Galvanomagnetic Effects in Antimony*

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The galvanomagnetic effects in antimony have been measured at low magnetic fields in the temperature range 50–300°K. It is shown that the behavior of the resistivity and the Hall coefficients at low temperatures is in qualitative agreement with the model of two overlapping bands as proposed by Windmiller and by Falicov and Lin. However, the initial increase in the Hall coefficient $\rho_{23,1}$ with temperature indicates the possibility of another hole band with the band edge lying close to the Fermi level.

INTRODUCTION

RECENTLY, the band structure of antimony has been investigated using the de Haas–van Alphen effect,[1–3] cyclotron resonance,[4] ultrasonic attenuation,[5–7] the Schubnikov–de Haas effect,[8–10] and galvanomagnetic effects.[11–14] The cyclotron resonance[4] and the de Haas–van Alphen-effect[3] data have been analyzed in terms of a Fermi surface consisting of two sets of closed pockets corresponding to electrons and holes, respectively. The band-structure calculations[15] for antimony are in accordance with the two-band model and show that the electrons are located in three equivalent pockets centered at the points L of the Brillouin zone (Fig. 1) while the holes are located in six equivalent pockets centered at points on the mirror plane σ near T. From the analysis of the de Haas–van Alphen effect, Windmiller[3] has estimated the carrier concentrations to be $N_e = 5.49 \times 10^{19}$ electrons/cm^3 and $N_h = 5.49 \times 10^{19}$ holes/cm^3 at liquid-helium temperatures.

In order to explain the room-temperature galvanomagnetic effects in antimony, Hall and Koenig[16] have proposed two sets of holes such that one set provides the Hall conductivity in the trigonal plane required to give positive Hall coefficient when the magnetic field is along the threefold axis while the other set has a small effective mass in the trigonal direction, thus making the second component of the Hall tensor positive. In the present work the galvanomagnetic coefficients have been measured at lower temperatures in order to arrive at a more conclusive model for the valence band in antimony.

EXPERIMENTAL DETAILS

High-purity antimony (69 grade) was purchased from Consolidated Mining and Smelting Company and a large single crystal was grown by pulling the ingot through a horizontal furnace in the helium atmosphere. Several samples in the approximate dimensions of 12 $\times 2.5 \times 2.5$ mm were prepared by first cleaving along the trigonal plane and then reducing them to the final size by grinding. The orientation of each sample was checked with both the Laue pattern and the light figure technique.

The samples were mounted on a lucite holder in either the horizontal or the vertical position. The current and the potential leads were made using No. 38 copper wires soldered directly onto the samples with a low-melting-point alloy.

The potentials were measured using a Leeds and Northrup potentiometer and a high-sensitivity dc null detector. The current passed through the samples was varied from 500 to 800 mA and the magnetic field from 100 to 8000 G. The over-all sensitivity of the electrical setup was such as to give an accuracy of ± 0.1 μV in the absolute measurement of the potential differences. The temperatures lower than the liquid-nitrogen tem-

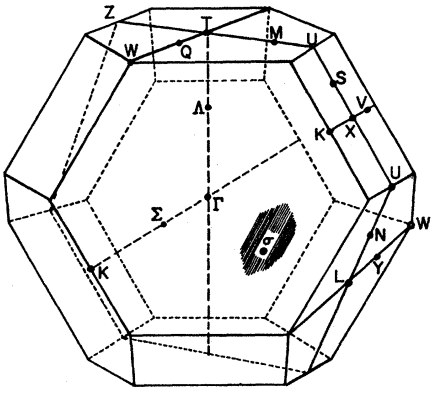

FIG. 1. The Brillouin zone for antimony (from Ref. 15).

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TABLE I. Experimental values of the galvanomagnetic coefficients of antimony [ρ_{ii}^0 in $10^{-6}\,\Omega$ cm, $\rho_{ij,k}$ in $10^{-10}\,\Omega$ cm/G; $\rho_{ij,kl}$ in $10^{-15}\,\Omega$ cm/G^2].

Temp. (°K)	ρ_{11}^0	ρ_{33}^0	$-\rho_{23,1}$	$-\rho_{12,3}$	$\rho_{11,22}$	$\rho_{11,33}$	$\rho_{23,11}$	$\rho_{11,11}$	$\rho_{33,33}$	$-\rho_{23,23}$	$\rho_{11,23}$	$\rho_{23,11}$
300	43	30	2.0	2.3	32	6.6	8.8	7.8	2.2	...	5.6	...
90	8.3	5.8	2.7	3.1	189	37	48	38	15	...	37	41
77	6.6	4.3	2.6	3.3	233	45	60	48	18	...	43	32
65	4.7	3.1	2.4	3.5	310	57	70	59	21	36	54	32
55	3.2	2.3	2.2	3.8	380	70	93	74	24	50	70	32
Approx. error (%)	5	5	5	5	15	10	10	10	10	25	25	25

perature were obtained by pumping on liquid nitrogen while liquid oxygen was used for the higher temperature. Complete galvanomagnetic measurements were thus made at four values of temperature in the range 50–95°K. Using a standard liquid-helium cryostat, higher temperatures were obtained by adjusting the helium gas pressure in the inner Dewar and filling the outer Dewar with liquid nitrogen. A vapor-pressure thermometer and an iron–constantan thermometer were used to measure the temperatures in the ranges 50–78°K and 78–300°K, respectively.

RESULTS

According to the phenomenological theory, the relation between the electric field and the current density is given by

$$E_i=\sum_j \rho_{ij}(\mathbf{H})J_j,$$

where the resistivity tensor components ρ_{ij} are functions of the magnetic field. At low magnetic fields, $\rho_{ij}(\mathbf{H})$ can be assumed to have the form

$$\rho_{ij}(\mathbf{H})=\rho_{ij}^0+\rho_{ij,k}H_k+\rho_{ij,kl}H_kH_1.$$

From the group-theoretical analysis of $3\bar{m}$ symmetry crystals, Okada[17] and Juretschke[18] have shown that each of the ρ_{ij} and $\rho_{ij,k}$ has two independent components, while $\rho_{ij,kl}$ has eight components. Following Zitter's work[19] on bismuth, it was sufficient to prepare two sets of samples, one set having its length along the trigonal axis and the other set with the length along a binary. Samples with these two orientations were sufficient to measure all 12 components of the resistivity tensor.

In all the measurements, the magnetic field was varied from 0.1 to 8 kG. Since at low temperatures the Hall and the magnetoresistance voltages showed considerable deviation from the linear and the quadratic dependence on the magnetic field, the coefficients were determined by extrapolation to zero field. Following this procedure it was possible to obtain a consistent set of resistivity tensor components at all temperatures. The results of the analysis are shown graphically in Figs. 2–5 and in Table I. These results are in reasonable agreement with the room-temperature data of Epstein and Juretschke[12] and the data of Öktü and Saunders[14] in

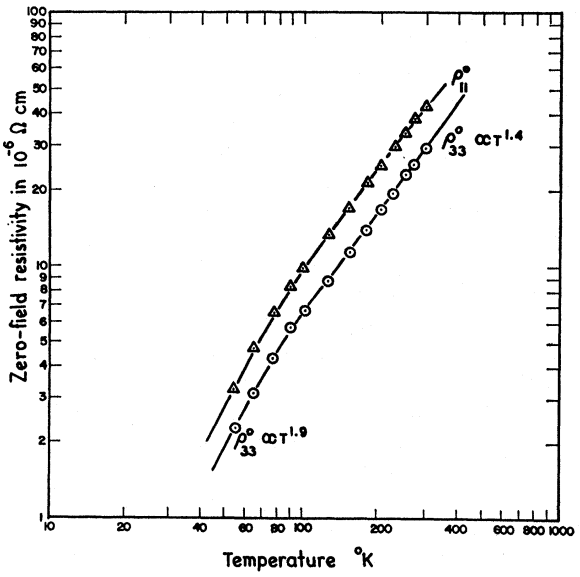

FIG. 2. Zero-field resistivity tensor components as a function of temperature.

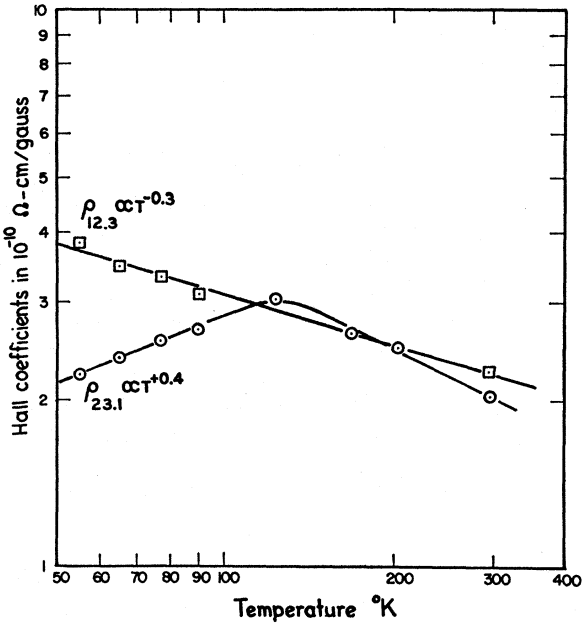

FIG. 3. Small-field Hall coefficients as a function of temperature.

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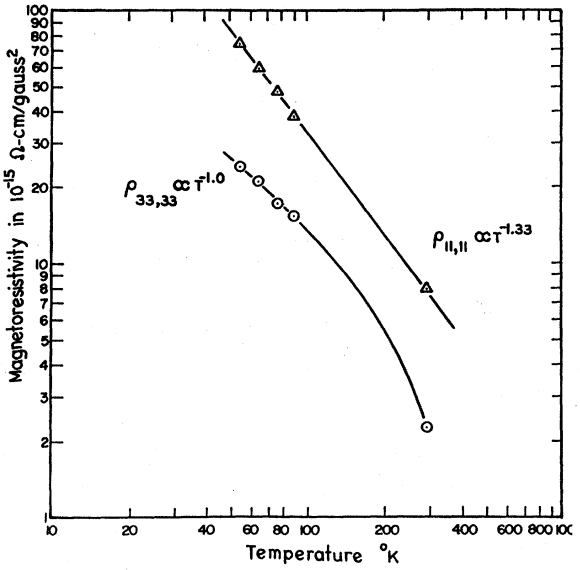

FIG. 4. Longitudinal galvanomagnetic coefficients $\rho_{ij,kl}$ as a function of temperature.

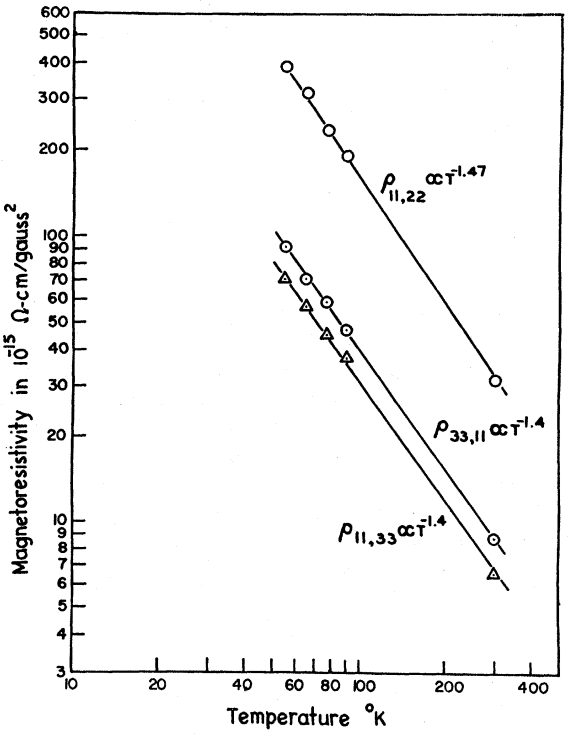

FIG. 5. Transverse galvanomagnetic coefficients $\rho_{ij,kl}$ as a function of temperature.

the temperature range 77–273°K, except for the maximum in the temperature dependence of ρ_{231} which has not been observed in the earlier measurements. The larger errors in the magnetoresistivity coefficients arise mainly from the larger uncertainty in the extrapolation to zero field.

INTERPRETATION AND DISCUSSION

As an initial step in interpreting the data, it is assumed that the Fermi surface in antimony consists of two sets of closed pockets corresponding to electrons and holes, respectively. The cyclotron resonance as well as de Haas–van Alphen effect show that both sets are tilted in the trigonal-bisectrix plane by approximately 4° and 36° from the trigonal axis. In accordance with the band-structure calculations, it is assumed in the present work that the small tilt pockets correspond to electrons having the effective-mass tensor components[4] $m_{11}=0.093$, $m_{22}=1.14$, $m_{33}=0.093$, and $|m_{23}|=0.082$, and the large tilt pockets contain holes with the mass components $m_{11}=0.068$, $m_{22}=0.63$, $m_{33}=0.34$, and $|m_{23}|=0.41$. For an isotropic relaxation time and an equal number of electrons and holes, the two components of the conductivity tensor are given by

$$\sigma_{11}^0=(Ne^2/2m_0)[(\alpha_{11}+\alpha_{22})\tau_e+(\beta_{11}+\beta_{22})\tau_h],$$
$$\sigma_{33}^0=(Ne^2/m_0)[\alpha_{33}\tau_e+\beta_{33}\tau_h],$$

where the α's and the β's are inverse effective-mass tensors components for electrons and holes, respectively, referred to the crystal axes coordinate system. The resistivity data in Fig. 2 show that $\rho_{11}^0/\rho_{33}^0\sim 1.5$. Using the values of the effective masses given above, this ratio would require $\tau_e\sim\tau_h$. The equality of the relaxation times for electrons and holes would further give the following ratio for the two Hall coefficients:

$$\frac{\rho_{12,3}}{\rho_{23,1}}=\frac{2\rho_{11}^0}{\rho_{33}^0}\frac{(\alpha_{11}\alpha_{22}-\beta_{11}\beta_{22})}{(\alpha_{11}+\alpha_{22})\alpha_{33}-\alpha_{23}^2-(\beta_{11}+\beta_{22})\beta_{33}+\beta_{23}^2}.$$

Again using Falicov and Lin's assignment and Datar's values of effective masses, the calculated value is $\rho_{12,3}/\rho_{23,1}\gtrsim 3$. The observed ratio in the present work (Fig. 3) shows this ratio of the Hall coefficients approaching the calculated value in the lower-temperature region. It appears from Steele's data[13] that $\rho_{12,3}$ at 4.2°K has almost the same magnitude as between 50–300°K, implying thereby that it is only $\rho_{23,1}$ which is varying significantly with temperature. Since both the electrons and holes observed in cyclotron resonance and de Haas–van Alphen effect have Fermi energies of the order of 0.1 eV, it is difficult to understand the increase in $\rho_{23,1}$ with increasing temperature on the basis of two overlapping bands alone. In order to explain the temperature variation of $\rho_{23,1}$ it becomes necessary to assume the presence of another hole band having the band edge close to the Fermi level and probably located at the point T in the Brillouin zone. Following the suggestion of Hall and Koenig, these holes with a low mass in the trigonal direction would provide a large Hall mobility when the magnetic field is along the binary or bisectrix axis. The increase in $\rho_{23,1}$ with increasing temperature would thus be a consequence of thermal excitation of

holes from one hole band to another. Contrary to Hall effect, the contributions of electrons and holes to conductivity are additive and a small number of new holes would make very little contribution to the temperature dependence of the electrical conductivity. The data in Figs. 2–5 indicate that the zero-field resistivity coefficients ρ_{ii}^0 are approximately proportional to $T^{1.9}$ and $T^{1.4}$ below and above 90°K, respectively, while most of the magnetoresistivity coefficients $\rho_{ijkl} \sim T^{-1.4}$. These variations are also in better agreement with the band-structure model of one conduction band overlapping with two valence bands as proposed above.

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Experimental Determination of the Effect of Hydrostatic Pressure on the Fermi Surface of Copper*

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We have measured the pressure derivatives of five cross-sectional areas of the Fermi surface of copper, using the fluid-He phase-shift method. The results are in excellent agreement with predictions of recent band-structure calculations by Davis, Faulkner, and Joy.

INTRODUCTION

A WEALTH of experimental data giving detailed information about the Fermi surface of copper is available in the literature. In particular, cross-sectional areas of the Fermi surface accurate to the order of 0.2% have been obtained recently from de Haas–van Alphen measurements.[1–3] Such Fermi-surface data constitute easily accessible experimental information of sufficient accuracy and quantity that it may be used to critically evaluate a band-structure calculation of a metal at least in the vicinity of the Fermi energy. However, most theoretical band-structure descriptions are in some sense parametrized to fit the experimental data, e.g., by the choice of the potential, adjustment of the exchange terms, or fitting pseudopotential coefficients. Pressure studies of the Fermi surface serve to add another dimension with which to test the physical significance of the theoretical description.

In a recent calculation,[4] using the Korringa-Kohn-Rostoker (KKR) formalism, Faulkner, Davis, and Joy have succeeded in obtaining essential agreement with the zero-pressure Fermi surface of Cu. In a subsequent paper,[5] these investigators calculated the band structure as a function of lattice parameter and gave values of the pressure derivatives of four cross-sectional areas of the Fermi surface. The pressure derivatives of two of these cross sections are available from the work of Templeton.[6] The purpose of this paper[7] is to present the pressure derivatives of the five cross-sectional areas (three additional cross sections plus the two given previously by Templeton) observable along the major symmetry axes [100], [110], and [111]. Because of the relative simplicity of the Fermi surface of the noble metals, these five experimental data constitute a rather complete description of the effect of pressure upon the Fermi surface of copper suitable for comparison with a theoretical description such as that of Davis *et al.*

The Fermi surface of copper consists of a spherical electron surface centered on Γ with interconnecting necks in the [111] directions.[3] With the magnetic field in the [111] direction, one observes a "belly" orbit and a "neck" orbit. In the [110] direction, the only extremal section gives rise to a hole orbit made up of the necks and spheres which resembles a "dogbone." A similar fourfold symmetric hole orbit known as the four-cornered "rosette" is observed in the [100] direction in addition to a "belly" orbit about the sphere. We have measured the pressure derivatives of the de Haas–van Alphen frequencies corresponding to these five cross-sectional areas.

EXPERIMENTAL

The samples were $\frac{3}{16}$-in.-diam$\times\frac{5}{8}$-in.-long right circular cylinders cut by spark erosion from a boule whose residual-resistance ratio ($R_{300°K}/R_{4°K}$) was about 4000. These samples were etched down with dilute HNO_3 so as to slip into the $\frac{1}{8}$-in.-bore Be-Cu bomb and were oriented along the appropriate symmetry axes to within 2 deg by standard back reflection x-ray techniques.

The de Haas–van Alphen oscillations were detected

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