Piezo-Galvanomagnetic Effects in Bismuth

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The electrical resistivity and Hall coefficient in single crystals of bismuth have been measured as a function of uniaxial stress along the trigonal axis at 4.2, 77, and 295°K. Values of elastoresistance and elasto-Hall coefficients have been calculated by combining the results of the present experiment with our earlier measurements of the pressure dependence of the galvanomagnetic effects. The data are analyzed in terms of a model consisting of a conduction band overlapping a valence band. The deformation potential components defining the strain dependence of the overlap energy ($E_0 = 0.03$ eV) are evaluated to be $E_1 = -2.7$ eV and $E_2 = +2.8$ eV.

INTRODUCTION

BISMUTH is a semimetal and its low electrical conductivity is ascribed to a small number of electrons and holes arising from the slight overlap of the conduction and valence bands. It has been shown[1] using various experimental data that the Fermi surface for electrons can be quite accurately described by three equivalent ellipsoids in momentum space, while for holes it consists of an ellipsoid of revolution about the trigonal axis. According to the present estimates, the total number of electrons (with a density of states mass $m_e^* \approx 0.05\ m_0$) is of the order of $4 \times 10^{17}/\text{cm}^3$ at 4.2°K, and is nearly equal to the number of holes ($m_h^* \approx 0.16\ m_0$) with the total overlap energy for parabolic bands being of the order of 0.03 eV. Using the piezoresistance[2] and the high pressure dependence of the resistivity[3] at room temperature, Keyes[4] has estimated the rate of change of the overlap energy per unit strain in the trigonal direction to be 3 eV. In the present work, we have measured the resistivity and the Hall coefficient as a function of uniaxial stress at lower temperatures, and have determined the deformation potential constants defining the strain dependence of the overlap energy using our earlier hydrostatic pressure measurements[5] and the present data.

EXPERIMENTAL DETAILS AND RESULTS

The experimental method consists of applying a uniaxial compressional stress Z to a high-purity zone-refined bismuth crystal ($r_{300°\text{K}}/r_{4.2°\text{K}} \approx 200$) along the trigonal direction. The crystals were cut into rectangular bars of 4 mm$\times$4 mm cross section and 8 mm in length. The changes in resistance and Hall voltage with applied stress were measured using an ac compensation method.[6] The maximum stresses used were 25 kg/cm^2. At higher stresses attempted, the crystals de-

veloped slipping. All the results were, therefore, obtained at lower stresses under elastic and reversible conditions. The maximum magnetic field strengths used were 100, 300, and 1500 G for 4.2, 78, and 300°K, respectively, so that higher order effects in the magnetic field are small.

The results of the measurements averaged over four samples are as shown in Table I. Both the resistivity and the Hall coefficient were found to increase linearly with increasing stress at all temperatures. The stress dependence of resistivity at 4.2°K was determined by extrapolating to zero magnetic field the corresponding values at magnetic fields between 20–100 G. The elastoresistance and elasto-Hall coefficient values were obtained using the results of the present experiment, the pressure dependence of the resistivity and Hall effect,[5] and the elastic constants.[7] The various elastoresistance and elasto-Hall coefficients are denoted by the symbols $m_{33}(ii)$ and $m_{13,2}(ii)$, respectively, where ii represents the direction of strain, and are given in Table II.

ANALYSIS AND DISCUSSION

The experimental results have been analyzed in terms of the electron and hole band model described in the Introduction. For the case of equal number of electrons and holes in bismuth, Abeles and Meiboom[8] have derived the following expressions:

For the resistivity

$$r_{33} = \frac{1}{N|e|(\mu_3 + \nu_3)}$$

and for the Hall coefficient   (1)

$$r_{13,2} = -\frac{1}{N|e|}\left[\frac{\frac{1}{2}(\mu_1 + \mu_2)\mu_3 - \nu_1\nu_3}{(\frac{1}{2}(\mu_1 + \mu_2) + \nu_1)(\mu_3 + \nu_3)}\right].$$

Since the hole mobility components ν_i are much smaller than those of the electron mobility μ_i, these expressions

[1] A. L. Jain and S. H. Koenig, Phys. Rev. **127**, 442 (1962).
[2] M. Allen, Phys. Rev. **42**, 848 (1932); **49**, 248 (1935).
[3] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **63**, 351 (1929).
[4] R. W. Keyes, Phys. Rev. **104**, 665 (1956).
[5] R. Jaggi, A. L. Jain, and H. Weibel, Phys. Letters **7**, 181 (1963).
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[7] Y. Eckstein, A. W. Lawson, and D. H. Reneker, J. Appl. Phys. **31**, 1534 (1960).
[8] B. Abeles and S. Meiboom, Phys. Rev. **101**, 544 (1956).

TABLE I. Experimental results.

Tempera-ture T °K	Resistivity[a] r_{33} 10^{-6} Ω cm	Hall coefficient[a] $r_{13,2}$ cm³/coul	Pressure derivatives[a]		Stress derivatives	
			$\dfrac{\delta r_{33}}{r_{33}\delta p}$ 10^{-4} cm²/kg	$\dfrac{\delta r_{13,2}}{r_{13,2}\delta p}$ 10^{-4} cm²/kg	$\dfrac{\delta r_{33}}{r_{33}\delta Z}$ 10^{-4} cm²/kg	$\dfrac{\delta r_{13,2}}{r_{13,2}\delta Z}$ 10^{-4} cm²/kg
4.2	0.63±0.06	−14.5 ±0.7	0.80±0.07	0.80±0.05	8.8 ±1.0	8.6±0.6
77	33 ±2	−9.9 ±0.6	0.31±0.08	0.50±0.03	1.6 ±0.1	5.6±0.2
295	136 ±3	−1.38±0.07	0.31±0.05	<0.1	0.35±0.03	1.9±0.2

[a] See Ref. 5.

can be approximated by

$$r_{33} \approx \frac{1}{N|e|\mu_3}$$

and

$$r_{13,2} \approx -\frac{1}{N|e|}.$$ (2)

The corresponding elastoresistance and elasto-Hall coefficient can, then, be expressed as

$$m_{33}(ii) = \frac{\delta r_{33}}{r_{33}\cdot\epsilon_{ii}} \approx \frac{\delta N}{N\epsilon_{ii}} - \frac{\delta\mu_3}{\mu_3\epsilon_{ii}}$$

and

$$m_{13,2}(ii) = \frac{\delta r_{13,2}}{r_{13,2}\epsilon_{ii}} \approx -\frac{\delta N}{N\epsilon_{ii}}.$$ (3)

According to Keyes[4] the dependence of the energy difference between the band extrema on the strain ϵ can be written in the form

$$E = E_0 + E_1(\epsilon_{11} + \epsilon_{22})E_2\epsilon_{33}.$$ (4)

Assuming that the electron and hole bands are parabolic, the change in the number of carriers at a finite temperature T is given by

$$\frac{\delta N}{N\epsilon_{33}} = \frac{E_2}{kT}\frac{1}{\dfrac{F_{1/2}(\zeta_e/kT)}{F_{1/2}'(\zeta_e/kT)} + \dfrac{F_{1/2}(\zeta_h/kT)}{F_{1/2}'(\zeta_h/kT)}},$$ (5)

where ζ_e and ζ_h are the electron and hole Fermi energies

TABLE II. Experimentally derived values of elastoresistance and elasto-Hall coefficient.

Tempera-ture T °K	Elastoresistance		Elasto-Hall coefficient	
	$m_{33}(11)$ $=\dfrac{\delta r_{33}}{r_{33}\epsilon_{11}}$	$m_{33}(33)$ $=\dfrac{\delta r_{33}}{r_{33}\epsilon_{33}}$	$m_{13,2}(11)$ $=\dfrac{\delta r_{13,2}}{r_{13,2}\epsilon_{11}}$	$m_{13,2}(33)$ $=\dfrac{\delta r_{13,2}}{r_{13,2}\epsilon_{33}}$
4.2	+138 ±23	−140 ±15	+134±14	−137±9
77	+18 ± 5	−29 ± 3	+88± 5	−87±3
295	−6.8± 2.8	−12.4± 8	+37± 8	−26±5

and are related by $\zeta_e + \zeta_h = E_0$. The various $F_{1/2}$ and $F_{1/2}'$ are the Fermi integrals and their first derivatives for electrons and holes. For an extremely degenerate gas, this reduces to

$$\delta N/N\epsilon_{33} = \tfrac{3}{2}(E_2/E_0).$$ (6)

Similar expressions can be derived for the other strain component ϵ_{11}. Taking the density-of-states masses of 0.05 m_0 and 0.16 m_0 for electrons and holes, respectively, and the total number of electrons to be 4×10^{17} cm⁻³ at 4.2°K, we have calculated, using expressions (5) and (6), that for a finite strain

$$(\delta N/N)_{4.2°K} = 1.4(\delta N/N)_{77°K}.$$ (7)

As can be seen from Tables I and II, our data are within the experimental errors in agreement with this expression and, therefore, support the model of one type of electron and one type of hole responsible for conduction at low temperatures. However, deviations from the relation (5) can be expected to occur at room temperature because of the possible thermal excitation of the carriers from the lower bands.

Furthermore, Table I shows that at 4.2°K, the pressure derivatives of resistivity and Hall coefficient are equal within the experimental errors, likewise both stress derivatives are the same. Consequently, in Table II, the corresponding elastoresistance and elasto-Hall coefficient at 4.2°K are equal within the experimental errors. This confirms that the effect of strain on the mobility at 4.2°K is very small and the entire change of resistivity and Hall coefficient is due to the change of carrier concentration.[5] At 77°K and room temperature, however, the difference between the two coefficients is in a direction which requires the effective mobility μ_3 to reduce with strain. This is as expected if there is increased thermal excitation of holes to the new oblate valence band discussed by Hall and Koenig.[9]

We can use the relations (3) and (6) to evaluate the coefficients E_1 and E_2 in Eq. (4). Choosing an overlap energy $E_0 = 0.03$ eV (disregarding its uncer-

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[9] J. J. Hall and S. H. Koenig, IBM J. Res. Develop. 8, 241 (1964).

tainty) and using our low temperature results (considering their experimental errors) we finally get $E_1 = -(2.7\pm0.3)$ eV and $E_2 = +(2.8\pm0.2)$ eV.

Note added in proof. It has been pointed out by Dr. S. H. Koenig that it is somewhat inappropriate to assume parabolic electron energy bands. Using more recent estimates of the total number of electrons $N = 3\times10^{17}/\text{cm}^3$ at $4.2°$K, he has suggested an effective parabolic Fermi energy for electrons to be 0.015 eV

such that expression (6) is validated. This gives an overlap energy $E_0 = 0.027$ eV and consequently (within $\pm10\%$) $E_1 = -2.4$ eV and $E_2 = +2.5$ eV.

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Hyperfine and Superhyperfine Structure of Manganese in SnO₂†

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The electron paramagnetic resonance spectrum of manganese in a single crystal of SnO₂ (cassiterite) was investigated at K and K_A band frequencies at a temperature of $77°$K. The manganese atoms occupy Sn^{4+} substitutional sites giving the same charge with a resulting spin ground state of $S = 3/2$. The hyperfine structure (HFS) with $I = 5/2$ and the superhyperfine structure (SHFS) show large anisotropies which can be explained by the relatively large values of D and E in the spin-Hamiltonian. The strong overlaps of the wave functions of the central manganese ion with those of the nearest-neighbor tins along the C axis accounts for the large SHFS, $a = 34$ G. An attempt to explain these data from the experimental evidence is given. The spin-Hamiltonian and the constants for the C axis and magnetic Z axis coincident are

$$H = \beta\mathbf{S}\cdot g\cdot\mathbf{H} + D[S_z^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + \mathbf{S}\cdot A\cdot\mathbf{I} + \sum_{i=1}^{2}\mathbf{S}\cdot a_i\cdot\mathbf{I}_{Sn}.$$

	$x[110]$	$y[110]$	$z[001]$	Tolerance
g	1.9879	1.9870	1.9907	±0.0003
A (gauss)	77.7	75.4	80.64	±0.5
a (gauss)	30.5	29.5	34.0	±0.5
D (kMc/sec)	26.436			±0.01
E (kMc/sec)	7.91			±0.01

In addition, the resonance results obtained for Mn^{4+} in SnO₂ are compared with those obtained for Cr^{3+} and V^{4+} in SnO₂ and for Cr^{3+}, V^{4+}, and Mn^{4+} in TiO₂.

INTRODUCTION

THE paramagnetic resonance spectrum of the ground state of Mn^{4+} in SnO₂ has been investigated to determine the constants of the applicable spin-Hamiltonian and to compare the experimental results with those obtained for certain other impirities in SnO₂ and in the rutile form of TiO₂.

SnO₂ is isomorphic to TiO₂ which has the rutile structure and belongs to the D_{4h}^{14} space group.[1] The lattice parameters of SnO₂ are $a = 4.737$ Å, $c = 3.185$ Å, and $u = 0.307$ with $c/a = 0.672$.[2] The c axis[2] is the fourfold axis and it is chosen to be the Z magnetic axis. The values for TiO₂ are $a = 4.594$ Å, $c = 2.959$ Å, $u = 306$, and $c/a = 0.644$.[2] There are two molecules of SnO₂ in each unit cell.

[1] R. W. C. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1960).

[2] Werner H. Baur, Acta Cryst. **9**, 515 (1956).