.

quantitative results were available to test the theoretical treatments. This was primarily due to the fact that the extreme quantum limit (to which the calculations apply) was not quite reached in this material. From the dHvA data, it can be shown that the charge carriers will all lie in the ground state for fields above 180 kG which was slightly above the maximum field achieved in this experiment. As predicted by Adams and Holstein²⁵ for degenerate carriers, the magnetoresistance in the vicinity of the quantum limit was observed to be temperature independent (between 4.2 and 1.4°K). This, however, is not a critical test of the theory.

With H parallel to the trigonal axis, several small Shubnikov-de Haas oscillations were observed in both the longitudinal and transverse magnetoresistance. These results were in agreement with the dHvA data.

The general behavior of the HFGM results in other orientations is shown in Figs. 2(b) and 3(b). Although remarks similar to those above apply in these cases also, several features may be noted in particular. At 4.2°K, a saturation of the longitudinal magnetoresistance is observed in the orientation $\vec{H} \parallel \vec{I} \perp$ trigonal axis. The calculated value of the classical saturation for this orientation of the ellipsoids is, again, in fair agreement with the observed value (see Fig. 3). However, it is not clear why the quantum-mechanical behavior is suppressed in this orientation. On examining the results of all orientations there is, in fact, no consistent behavior in the relative onset of the quantum limit. It is likely that in the many-valley model where, in general, each ellipsoid may "enter" the quantum limit at a different field value, the onset of the quantum limit may be complicated. (In this regard,

a redistribution of carriers among the various valleys might also occur.) The classical saturation at 4.2°K probably results from the fact that in this orientation at least four of the six ellipsoids exhibited larger cyclotron effective masses (and therefore have higher quantum limits) than in the case of H parallel to the trigonal axis where the quantum behavior was observed.

IX. DISCUSSION

The comparison of our LFGM results with those of Drabble²⁹ and Efimova *et al.*,¹² but largely the recent work of Ashworth *et al.*,¹ shows that the effective-mass-relaxation-time parameters obtained from the analysis are dependent upon the carrier concentration. Although Drabble did not obtain the same parameters in his results for samples of different hole concentrations, we have found that his values obtained from the low-concentration sample ($p \sim 3.5 \times 10^{18} \text{ cm}^{-3}$) (calculated assuming a scalar τ) at 77°K are in qualitative agreement with the dHvA data. It appears, therefore, that near this carrier concentration and temperature in p -type Be_2Te_3 acoustical scattering is nearly isotropic. At higher carrier concentrations (corresponding to the as-grown state), however, concentration-dependent anisotropies in $\alpha\tau$ occur.

The principle reason for concluding that $\alpha\tau$ depends on the carrier concentration rather than a breakdown of the model itself is that the consistency relations [Eqs. (5)] in much of the reported work are largely satisfied. These relations, which test the interdependence of the LFGM tensor components, comprise the essential test for the applicability of this model.

Ashworth *et al.*¹ have concluded from their observed carrier-concentration dependence of certain magnetoresistance ratios that a two-band model must be applied for the high-concentration samples. (The consistency relations were apparently not tested in this work.) For n -type material other experiments³⁰ support this conclusion; for p type, the authors find their galvanomagnetic evidence less satisfactory. This suggestion of a second populated band, as an alternative to a concentration dependent $\alpha\tau$, may apply to very heavily doped samples. However, our sample, which should have had a second populated valence band according to Ashworth *et al.*,¹ showed no indication of such. We list below the relevant experimental results. (i) In dHvA experiments with fields up to 200 kOe no evidence of a new Fermi-surface sheet was found. If such carriers existed their $\omega_c\tau$ must be less than unity at these fields, corresponding to mobilities ($< 500 \text{ cm}^2/\text{V sec}$) smaller by a factor of ~ 15 than the reported carriers. These would not be expected to have marked effects upon the transport properties. However, if the additional car-

riers occupy a small Fermi volume they may pass into the quantum limit before 200 kOe and not be observable in dHvA studies. (ii) From dHvA studies the carrier concentration per ellipsoid was found to be $1.13 \times 10^{18} \text{ cm}^{-3}$. The concentration for all ellipsoids (by symmetry) is expected to be three or six times this value. The total concentration obtained in the LFGM analysis agrees to within several percent (less than the estimated errors) with the factor 6. Either of the two measured Hall coefficients in this case would reveal additional carriers irrespective of their mobility, and modified only somewhat (usually less than a factor of 3) by the mass-relaxation-time anisotropy. (iii) The high-field (160 kOe) Hall coefficient under both classical and quantum conditions also shows no additional carriers in excess of the dHvA results. (At least for the classical condition these results are further independent of the anisotropies of m^* and τ .) (iv) Effective masses and anisotropies deduced from optical behavior^{31,32} assuming a single band are also in agreement with the results obtained here. It is concluded that in our sample carriers from a second populated valence band must

number less than 10% of the total.

The results of Ashworth *et al.*¹ for *p*-type samples, it seems, could be explained equally in terms of a concentration-dependent $\alpha\tau$. For *n*-type Be_2Te_3 , also investigated by these workers, some information on the concentration dependence of α is available³⁰ and it is found to be small. For *p*-type Bi_2Te_3 less data are available leaving the question somewhat open.

The possibility of a nonparabolic band structure may also be considered in this regard. (This has been suggested by Goldsmid³³ for *n*-type Bi_2Te_3 .) Since the Fermi energy was only about $\frac{1}{8}$ of the (indirect) energy gap, very large changes in the effective masses at carrier concentrations lower than ours should not occur. For larger carrier concentrations, a variation may be expected and some anomalous behavior is observed, but other complications arise from the defect state of the crystal.

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¹⁷The value of B is not very sensitive to the assumptions in its calculation.

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²⁷Small irregularities in the HFGM coefficients were sometimes observed above 100 kOe at fields corresponding to low-order Landau levels. Except in those cases where they were recognized with some clarity, these irregularities have been smoothed out in the graphical representation.

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