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ABSTRACT

Galvanomagnetic measurements have been made in single crystals of n-type bismuth-antimony alloys as a function of concentration in the range 0 - 13 at % Sb. The data have been analyzed in terms of two band model. The ratio of the two resistivity components P_{33}/P_{11} suggests that the electrons in the lower concentration alloys are located at the same points in the Brillouin zone as those for pure bismuth and that the ratio of the various mobility components is not much influenced on alloying bismuth with antimony.

INTRODUCTION

Bismuth and antimony are well known for their semi-metallic behavior. However, when bismuth is alloyed with antimony, there is a continuous change from semi-metallic to semiconducting behavior.[1,2] Alloys at both ends of Bi - Sb phase diagram have overlapping valence and conduction bands, but the alloys containing between 5 and 40 at % Sb have been shown to have a small energy gap. Recently there has been considerable interests in the thermoelectric and thermomagnetic properties[3,4] of these alloys. So far the previous studies have not been sufficiently extensive to yield the information about the various parameters characterizing the electron and hole bands in these alloys. In the present work the variation of the electrical resistivity and Hall Effect tensors has been investigated as a function of alloy composition at liquid helium temperature.

Results of the present investigation have been discussed in terms of the band structure model for bismuth.[5] According to this model the Fermi surface of electrons in bismuth consists of three electron ellipsoids which are really six half-ellipsoids centered on the pseudo-hexagonal faces of the Brillouin zone (points L, Figure 1). The hole Fermi surface is represented by a single ellipsoid which is composed of two half-ellipsoids centered on the hexagonal faces of the Brillouin zone (points H, Figure 1). The effect of adding antimony to bismuth is to displace the hole band at H downward with respect to the pair of light mass bands at the point L. The results of the present experiments indicate that this model is at least sufficient to explain the observed mobility anisotropy of electrons in the alloys containing less than 12 at % Sb.

EXPERIMENTAL DETAILS

The alloys used in this work were prepared from Cominco's zone-refined 69 grade bismuth and antimony. Single crystals of high homogeity were grown by using the zone levellin method described elsewhere.[(1)] Since the galvanomagnetic properties in the semiconducting range are very sensitive to the concentration of the alloys, the present work was carried out on single crystal plates of dimensions 8 x 8 x 3 mm. The orientation of the plates was such that the current could be sent along either the binary or the trigonal directions. The samples were cut and oriented using the cleavage and the Lane pattern methods. Composition of the alloys was determined chemically.

For electrical measurements, the current flow direction used was either the binary or the trigonal. Thus by using the sample in the form of plates, it was possible to measure both the components of the electrical resistivity and the Hall effect tensors on the same sample. In order to make the electrical connections, thin copper films were deposited by evaporation and the current leads were soldered with a low melting point solder directly onto the copper films.

The electrical measurements were made at liquid helium and room temperatures using the conventional d.c. techniques. All voltages were measured by type K-3 Leeds and Northrup potentiometer and d.c. electronic null detector. The maximum current and the magnetic field used were 30 mamp and 200 gauss respectively.

RESULTS AND DISCUSSION

Measured values of the resistivity and Hall effect components at 4.2°K are shown in Table 1 as a function of antimony concentration. The sign of the Hall effect components indicates that the carriers responsible for conduction in these samples containing 5 - 12 at % Sb are primarily electrons. Assuming that these electrons are located at the points marked L in the Brillouin zone and using the 3-ellipsoid model for electrons, the electrical resistivity and Hall effect components are given by

$$P_{11} = \frac{2}{eN\,(u_1 + u_2)}$$

$$P_{33} = \frac{1}{eNu_3}$$

$$R_p = -\frac{1}{eN}\left[\frac{4u_1u_2}{(u_1 + u_2)^2}\right]$$

$$R_s = -\frac{1}{eN}\left[1 - \frac{u_4^{\,2}}{(u_1 + u_2)\,u_3}\right]$$

where N is the total number of electrons and the u's are the components of the electron mobility tensor in the crystal axis coordinate system such that

$$\tilde{u} = \begin{bmatrix} u_1 & 0 & 0 \\ 0 & u_2 & u_4 \\ 0 & u_4 & u_3 \end{bmatrix}$$

If the general shapes of the conduction band in bismuth is assumed to emain unchanged on alloying such that $m_2 > m_1, m_3$ and $u_1, u_3 >> u_2, u_4$ we an reduce the above expressions for low magnetic fields to

$$P_{11} \sim \frac{2}{eNu_1}$$

$$P_{33} = \frac{1}{eNu_3}$$

$$R_s \sim -\frac{1}{Ne}, \quad R_p \sim -\frac{4}{Ne}\frac{u_2}{u_1}$$

In the high field limit $R_p \to R_s \to \frac{1}{Ne}$.

If the samples are p-type, then the similar expressions for holes at the point T will be

$$P_{11} = \frac{1}{eP\nu_1}$$

$$P_{33} = \frac{1}{eP\nu_3}$$

$$R_s = R_p = +\frac{1}{eP}$$

where P is the total number of holes and ν_1 and ν_3 are the mobilities in the basal plane and along the trigonal direction respectively.

From the galvanomagnetic effects data at 4.2°K, Zitter[6] has estimated the following values for components of the electron and hole mobility tensor:

$$u_1 = 4.30 \times 10^7 \ cm^2/v.sec$$

$$u_2 = 0.06 \times 10^7 \ cm^2/v.sec$$

$$u_3 = 3.00 \times 10^7 \ cm^2/v.sec$$

$$u_4 = 0.34 \times 10^7 \ cm^2/v.sec$$

$$\nu_1 = 1.20 \times 10^7 \ cm^2/v.sec$$

$$\nu_3 = 0.10 \times 10^7 \ cm^2/v.sec$$

If the general form of the mobility tensors remains unchanged on alloying with antimony except for the reduction of all mobility components by a constant factor for a given concentration, then the ratio P_{33}/P_{11} would lie close to 0.7 for n type and $P_{33}/P_{11} \approx 12$ for p-type alloys. The present data indicate that the measured values of P_{33}/P_{11} have a spread of values from 0.5 to 0.7 for n-type Bi - Sb alloys having concentration from 5 to 10 at % Sb. Along with the preliminary measurements of the Hall coefficients, it is possible to conclude that the electrons in alloys having less than 10 at % Sb are located at the same points in the Brillouin zone as in the case of pure bismuth and that the ratio of the mobility components for electrons is not changed significantly from that in bismuth. At present it is of considerable interest to check the validity of the above stated relations for p-type alloys.

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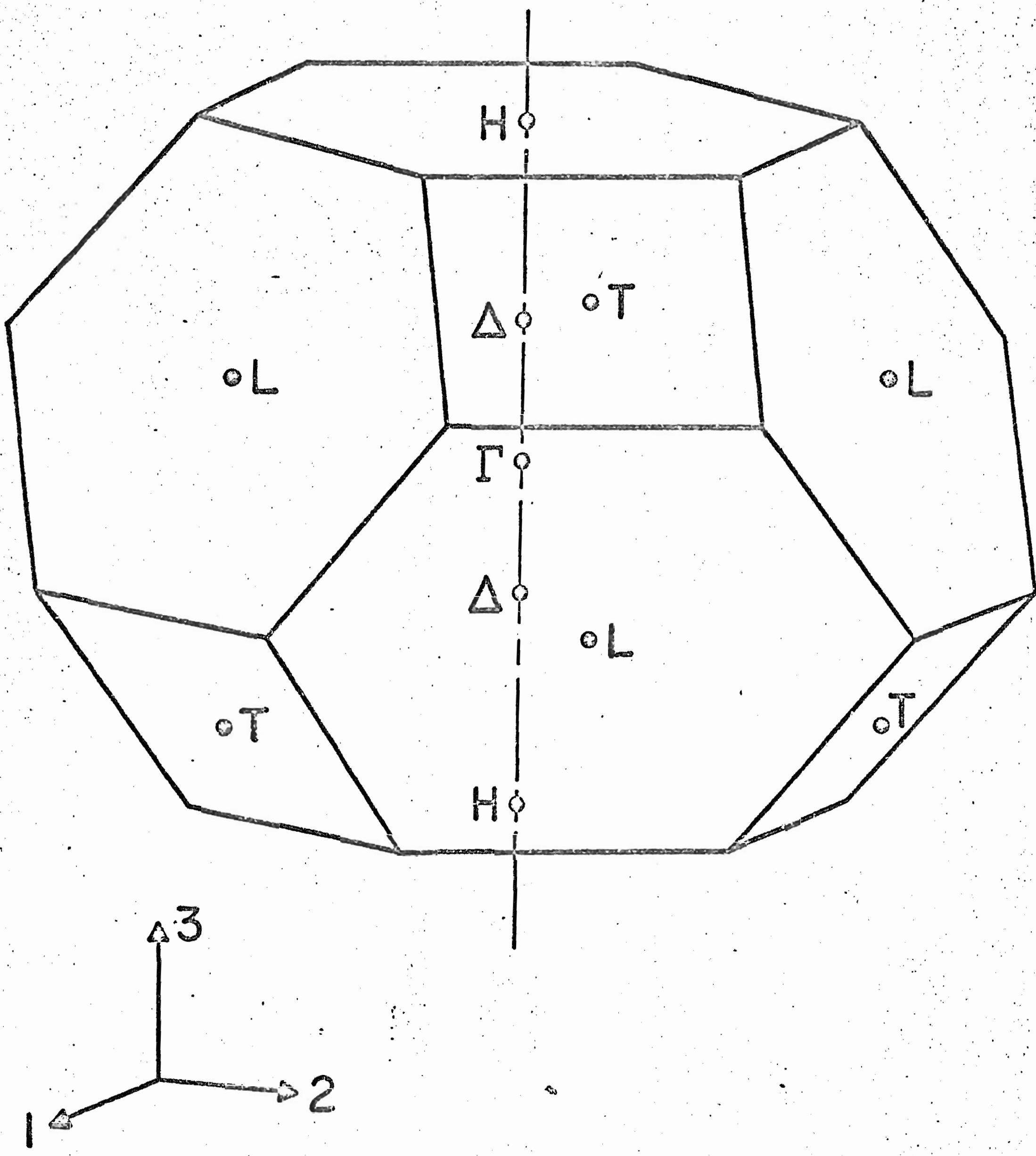

FIRST BRILLOUIN ZONE

TABLE 1

Resistivity and Hall effect in n-type Bi - Sb alloys at 4.2°K. P_{11} nd P_{33} are the resistivity components measured with current flowing along inary and trigonal axes respectively. R_p and R_s are the Hall components easured with the magnetic field parallel and perpendicular to the trigonal xis.

Conc. at % Sb	P_{33} μΩ-cm	P_{11} μΩ-cm	P_{33}/P_{11}	R_s cm^3/C	R_p cm^3/C
4.1	42	42	1.00	-	-
5.0	96	90	1.06	-	-
6.1	118	252	0.47	-150	-10
7.5	451	654	0.69	-	-
10.0	530	1020	0.52	-850	-52
10.3	582	1264	0.46	-	-
11.0	1988	2128	0.94	-	-
13.5	4030	3528	1.14	-	-