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GALVANOMAGNETIC, THERMOELECTRIC AND THERMOMAGNETIC

PROPERTIES OF Sn-DOPED AND Te-DOPED

BI$_{88}$SB$_{12}$ AND BI$_{95}$SB$_{5}$ ALLOYS

by

Sheng San Li

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
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Doctor of Philosophy
in
Electrical Engineering

Thesis Director's signature:

[Signature]

Houston, Texas
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INTRODUCTION

Recently considerable attention has been directed towards thermoelectric and thermomagnetic energy conversion, particularly for low temperature refrigeration. The Ettingshausen effect is used for thermomagnetic refrigeration, and the Peltier effect is used for thermoelectric refrigeration.* Goldsmid (9) has derived an expression for the maximum coefficient of performance for thermoelectric refrigeration. The coefficient of performance is defined as the rate of cooling at the heat source, divided by the rate of expenditure of electrical energy. The maximum coefficient of performance for a given temperature difference and for a given mean temperature \( T_M \) is given by (9):

\[
\dot{\Phi}_{\text{max}} = \frac{T_C}{T_H - T_C} \cdot \frac{\sqrt{1 + Z T_M} - T_H/T_C}{\sqrt{1 + Z T_M} + 1}
\]

Where \( T_C \) is the heat source temperature, \( T_H \) is the heat sink temperature, \( T_M = (T_H + T_C)/2 \), and \( Z \) is the figure of merit of the material and is given by:

\[
Z = \frac{\alpha^2 \sigma}{k}
\]

\( \alpha \) is the Seebeck coefficient, \( \sigma \) is the electrical conductivity, and \( k \) is the thermal conductivity.*

* details see chapter V
The figure of merit depends entirely upon the properties of the materials. It depends on the mobility, the effective mass of the carriers and the thermal conductivity of the materials.

The usual objective of research on the thermoelectric or thermomagnetic materials is to find materials for which the value Z is as high as possible. By performing the transport measurements (resistivity, Hall, Seebeck, Nernst, and thermal conductivity), one can easily obtain the required information for determining the feasibility of the tested materials for thermoelectric or thermomagnetic refrigeration.

Weaver et al. (22) have found that Bi-Sb alloys are promising as materials for the Ettingshausen cooling as well as for the Peltier cooling. They reported a value for $Z_E^*$ (Ettingshausen) at 80°K equal to $5 \times 10^{-3}/°K$ for an alloy containing 5% antimony. Smith et al. (31) have found a value for $Z^*$ (Peltier) at 80°K equal to $5.2 \times 10^{-3}/°K$ for Bi$_{88}$Sb$_{12}$ alloy. The figure of merit for these alloys decreases with increasing temperature at higher temperatures.

This research deals with the measurements of resistivity, Hall, Nernst, Seebeck, and Magneto-Seebeck coefficient on the Sn-doped and Te-doped Bi$_{88}$Sb$_{12}$ and Bi$_{95}$Sb$_{5}$ alloys. By performing these measurements, our purpose is to ascertain the transport properties of these doped alloys and to find out the feasibility of using them for thermoelectric and thermomagnetic cooling between 80 and 300°K.

* see chapter V
In chapter I, a general review of the transport properties of bismuth and Bi-Sb alloys between 80 and 300°K is made. Different expressions for the transport coefficients of bismuth obtained by A & M * are quoted. (2)

In chapter II, theoretical expressions for the transport coefficients of Sn-doped and Te-doped Bi-Sb alloys are derived and discussed. These expressions are also compared with the expressions for bismuth obtained by A & M (2).

In chapter III, a general description for the experimental setup and the measuring technique is made.

In chapter IV, the experimental results for the Sn-doped and the Te-doped Bi-Sb alloys, between 80 and 300°K, are analyzed and discussed. The results are compared with the previous results for bismuth and Bi-Sb alloys obtained by other authors. (1,2,4) Band-models for Sn-doped and Te-doped Bi-Sb alloys are proposed in terms of the experimental results. To explain the results, a heavy-hole band is postulated for these alloys.

In chapter V, a brief description on thermoelectric and thermomagnetic refrigeration is made. A comparison between thermoelectric and thermomagnetic cooling is also made. The figure of merit for bismuth and Bi-Sb alloys are listed and discussed.

* A & M refers to Abeles and Meiboom (2)
In this work, most of the experimental results can be properly explained by the obtained theoretical expressions. Tensor components of the electron mobility are found from the Hall coefficient and the resistivity measurements on Te-doped and Sn-doped Bi-Sb alloys between 80 and 300°K. The results are also compared with the previous results for bismuth and Bi-Sb alloys obtained by other authors.\(^{(2,9)}\) Scattering mechanism are studied for both Te-doped and Sn-doped Bi-Sb alloys. It is found that the temperature dependence of the Nernst coefficient and of the mobility can be used for determining the type of scattering for the Te-doped Bi-Sb alloys between 80 and 300°K.

The thermoelectric and thermomagnetic figure of merit for bismuth, Bi-Sb alloys and Sn-doped Bi-Sb alloys are compared and discussed. It is found that Sn-doped Bi\(_{95}\)Sb\(_{5}\) alloy shows promising results for thermoelectric refrigeration between 80 and 300°K.

Although this research has not explored completely all the transport properties associated with both electrons and holes, it does form a basic contribution to an understanding of the transport properties associated with the electrons in Te-doped Bi-Sb alloys between 80 and 300°K. This may lead to further investigation to improve the figure of merit for both thermoelectric and thermo-magnetic cooling schemes.
CHAPTER I
GENERAL REVIEW OF BISMUTH AND
BISMUTH-ANTIMONY ALLOYS

I-1 Bismuth

Bismuth is a semimetal which has a crystal structure based on the rhombohedral lattice with two atoms per unit cell. Most of the electrical and thermal properties of bismuth are anisotropic and can be described with reference to the trigonal axis and two equivalent binary axes lying in a plane perpendicular to the trigonal axis as shown in Fig. I.1-a.

The semimetallic properties of bismuth are caused by slightly overlapping conduction-valence bands. The conventional model is represented by a single-hole band on the trigonal axis with a density of states-effective mass of $0.16 m_0$. Overlapping three- or six-electron ellipsoids are located on the binary axes, but tilted slightly out of the basal plane ($5^\circ$) as shown in Fig. I.1-b.

Many other more-complicated models have been proposed because of a vast and somewhat confusing amount of published information on the band structure and electrical properties of bismuth. However, there now appears to be relatively consistent agreement on the value for the effective mass of electrons on the Fermi surface.
Figure I.1-a  Unit Cell of Bismuth

Figure I.1-b  Fermi Surface of Bismuth
Further verification concerning the exact number of equivalent electron constant energy surfaces has been impeded by recent and often contradictory observations relating to the total electron concentration and the magnitude of the direct optical-band gap between the conduction-band minimum and the valence band.

The present situation is summarized in Table I where $\alpha_1, \alpha_2$ and $\alpha_3$ are the eigenvalues of the reciprocal effective mass tensor; $(m^*)/m_o = (\alpha_1 \alpha_2 \alpha_3)^{-1/3}$ is the density of states effective mass for a parabolic band, $E_F$ is the Fermi energy, $E_g$ is the value of optical band gap, and $N$ is the total electron concentration.

<table>
<thead>
<tr>
<th>Method or model</th>
<th>$\alpha_1$</th>
<th>$\alpha_2$</th>
<th>$\alpha_3$</th>
<th>$(m^*)/m_o$</th>
<th>$E_F$(eV)</th>
<th>$E_g$(eV)</th>
<th>$N/10^{17}$</th>
</tr>
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<tr>
<td>de Hass-van Alphen ($^{24}$)</td>
<td>417</td>
<td>0.396</td>
<td>40.8</td>
<td>0.053</td>
<td>0.018</td>
<td></td>
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<tr>
<td>Cyclotron absorption ($^{25}$)</td>
<td>167</td>
<td>0.99</td>
<td>101</td>
<td>0.039</td>
<td>0.018</td>
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<td>Infrared absorption ($^{26}$)</td>
<td>133</td>
<td>0.59</td>
<td>91</td>
<td>0.052</td>
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<td>4.4</td>
<td></td>
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<tr>
<td>de haas-van Alphen ($^{27}$)</td>
<td>202</td>
<td>0.86</td>
<td>71</td>
<td>0.043</td>
<td>0.022</td>
<td>0.046</td>
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<td>4.1</td>
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<tr>
<td>Cyclotron and optical absorption ($^{28}$)</td>
<td>119</td>
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<td>103</td>
<td>0.052</td>
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<td>3.9</td>
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<td>Infrared reflectivity ($^{30}$)</td>
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<td>0.027</td>
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The most comprehensive measurements on the thermoelectric properties of single crystals of pure bismuth have been carried out by Gallo et al. ($^1$) They determined the electrical conductivity,
thermal conductivity and Seebeck coefficient, with current flow and temperature gradient parallel to and perpendicular to the trigonal axis, in the temperature range 80 to $300^\circ$K. The results of their measurements are shown in Fig. I.1–c. A notable fact is that the Seebeck coefficient and ratio of electrical to thermal conductivity are both appreciably greater along the trigonal direction than along the basal plane.

I.2 Antimony

Antimony and bismuth have the same crystal symmetry. Similar measurements to those of Abeles and Meiboom have been carried out on antimony by Freedman and Juretsheke.(3) They showed that the conduction band of this element is also of the three valley type. However, the directions of the highest and lowest effective mass are interchanged and the tilt of the mass of the ellipsoids is more substantial in antimony than in bismuth. The valence band of antimony, however, is of the three-valley type and the constant energy surfaces, though almost spheroidal, are tilted by about $60^\circ$ from the trigonal axis. The overlap of the conduction band and valence bands is much greater for antimony than for bismuth and the Seebeck coefficient is only about $30 \mu V/^\circ$C. Therefore, antimony is less likely to be a useful thermoelectric material when compared to bismuth.
Fig. 1.1-c Seebeck coefficient ($\alpha$), electrical resistivity ($\rho$) and thermal conductivity ($k$) versus temperature for bismuth (after Gallo et al. (1))
I-3 Bismuth-Antimony alloys

Little or no improvement in the figure of merit for bismuth can be achieved if the element is doped with an element of some other group of the periodic table (lead and tin act as acceptor impurities and tellurium acts as a donor impurity). This is because an increase in the number of electrons decreases their partial Seebeck coefficient while an increase in the number of holes enhances the bipolar effects. However, the addition of antimony does not alter the balance between the number of electrons and holes, it does alter the overlap of the bands.

Jain (4) measured the electrical conductivity and Hall coefficient as a function of temperature for single-crystal Bi-Sb alloys having a wide range of compositions and showed that the energy gap is positive when the concentration of antimony lies between about 5 and 40 percent. (Fig I-3) The energy gap reaches its maximum value of about 0.014eV when the concentration of antimony is about 12 percent. It appears that there is a change from bismuth-like valence band structure to an antimony-like valence band structure when the concentration of antimony exceeds 12 percent.(5) However, the alloys which are of greatest interest for thermoelectric and thermo-magnetic cooling contain less than 12% antimony and retain bismuth-like band structures for both the valence and conduction bands. (6-7)
The addition of antimony to bismuth is beneficial, from the point of view of thermoelectric cooling for two reasons: (1) the increase of energy gap (or decrease of band overlap) allows higher Seebeck coefficients to be reached; (2) the formation of a solid solution leads to a considerable reduction in the lattice thermal conductivity. Thus, observations on the magneto-thermal resistance effect show that the lattice thermal conductivity along the basal planes at 300 K is reduced from 0.11 to 0.029 W/cm-°C on adding 6% antimony to bismuth. (5)

![Graph](image)

Fig. 1-3 Activation energy $E_g$ vs. concentration of Sb (4)
I.4 Transport theory in Bismuth

The theory will be divided into two parts: the first is essentially phenomenological; while the second part bases the details of the transport process on the Boltzmann equation and the shape of the Fermi surface. The second part will be introduced and discussed in a later section.

The phenomenological theory begins with a generalized Ohm's law for a crystalline solid.

\[ E_i = \sum_j \rho_{ij}(H) J_j \]  

(1-1)

relating components of the electric field and the current density through a resistivity tensor whose components are functions of the magnetic field. For small magnetic fields, the expression

\[ \rho_{ij}(H) = \rho^{\circ}_{ij} + \rho_{ij,k} H_k + \rho_{ij,kl} H_k H_l + \ldots \]  

(1-2)

is assumed valid, and the only restrictions on (1-2) are the requirements of crystal symmetry and the Onsager relations. (32)

It is found that the tensors \( \rho_{ij} \) and \( \rho_{ij,k} \) each have only two independent components while \( \rho_{ij,kl} \) has eight. Therefore, to a second order in magnetic field, there is a total of 12 independent resistivity tensor components.

In bismuth, each electron ellipsoid has two of its principle axes slightly tilted (5°) from the crystal axes. In fact, the electron energy surfaces are not strictly ellipsoidal and the conduction band is non-parabolic. It has been a common practice
to interpret the experimental data in terms of the parabolic bands and relaxation time approximation. In order to interpret their galvanomagnetic experiments, Abeles and Neiboom (2) used a simplified model which neglects the tilt of the ellipsoids and assumes that the relaxation time is energy independent.

The conductivity and other transport coefficients based on equation (1-1) were given by A & M (2) with the following expressions for $\sigma_{ij}$, $R_{ij}(l)$, $\rho_{ij}(l)$:

i) **Conductivity components:**

\[
\sigma_{ii} = \sigma_{zz} = Ne\left(\mu_1 + \mu_3\right) + Pe \frac{1}{\mu_3} = \sigma_{ii}^e + \sigma_{zz}^h
\]

\[
\sigma_{33} = Ne\mu_3 + Pe \sqrt{3} = \sigma_{33}^e + \sigma_{33}^h
\]  

\[
\tag{1-3}
\]

ii) **Hall coefficients:**

\[
R_{12}(3) = -R_{21}(3) = \frac{e}{\sigma_{ij}} \left(N\mu_1\mu_2 - Pe \frac{1}{\mu_3} \right)
\]

\[
R_{33}(l) = -R_{33}(l) = R_{13}(2) = -R_{23}(2) = \frac{e}{2\sigma_{ij} \sigma_{33}} \left[N\mu_1\mu_2 + 2 Pe \sqrt{3} \left(\mu_1 + \mu_3 \right) \right]
\]

\[
\tag{1-4}
\]

iii) **Transverse magneto-resistance coefficients:**

\[
\rho_{ii}(2) = \frac{Ne\mu_3}{8 \sigma_{ii} \sigma_{33}} \left[\sigma_{33}^e + 2 Pe \sqrt{3} \left(\mu_1 + \mu_3 \right) \right] \left[\sigma_{33}^h + 2 Pe \sqrt{3} \left(\mu_1 + \mu_3 \right) \right]
\]

\[
\rho_{11}(3) = \frac{e^2 N}{4 \sigma_{ii} \sigma_{33}} \left[\sigma_{33}^e \left(\mu_1^2 \right) + 2 Pe \sqrt{3} \left(\mu_1 + \mu_3 \right) \right] \left[\sigma_{33}^h \left(\mu_1^2 \right) + 4 Pe \sqrt{3} \mu_3 \right]
\]

\[
\rho_{33}(l) = \frac{e^2}{2 \sigma_{ii} \sigma_{33}} NP \sqrt{3} \left(\mu_1 + \mu_3 \right) \left(\mu_3 + \sqrt{3} \right) \right]
\]

\[
\tag{1-5}
\]
where, \( N = 3n \) is the total number of electrons per unit volume
\( P \) is the total number of holes per unit volume
\( i \) denotes the direction of voltage drop
\( j \) denotes the direction of current flow
\( 1, 2 \) and \( 3 \) denotes binary, bisectrix and trigonal axis
\( \mu \) and \( \lambda \) are the electron and hole mobility, respectively.

\[ I-5 \textbf{ Scattering Mechanism: Acoustic lattice scattering} \]

In the pure crystal the scattering of the charge carriers is due to the vibrations of the lattice. The simplest form of lattice scattering would occur if there were only one atom per unit cell. The vibrations would then be solely of the acoustic type. In fact, acoustic mode lattice scattering is predominant in a number of semiconductors in which there is more than one atom per unit cell even when these atoms are not all of the same species.

Acoustic-mode lattice scattering can be attributed to the local changes in density, brought about by the thermal vibrations which, in turn, lead to fluctuations in the strength of the periodic potential through which the charge carriers move. The deformation-potential method of calculating the scattering by acoustic lattice vibrations has been developed by Bardeen and Shockley.\( ^{(10)} \) It leads to an expression for the relaxation time.

\[
\tau = \frac{\hbar^4 v^2}{(8\pi^2)^{3/2} K T^4} \cdot \frac{E^{-\frac{1}{2}}}{\mu^{3/2}} \tag{1-6}
\]

where, \( v \) is the velocity of longitudinal sound waves.
ρ is the density
Δ is the deformation-potential constant
h is the Plank constant
E is the energy of charge carriers
m* is the effective mass of charge carriers

By combining the relation between 7 and the mobility, it is found that the mobility is given by:

$$\mu = \left\{ \frac{(8\pi)^2 e^2 k_B T^2}{3 \kappa^{\frac{1}{2}} \Lambda^2} \right\} m^{* -\frac{1}{2}} T^{-\frac{3}{2}}$$

(1-7)

Equation (1-6) shows that, for acoustic scattering, the scattering parameter λ is equal to -0.5 (γ = A/Δ). The mobility is proportional to Τ^−3/2 and to m^*−5/2.

There are a number of semiconductors in which the mobility varies with temperature more rapidly than as Τ^−3/2. In some cases, e.g., the compounds of lead with sulphur, selenium, and tellurium the mobility varies approximately as Τ^−5/2. It has been suggested that the scattering is due to two-phonon processes. (11) When two phonons are involved in the collisions the mobility is proportional to Τ^−2 so that, with λ equal to -1, the mobility varies as Τ^−5/2.

It is postulated that two-phonons processes can sometimes predominate over one-phonon processes since the number of modes that can take part in the latter are severely limited.
CHAPTER II

DESCRIPTION OF THE TRANSPORT PROPERTIES

IN Sn-DOPED AND Te-DOPED Bi-Sb ALLOYS

II.1 Resistivity

Zero field resistivity of doped Bi-Sb alloys can be described in terms of anisotropic carrier mobilities as for bismuth. Conductivities along the three axes of the crystal, the binary, the bisectrix and the trigonal (1, 2 and 3 respectively) are given by: (for two carriers model)

\[\sigma_{ii} = \sigma_{zz} = N e \left(\frac{\mu_e + \mu_h}{2}\right) + \rho e \nu_i = N e \mu_1 + \rho e \nu_1\]

\[\sigma_{33} = N e \mu_3 + \rho e \nu_3\]

(2-1)

where \(\mu_1 = \left(\frac{\mu_e + \mu_h}{2}\right)\) is the electron mobility along basal plane

\(\nu_1\) is the hole mobility along basal plane

N & P are the total number of electrons and holes per unit volume, respectively.

It will be seen later that for Sn-doped Bi-Sb alloys, the number of electrons and holes are still comparable and the two-carrier model as equation (2-1) is necessary for interpreting the results. For Te-doped Bi-Sb alloys the number of electrons is much larger than the number of holes (i.e. N >> P), and hence the single carrier model can be used for the interpretations.

Thus,

\[\sigma_{ii}^e = N e \mu_e\]

\[\sigma_{33}^e = N e \mu_3\]

(2-2)
For intrinsic semiconductors, the number of electrons and holes is equal, and the number of charge carriers vary with temperature as:

\[ n \propto T^{3/2} F_4(\eta) \]

and for the non-degenerate case:

\[ n \propto T^{3/2} \exp(-E_g/2kT) \]  \hspace{1cm} (2-3)

where, \( E_g \) is the energy band gap of the semiconductors. The mobility varies as \( T^{-3/2} \) for acoustic-mode lattice scattering. In this case, the conductivity varies as:

\[ \sigma \propto \exp(-E_g/2kT) \]  \hspace{1cm} (2-4)

Equation (2-4) explains why the resistivity should decrease with increasing temperature for a semiconductor (with positive \( E_g \)), and should increase with temperature for a semimetal (with negative \( E_g \)). Jain (4) has pointed out, from resistivity measurements in undoped Bi-Sb alloys, that for percentage of Sb above 5%, the alloys become semiconductors. Calculation of band gap, by equation (2-4), is shown in Fig (1-3) for different percentages of antimony.

II.2 Hall Coefficient

Equation (1-4) expressed two independent Hall coefficients for Bismuth in terms of mobilities and carrier concentrations. These
expressions can also be obtained in a simple way as follows.

The low field Hall coefficients for an isotropic material with mixed-conduction was given by Putley (12) as follows:

$$R = \frac{R_e \sigma^2 + R_h \sigma^2}{(\sigma_e + \sigma_h)^2} \quad (2-5)$$

The corresponding anisotropic expression is:

$$R_{yx} = \frac{\sigma_x^e \sigma_y^e R_{yx}^e + \sigma_x^h \sigma_y^h R_{yx}^h}{(\sigma_x^e + \sigma_x^h)(\sigma_y^e + \sigma_y^h)} \quad (2-6)$$

where the superscript \( e \) denotes electrons, and \( h \) is for holes.

\( y \) is the direction of Hall voltage,
\( x \) is the direction of current flow,
\( z \) is the direction of magnetic field.

If the Hall voltage is measured along trigonal axis, the current flows along binary axis and the magnetic field is along bisectrix.

Then equation (2-6) can be rewritten as follows:

$$R_{31} = \frac{\sigma_{xx}^e \sigma_{yy}^e R_{31}^e + \sigma_{xx}^h \sigma_{yy}^h R_{31}^h}{(\sigma_{xx}^e + \sigma_{xx}^h)(\sigma_{yy}^e + \sigma_{yy}^h)} \quad (2-7)$$

The partial Hall coefficients \( R_{31}^e \) and \( R_{31}^h \) are given by Goldsmid(13),

$$R_{31}^e = -\frac{1}{N_e} \quad , \quad R_{31}^h = \frac{1}{P_e} \quad (2-8)$$

And the partial conductivities \( \sigma^e \) and \( \sigma^h \) are given as follows:

$$\sigma_{xx}^e = N_e \mu_e \quad , \quad \sigma_{xx}^h = P_e \nu, \quad \sigma_{yy}^e = N_e \mu_3 \quad , \quad \sigma_{yy}^h = P_e \nu_3 \quad (2-9)$$
Substituting equation (2-7) and (2-8) into (2-9), we have:

\[ R_{31} = \frac{1}{N\varepsilon} \cdot \frac{-\mu_3 \mu_3 + \frac{P}{N} \nu_3 \nu_3}{(\mu_3 + \frac{P}{N} \nu_3)(\mu_3 + \frac{P}{N} \nu_3)} \] (2-10)

which turns out to be the same as equation (1-4) obtained by A & M (2). The corresponding expression for the Hall mobility is given by (2-11):

\[ R_{31} \sigma_{ij} = \frac{-\mu_3 \mu_3 + \frac{P}{N} \nu_3 \nu_3}{(\mu_3 + \frac{P}{N} \nu_3)} \] (2-11)

For Te-doped Bi-Sb alloys, since \( N \gg P \), it is reasonable to assume \( \mu_3 \gg \frac{P}{N} \nu_3 \) and \( \mu_3 \nu_3 \gg \frac{P}{N} \nu_3 \nu_3 \). Thus, equation (2-11) can be reduced to (2-12):

\[ R_{31} \sigma_{ij} \gg 1/\mu_3 = 1/\mu \] (2-12)

For Sn-doped Bi-Sb alloys, equation (2-12) is valid because the number of electrons and holes is still comparable.

Similarly, if the Hall voltage is measured along the bisectrix axis, the current flows along the trigonal axis and the magnetic field is along the binary axis. Then, equation (2-6) can be rewritten as follows:

\[ R_{23} = \frac{\sigma_{22}^e \sigma_{33}^e R_{23}^e + \sigma_{22}^p \sigma_{33}^p R_{23}^p}{(\sigma_{22}^e + \sigma_{22}^p)(\sigma_{33}^e + \sigma_{33}^p)} \] (2-13)

The partial Hall coefficients and the partial conductivities in (2-13) are given by Goldsmid (13) as follows:

\[ \sigma_{22}^e = N e \mu_2 \quad , \quad \sigma_{33}^e = N e \mu_3 \]

(2-14)

\[ \sigma_{22}^p = N e \mu_2 \quad , \quad \sigma_{33}^p = N e \nu_3 \]

\[ R_{23}^e = -\frac{1}{N e} \quad , \quad R_{33}^p = \frac{1}{N e} \]
Substituting equation (2-14) into (2-13), we have:

\[- R_{33} = \frac{1}{N e} \cdot \frac{-\mu_3 \mu_3 + \frac{P}{N} \nu_3 v_3}{(\mu_3 + \frac{P}{N} \nu_3)(\mu_3 + \frac{P}{N} \nu_3)} \tag{2-15}\]

The corresponding expression for the Hall mobility is given by:

\[R_{33} \sigma_{33} = \frac{-\mu_3 \mu_3 + \frac{P}{N} \nu_3 v_3}{(\mu_3 + \frac{P}{N} \nu_3)} \tag{2-16}\]

For Te-doped Bi-Sb alloys and the Sn-doped Bi-Sb alloys, with the same argument as above, equation (2-16) can be reduced to (2-17):

\[R_{33} \sigma_{33} \approx \frac{1}{\mu_3} \tag{2-17}\]

If the Hall voltage is measured along the bisectrix axis, the current is along the binary axis and the magnetic field is along the trigonal axis. Then, equation (2-6) can be written in the following form:

\[R_{21} = \frac{\sigma_{21} \sigma_{31} R_{21}^e + \sigma_{21} \sigma_{31} R_{31}^e}{(\sigma_{11}^e + \sigma_{11}^* \sigma_{33}^e \sigma_{33}^*)} \tag{2-18}\]

The partial Hall coefficients in equation (2-18) are given by (13) as follows:

\[R_{21}^e = -\frac{\mu_3 \mu_3}{N e \mu_2^2}, \quad R_{21}^r = \frac{1}{P e} \tag{2-19}\]

Substituting equations (2-9) and (2-19) into (2-18), we have:

\[R_{21} = \frac{1}{N e} \cdot \frac{-\mu_3 \mu_3 + \frac{P}{N} \nu_3 \nu_3^2}{(\mu_3 + \frac{P}{N} \nu_3)^2} \tag{2-20}\]

which turns out to be the same as equation (1-4) obtained by A & M (2).
For Te-doped Bi-Sb alloys, with the same argument as above, equation (2-20) reduced to (2-21):

\[ R_{21} = \frac{1}{Ne} \frac{-\mu_r \mu_z}{\mu_z^2} = \frac{-A}{Ne} \frac{\mu_r \mu_z}{(\mu_r + \mu_z)^2} \]  

(2-21)

Equation (2-15) and (2-20) are expressions for two independent Hall coefficients. To estimate the magnitude of these two constants, it is necessary to examine the mobility data on Bismuth given by A & M at 80²K and 300²K. From their results (Fig.4.3), it was found that mobility-ratios are almost constant with temperature.

The electron to hole mobility ratio \( \mu_r/\mu_z \), along trigonal axis, is 10, while the ratio \( \mu_r/\mu_z \), along the basal plane, is 2.1. It turns out that \( R_{31} \) varies inversely with carrier concentration and is very insensitive to the changes in electron mobility and hole mobility ratio. While, for \( R_{21} \), since \( \mu_r \gg \mu_z \), changes in mobility ratio \( \mu_r/\mu_z \) affects the magnitude of \( R_{21} \).

II.3 Seebeck coefficient

The Seebeck coefficient is defined as:

\[ \alpha = \frac{2}{q} \frac{\partial S}{\partial x} \bigg|_{J_x = 0} \quad \text{(one dimensional case)} \]  

(2-22)

where \( S \) is the Seebeck coefficient

\( q \) is electronic charge

\( J_x \) is the current density

Based on the Boltzmann transport equation, it is found that the
Seebeck coefficient for extrinsic materials - with single type of charge carrier (either electrons or holes) is given by:

\[ \alpha_{e,h} = \pm \frac{1}{eT} \left( \frac{f}{k_e} - \frac{K_1}{K_0} \right) \]  (2-23)

where: positive sign denotes charge carriers are quasi-free electrons. 
negative sign denotes charge carriers are holes.

and,

\[ K_0 = \frac{8\pi}{3} \left( \frac{2}{k_e} \right)^{\frac{3}{2}} \frac{1}{M^{\frac{3}{2}}} \frac{1}{T} \tau_0 \left( \frac{\lambda + \epsilon}{2} \right)^{\lambda + \frac{3}{2}} F_{\lambda + \frac{1}{2}} \]

\[ K_1 = \frac{8\pi}{3} \left( \frac{2}{k_e} \right)^{\frac{3}{2}} \frac{1}{M^{\frac{3}{2}}} \frac{1}{T} \tau_0 \left( \frac{\lambda + \epsilon}{2} \right)^{\lambda + \frac{5}{2}} F_{\lambda + \frac{3}{2}} \]  (2-24)

\[ F_\gamma(s) = \int_0^\infty \int_0^r f_0 \, dS \]  is the Fermi integral

\[ f_0 = 1 / \left( \exp \left( \frac{E - \epsilon}{kT} \right) - 1 \right] \]  is the Fermi distribution function

Substituting \( K_0 \) and \( K_1 \) into equation (2-23), we have:

\[ \alpha_{e,h} = \pm \frac{1}{eT} \left( \frac{f}{k_e} - \frac{\left( \frac{\lambda + \epsilon}{2} \right)^{\lambda + \frac{3}{2}} F_{\lambda + \frac{1}{2}} (3)}{\left( \frac{\lambda + \epsilon}{2} \right)^{\lambda + \frac{5}{2}} F_{\lambda + \frac{3}{2}} (3)} \right) \]  (2-24)

where \( \gamma = \frac{\lambda}{kT} \) is the reduced Fermi energy

For the nondegenerate case, equation (2-24) can be reduced to (2-25):

\[ \alpha_{e,h} = \pm \frac{1}{eT} \left[ \frac{\gamma}{\left( \frac{\lambda + \epsilon}{2} \right)} \right] \]  (2-25)

The above expressions assume that only one type of charge is present in the conductor. However, in an intrinsic semiconductor or semimetal, both negative quasi-free electrons and positive holes are present.

Bipolar effects corresponding to both intrinsic and mixed conduction can be found in semimetals as well as semiconductors.

In this case, the Seebeck coefficient is given by:
\[ \alpha = \frac{\alpha_e \sigma_e + \alpha_h \sigma_h}{\sigma_e + \sigma_h} \]  

(2-26)

where \( \alpha_e \) and \( \alpha_h \) are the partial Seebeck coefficient of electrons and holes, respectively.

\( \sigma_e \) and \( \sigma_h \) are the partial conductivity of electrons and holes, respectively.

For Sn-doped Bi-Sb alloys, the expression for the Seebeck coefficient in equation (2-26) is required for interpretation of the experimental results. For the Te-doped Bi-Sb alloys, equation (2-23) can be used for the interpretations.

II.4 Magneto-Seebeck Coefficient

It is found that the Seebeck coefficient of a material changes in a transverse magnetic field. In the case of single type of charge carriers, the Seebeck coefficient increases in magnitude as the magnetic field increased and saturates at high fields. For the extrinsic case, the Seebeck coefficient can be expressed as:

\[ \alpha_{e,h}(H) = \frac{1}{T_e} \left( \frac{\gamma_0 \gamma_i + \gamma_o \gamma_i}{\gamma_o \gamma_i + \gamma_i^2} - \frac{1}{\gamma} \right) \]  

(2-27)

where:

\[ \gamma_0 = -\frac{2T}{3m^*} \int_0^\infty \frac{q(E) E^2}{1 + \beta^2} \frac{2T}{E} \, dE \]

\[ \gamma_i = -\frac{2T}{3m^*} \int_0^\infty \frac{q(E) E^2}{1 + \beta^2} \frac{2T}{E} \, dE \]

\[ \gamma_1 = -\frac{2T}{3m^*} \int_0^\infty \frac{q(E) E^2}{1 + \beta^2} \frac{2T}{E} \, dE \]

\[ \gamma_0' = -\frac{2T}{3m^*} \int_0^\infty \frac{\beta q(E) E^2}{1 + \beta^2} \frac{2T}{E} \, dE \]

\[ \gamma_i' = -\frac{2T}{3m^*} \int_0^\infty \frac{\beta q(E) E^2}{1 + \beta^2} \frac{2T}{E} \, dE \]  

(2-28)
\[ g(E) = \frac{4\pi}{h^3} (2m^*)^{3/2} E^{1/2} \] is the density of states

\[ \tau = \tau_0 E^\lambda \] is the relaxation time of charge carriers

\[ \beta = \frac{eH}{m^*} \] \( (\beta \ll 1 \text{ at low magnetic field}) \)

The first term within the parentheses of equation (2-27) represents the average kinetic energy carried by the electrons or holes. This kinetic energy term is increased upon application of a magnetic field if the scattering parameter \( \lambda \) is negative and decreases in a magnetic field if \( \lambda \) is positive. For a nondegenerate semiconductor in a very strong magnetic field the rise in magnitude of the Seebeck coefficient is \(-\lambda (k/e)\), \(k/e\) being equal to about 86 \(\mu V/\circ C\). The change in the Seebeck coefficient is somewhat less for a partially degenerate semiconductor and becomes very small when the material is completely degenerate.

The magneto-Seebeck effect is more complicated for an intrinsic material like bismuth. The Seebeck coefficient for an intrinsic material is given by equation (2-26). \( \alpha_e \) and \( \alpha_h \) increase with increasing magnetic field and are of opposite sign, while \( \xi_e \) and \( \xi_h \) decrease with increasing magnetic field due to magneto-resistance effect. Thus, for an intrinsic material, the Seebeck coefficient shows a complicated behavior with magnetic field.

For bismuth, using the magneto-conductivity expressions given by Abeles & Meiboom (2), the expression for \( \alpha \) as a function of magnetic field becomes:

\[
\alpha_{12}(H) = \frac{\alpha_e + (\frac{J_e}{\mu_e^*}) \left[ \frac{1 + \mu_e^* \mu_h^* H^2}{1 + J_e \eta_e H^2} \right] \alpha_h \beta_e \beta_h}{1 + (\frac{J_h}{\mu_h^*}) \left[ \frac{1 + \mu_e^* \mu_h^* H^2}{1 + J_h \eta_h H^2} \right] \beta_e \beta_h} \quad (2-29)
\]
where,
\[
\sigma = \frac{N e \mu_{\perp}}{1 + \mu_{\parallel} \mu_{\perp} H^2}, \quad \sigma_{\parallel} = \frac{\rho e J_1}{1 + \mu_{\parallel} \mu_{\perp} H^2}
\]

I parallel Binary axis (1)

H parallel to Bisectrix axis (2)

II.5 Nernst Coefficient

The Nernst coefficient \( Q \) is defined by the equation

\[
Q = \frac{E_y}{H_z \frac{\partial T}{\partial \chi}} \bigg|_{J_y, J_z = 0, \nabla J_y = 0}
\]  

(2-30)

The units for the Nernst coefficient are cm\(^2\)/sec-\(0\)K, or m\(^2\)/sec-\(0\)K. This is the transverse voltage obtained when there is a temperature gradient along the sample placed in a magnetic field which is in the direction perpendicular to the other two components. The sign of Nernst coefficient in an extrinsic material (or single type carrier) depends on the type of scattering mechanism. For example, if the charge carriers are scattered by acoustical mode lattice vibration, then the Nernst coefficient will be negative. On the other hand, if the charge carriers are scattered by the impurity ions the sign of Nernst coefficient is positive. It does not depend on the type of charge carriers. The Nernst coefficient for single charge carriers is given by Putley (12) as follows: ...

(for low magnetic field)
\[ Q = \frac{(k/e) \cdot \lambda \cdot r \cdot \mu_H}{(2-31)} \]

where, \( \lambda \) is the scattering parameter of charge carriers

- \( 0 < r \leq 3\pi/8 \), \( r = 3\pi/8 \) for the nondegenerate case.
- \( r = 0 \) for the completely degenerate case.

\( \mu_H \) is the Hall mobility of charge carriers.

From equation (2-31), it is found that the small magnitude of the Nernst field is not only due to the small value of the carrier mobility but also due to the partial degeneracy of the carriers.

The Nernst coefficient of an intrinsic semiconductor or semimetal is the sum of two terms. One term depends on the details of the scattering mechanism just as in an extrinsic semiconductor. The other term has its origin in the bipolar effects. The physical origin of this bipolar effect is due to the creation and annihilation of electron-hole pairs. At this point it is pertinent to mention the Ettingshausen effect, as the Nernst and Ettingshausen effects are related by the thermodynamic relation:

\[ PK = QT \quad (2-32) \]

where \( P \) is the Ettingshausen coefficient,

and \( K \) is the thermoconductivity.

The origin of the Ettingshausen effect in an intrinsic semiconductor can be seen from Fig.2.5.
The applied electric field causes electrons to flow in one direction while positive hole flow in the opposite direction. Then, on application of the magnetic field both type of carriers tend to move in the same transverse direction. Electron-hole pairs are created at the cold face, drawing energy from the lattice vibrations, and are annihilated at the hot face, where they give up their ionization energy once again to the lattice. This bipolar effect is very large compared to the single carrier effect in the extrinsic case. Hence the Nernst effect is very large for an intrinsic material.

The expression for the Nernst coefficient, in an intrinsic material, is given by Putley as follows: (in low magnetic field)

\[ Q = \frac{Q_e \sigma_e (\sigma_e + \sigma_i) + Q_h \sigma_i (\sigma_e + \sigma_i)}{(\sigma_e + \sigma_i)^2} + \frac{\sigma_e \sigma_i (\sigma_e - \sigma_i)}{(\sigma_e + \sigma_i)^2} \]

\[ (\text{single carrier term}) \quad (\text{bipolar term}) \]  

(2-33)
where, \( Q^e \) and \( Q^h \) are the partial Nernst coefficient.
\( R^e \) and \( R^h \) are the partial Hall coefficient.

Corresponding anisotropic expression is

\[
Q_{\gamma x} = \frac{\delta_x \delta_y Q_{\gamma x}^e + \delta_x \delta_y Q_{\gamma x}^h}{\delta_x \delta_y} + \frac{(\alpha^e - \alpha^h)(\delta_y \delta_x R_{\gamma x}^e - \delta_y \delta_x R_{\gamma x}^h)}{\delta_x \delta_y}
\]

(2-34)

In the case of Bismuth or Bi-Sb alloys, if the temperature gradient is along the binary and the magnetic field is along the bisectrix axis, then the Nernst coefficient can be expressed by:

\[
Q_{31} = \frac{\delta_1 \delta_3 Q_{31}^e + \delta_1 \delta_3 Q_{31}^h}{\delta_1 \delta_3} + \frac{\delta_1 \delta_3 (\alpha^e - \alpha^h)(\delta_3 \delta_3 R_{31}^e - \delta_3 \delta_3 R_{31}^h)}{\delta_1 \delta_3}
\]

(2-35)

where, \( R_{31}^e = -\frac{i}{Ne} \), \( R_{31}^h = \frac{i}{Pe} \)

\( Q_{31}^e = (\frac{\delta_3}{\delta_1}) \cdot \gamma \cdot (R_{31}^e \delta_3) = (\frac{\delta_3}{\delta_1}) \cdot \gamma \cdot \mu_\perp \)

\( Q_{31}^h = (\frac{\delta_3}{\delta_1}) \cdot \gamma \cdot \mu_\perp \)

\( \delta_1 \delta_3 = Ne \mu_\perp \), \( \delta_1 \delta_3 = Pe \mu_\perp \)

(2-36)

Substituting above expressions into equation (2-35), we have:

\[
Q_{31} = (\frac{\delta_3}{\delta_1}) \cdot \gamma \cdot \frac{\mu_\perp \mu_3 + (\frac{P}{N}) \mu_\perp \nu_3}{\mu_3 + (\frac{P}{N}) \nu_3} + \frac{(\frac{P}{N})(\alpha^h - \alpha^e)\mu_\perp \nu_3 (\mu_3 + \nu_3)}{(\mu_3 + (\frac{P}{N}) \nu_3) (\mu_3 + (\frac{P}{N}) \nu_3)}
\]

(2-36)

For Te-doped Bi-Sb alloys, \( N \gg P \), equation (2-36) reduce to (2-31):

\[
Q_{31}^e = (\frac{\delta_3}{\delta_1}) \cdot \gamma \cdot \mu_\perp
\]

(2-31)
CHAPTER III
EXPERIMENTAL DETAILS

III. 1 Sample Preparation

Sn-doped and Te-doped Bi-Sb alloys were bought from Semi-elements, Inc. and were 99.9999 % pure. The method of growth for these Bi-Sb single crystal alloys is the floating zone technique. The directions of the crystal axis were determined by the characteristics of the cleavage planes as seen on the basal plane. The dopant concentrations were certified by Semi-Element Inc. and these concentrations were very close to our specifications when Te-doped and Sn-doped Bi-Sb alloys were checked using Hall coefficient measurements at 80 K.

All sample cutting was done by using an electrical discharge machine which reduces the possibility of straining the samples. Measurements were made on oriented bars of typical dimensions $\frac{1}{2}'' \times \frac{1}{8}'' \times \frac{1}{16}''$.

The samples were then lapped with # 600 grit silicon carbide powder and etched with nitric acid about 3 minutes and then washed with hydrochloride acid to remove the oxide layer formed on the surface. The length of the sample was made three or four times greater than the width in order to remove end effects.
A typical sample is shown in Fig. 3.1.

![Diagram](image)

**Fig. 3.1**  typical sample

### III.2 Contacts

5 mil Copper-Constantan thermocouple wires were attached to the samples as shown in Fig. 3-1. Wood's metal solder (low melting point alloy) was used for attaching thermocouples and electrical leads to the sample. Precautions were taken to ensure that the solder spot was small enough and far enough from the ends of the samples to eliminate effects due to shorting the Hall voltage. The ends of the samples were soldered with Wood's metal to the copper block connected to the heater and heat sink.

### III.3 The Cryostat and the Magnet

A low temperature cryostat shown in Fig.3.3-a and Fig.3.3-b was used for measuring the resistivity, the Hall coefficient, Seebeck coefficient, Nernst coefficient, Magneto-resistance and Magneto-Seebeck coefficient. The cryostat dewar system is suspended between the pole faces of the magnet, so that the sample inside the cryostat is in a uniform magnetic field. All the electrical
Fig. 3.3-a. The Cryostat
Fig. 3.3-b. The Sample Chamber
connections from the sample are brought out from the top flange through glass to metal feed throughs. The center portion of this cryostat is made of glass, while the lower portion which is dipped in liquid nitrogen is made of copper so that very little heat is transferred to this portion from the top. The cryostat is evacuated by a mechanical and a diffusion pump, which are connected in series. The heater is made of nichrome wire wound on a copper cylinder.

The magnet is a 9-in. (22.86 cm) Varian electromagnet, type 340L, with pole pieces tapered to 6 in. and a pole gap of 3 in. The range of magnetic field is 40-10000 gauss. Each magnet of the V-340L has two water-cooled low impedance (one-eighth ohm) coils connected in series and mounted in a trunnion-supported yoke. Precision-finished butt joints on the yoke members are joined by bolts and nuts rather than welded. This method of fabrication avoids the large fringe magnetic fields produced by welds, and the field homogeneity distortion caused by the aging of welded cast joints. The magnet has a yoke which may be locked in any position from horizontal through a 135-degree arc. (360° rotation about pole gap vertical axis with a V-342L base).

III.4 Measurements:

The apparatus of Fig. 3.3 was used to measure the electrical resistivity, Hall coefficient, Seebeck coefficient and Nernst coefficient
of the sample. The temperatures were measured with copper-Constantan thermocouples which were soldered to the sample before being brought out of the cryostat. All of the measurements were made with a Leeds and Northrup K-3 potentiometer and an accurate ammeter (± 0.1% error).

The isothermal electrical resistivity was measured by passing a direct current of 100 ma. through the sample. A reversing procedure was used to eliminate thermoelectric effects. The potential drop across the sample was measured across the copper leads of the thermocouples attached to the sample. Room temperature resistivity measurements on two different samples with same composition indicated that the contact resistance and the inhomogeneity effect were less than 5%. In measuring the Hall coefficient and the magneto-Seebeck coefficient, both the current and the magnetic field were reversed and the average value was taken. The sign of the Hall voltage was determined by the sign of the potential developed in the I x H direction, which is according to convention. Careful field-reversing procedures were used in order to eliminate hysteresis effects. For fields below 1000 gauss, the field was continuously monitored by using an incremental type Gaussmeter.

The Seebeck coefficient and the Nernst coefficient were measured by establishing a steady-state temperature gradient across the sample. In this case, temperature differences of 10°-15°C were used so that the experimental error arising from the fluctuation of temperature in the
heater and the environment can be minimized. The Seebeck voltage was measured across the copper leads of the thermocouples and the temperature differences were measured from the thermocouples. The absolute Seebeck coefficient of the sample was found by making a correction for the small absolute Seebeck coefficient of copper (\(\sim 4 \mu V\)). In measuring the Nernst and Magneto-Seebeck coefficient, the magnetic field was varied after the steady state temperature difference was established.

In the case of the Magneto-Seebeck coefficient measurement, no "Umkehr effect" should be observed (15) for our chosen orientation. The appearance of a different Seebeck coefficient on reversal of the magnetic field is known as the "Umkehr effect". By properly orienting the crystal, the Umkehr effect was made to vanish. In fact, this method was used to orient the crystal axis, with respect to the magnetic field. All measurements were made in a vacuum cryostat and by dip-stick techniques in liquid \(N_2\).
CHAPTER IV

RESULTS AND ANALYSES

IV.1 Resistivity

Fig. 4.1-a and Fig. 4.1-b show resistivity versus temperature in the range of 80°K to 300°K, for Sn-doped and Te-doped Bi$_{88}$-Sb$_{12}$ and Bi$_{95}$-Sb$_5$ alloys with the current flow along the binary axis. These results are compared with the previous results of undoped Bi$_{95}$-Sb$_5$ and Bi$_{88}$-Sb$_{12}$ alloys obtained by Wolfe and Smith (h), and also compared with the result of Te-doped Bi$_{85}$-Sb$_{15}$ alloys obtained by Brown and Silverman (8).

From the results, it is interesting to note that for both Sn-doped Bi-Sb alloys, the resistivity shows semiconductor behavior (resistivity decreases with increasing temperature) for temperature below 135°K, while for both Te-doped Bi-Sb alloys, the resistivity shows semi-metallic behavior (resistivity increases with temperature). It was pointed out by Jain (4) that the undoped Bi-Sb alloys become semiconductors if the percentage of antimonide atoms exceeds 5% (as shown in Fig. 1-3). The present results indicate that this is not necessarily so for both Sn-doped and Te-doped Bi-Sb alloys.

Fig. 4.1-c and Fig. 4.1-d show resistivity versus temperature from 80°K to 300°K, for Sn doped and Te-doped Bi$_{88}$-Sb$_{12}$ alloys with current flow along binary and trigonal axis, respectively.
Fig. 4.1-a Resistivity versus temperature (°K)
Fig. 4.1-b Resistivity versus temperature (°K)
Fig. 4.1-c  Resistivity versus $10^3/T$ (°K$^{-1}$)
Te doped Bi$_{88}$Sb$_{12}$
• Current // trigonal
△ Current // binary

Fig. 4.1-d  Resistivity versus $10^3/T$ (°K$^{-1}$)
Sn doped Bi$_{88}$Sb$_{12}$
• Current // trigonal
△ Current // binary
Since these alloys are highly anisotropic materials, the resistivity \( \rho_{11} \) (I // Binary) and \( \rho_{33} \) (I // Trigonal) for Sn-doped Bi\(_{88}\)-Sb\(_{12}\) alloys has the following ratios:

\[
\frac{\rho_{33}}{\rho_{11}} \approx 3 \quad \text{at} \quad T = 77^\circ\text{K}
\]

\[
\frac{\rho_{33}}{\rho_{11}} \approx 2.25 \quad \text{at} \quad T = 300^\circ\text{K}
\]

and, for Te-doped Bi\(_{88}\)-Sb\(_{12}\) alloys:

\[
\frac{\rho_{33}}{\rho_{11}} = \frac{1.25}{0.72} = 1.74 \quad \text{at} \quad T = 77^\circ\text{K}
\]

\[
\frac{\rho_{33}}{\rho_{11}} \approx \frac{2.2}{1.3} = 1.69 \quad \text{at} \quad T = 300^\circ\text{K}
\]

The above results indicate that the mobility of electrons along binary axis (\( \mu_{\perp} \)) is higher than along the trigonal axis (\( \mu_{\parallel} \)).

### IV.2 Hall Coefficient \( R_{31} \) and the electron concentrations

In this section, the experimental results of the Hall coefficient for Sn-doped and Te-doped Bi-Sb alloys will be interpreted in terms of the theoretical expressions described in section (II-2). The Hall coefficient \( R_{31} \) (I//1, H//2) in equation (2-15) can be rewritten as follows:

\[
R_{31} = \frac{1}{Ne}\left[ \frac{(-1 + \frac{P}{N\mu_{\perp}} \frac{\nu_{\perp}}{\mu_{\perp}})}{\left(1 + \frac{P}{N\mu_{\parallel}} \frac{\nu_{\parallel}}{\mu_{\parallel}}\right) \left(1 + \frac{P}{N\mu_{\parallel}} \frac{\nu_{\parallel}}{\mu_{\parallel}}\right)} \right]
\]  (2-15)
The electron mobilities ($\mu_1$ & $\mu_3$) are higher than the hole mobilities ($\nu_1$ & $\nu_3$) as per A & M mobilities data for bismuth. (see section II.2)

This is also true even for Bi-Sb alloys. (13)

For Te-doped Bi-Sb alloys, since $N \gg P$, equation (2-15) can be reduced to:

$$R_{31} = -\frac{1}{N_0} \quad (2-15-a)$$

which indicates that $R_{31}$ is inversely proportional to the carrier concentration ($N$) and is independent of the carrier mobility ratios.

For Sn-doped Bi-Sb alloys, the alloys are N-type intrinsic and $\mu_1 > \nu_1$, $\mu_3 > \nu_3$, therefore, it is reasonable to assume that the variation of $R_{31}$ with the whole bracket of equation (2-15) can be neglected. Thus, $R_{31}$ is also inversely proportional to $N$, or $R_{31} \approx -\frac{1}{N_0}$. The variation of the Hall coefficient $R_{31}$ with temperature for Sn-doped and Te-doped Bi-Sb alloys measured with the current parallel to the binary axis and the magnetic field parallel to the bisectrix axis is shown in Fig. 4.2-a to Fig. 4.2-f (for low field and high field limit).

Fig. 4.2-a shows that the Hall coefficient $R_{31}$ for Sn-doped Bi-Sb alloys depends strongly on temperature. The Hall coefficient $R_{31}$ for Te-doped Bi-Sb alloys depends weakly on temperature as shown in Fig. 4.2-b. The reason for this is that at intermediate temperature (kT of the order of magnitude of the band gap) the introduction of acceptor levels (Sn atoms) will cause a reduction in the number of electrons and an increase in the number of holes. At high
temperature the effect of the acceptor levels is small. (2) In fact, the Hall coefficient \( R_{31} \) for Sn-doped and Te-doped Bi-Sb alloys is nearly equal at room temperature, which means that the carrier concentrations at room temperature are nearly equal for both Sn-doped and Te-doped Bi-Sb alloys. (see Fig. 4.2-a and Fig.4.2-b)

The variation of the Hall coefficient \( R_{31} \) with the magnetic field for Sn-doped and Te-doped Bi-Sb alloys is shown in Fig.4.2-g to Fig. 4.2-m. It is seen from all these curves that \( R_{31} \) saturates at high magnetic field and depends on the scattering mechanism at low magnetic field. The electron concentrations are figured out for the high field limit. Fig.4.2-n shows the variation of electron concentrations with temperature for Sn-doped and Te-doped Bi-Sb alloys. The electron concentrations obtained from the present Hall coefficient data \( R_{31} \) for Sn-doped and Te-doped Bi-Sb alloys, and for bismuth obtained by A & M (2) are listed in table (II) for comparison.

Table II Electron Concentrations (cm\(^3\))\(^{-1}\)

<table>
<thead>
<tr>
<th>Material</th>
<th>( T = 80^\circ K )</th>
<th>300(^\circ) K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth (2)</td>
<td>( 4.6 \times 10^{17} )</td>
<td>( 2.2 \times 10^{18} )</td>
</tr>
<tr>
<td>Sn-doped Bi(<em>{95})Sb(</em>{5})</td>
<td>( 3.48 \times 10^{17} )</td>
<td>( 6.6 \times 10^{18} )</td>
</tr>
<tr>
<td>Sn-doped Bi(<em>{88})Sb(</em>{12})</td>
<td>( 7.6 \times 10^{17} )</td>
<td>( 7.8 \times 10^{18} )</td>
</tr>
<tr>
<td>Te-doped Bi(<em>{88})Sb(</em>{12})</td>
<td>( 4.8 \times 10^{18} )</td>
<td>( 9.2 \times 10^{18} )</td>
</tr>
</tbody>
</table>
Fig. 4.2-a  Hall coefficient versus $10^3/T$ ($^\circ$K)$^{-1}$
Fig. 4.2-b Hall coefficient versus $10^3/T$ ($^\circ$K)$^{-1}$

Te doped Bi$_{88}$Sb$_{12}$

- $I \parallel 1, H \parallel 2$
- $I \parallel 3, H \parallel 1$

($H = 500$ gauss)

Fig. 4.2-c Hall coefficient versus $10^3/T$ ($^\circ$K)$^{-1}$

Te doped Bi$_{95}$Sb$_5$

- $I \parallel 1, H \parallel 2$

($H = 500$ gauss)
Fig. 4.2(d) Hall coefficient versus $10^3/T (^{°}K)^{-1}$
Fig. 4.2-e  Hall coefficient versus $10^3/T \ (^\circ \text{K})^{-1}$
Te doped Bi$_{83}$Sb$_{12}$

- I // 1, H // 2
- I // 3, H // 1
  ($H = 10^4 \text{ gauss}$)

Fig. 4.2-f  Hall coefficient versus $10^3/T \ (^\circ \text{K})^{-1}$
Te doped Bi$_{95}$Sb$_5$
I // 1, H // 2
($H = 10^4 \text{ gauss}$)
Fig. 4.2-g  Hall coefficient versus $H$ (Kilogauss)
Sn doped Bi$_{95}$Sb$_5$
I $// l$, H $// 2$
Fig. 4.2-h  Hall coefficient versus H (Kilogauss)
Te doped Bi₉₅Sb₅
I // 1, H // 2

Fig. 4.2-i  Hall coefficient versus H (Kilogauss)
Sn doped Bi₉₅Sb₅
I // 1, H // 3
Fig. 4.2-j  Hall coefficient versus H (Kilogauss)
Sn doped Bi$_{88}$Sb$_{12}$
I // 3, H // l
Fig. 4.2-k  Hall coefficient versus H (Kilogauss)
Sn doped Bi$_{38}$Sb$_{12}$
I // 1, H // 2
Fig. 4.2-1  Hall coefficient versus H (Kilogauss)
I // 1, H // 2
Te doped Bi$_{88}$Sb$_{12}$

Fig. 4.2-m  Hall coefficient versus H (Kilogauss)
Te doped Bi$_{88}$Sb$_{12}$
I // 3, H // 1
Fig. 4.2-n Electron Concentrations versus $10^3 / T (°K)^{-1}$

- Sn doped Bi$_{88}$Sb$_{12}$
- Sn doped Bi$_{95}$Sb$_5$
- Te doped Bi$_{88}$Sb$_{12}$
The variation of the Hall coefficient $R_{21}$ with magnetic field for Sn-doped $\text{Bi}_{92}\text{Sb}_5$ alloy at $80^\circ\text{K}$ is shown in Fig. 4.2-i. $R_{21}$ is small and positive for bismuth, since $J_1$ is slightly larger than $\mu_i \mu_1$. In fact, the experimental results show that this is indeed so for both Sn-doped and Te-doped Bi-Sb alloys. This can be explained as follows: For Sn-doped Bi-Sb alloys, $R_{21}$ is given by equation (2-20)

$$R_{21} = \frac{1}{Ne} \cdot \frac{-\mu_i \mu_1 + \frac{P}{N} J_1}{(\mu_1 + \frac{P}{N} J_1)^2}$$

(2-20)

The magnitude of $R_{21}$ depends on the difference between $J_1$ and $\mu_i \mu_1$. $R_{21}$ is positive and small at $80^\circ\text{K}$ because $J_1$ is slightly greater than $\mu_1 \mu_1$ and $P > N$. However, it is found that $R_{21}$ is nearly equal to zero at $300^\circ\text{K}$ because $N$ is greater than $P$ near room temperature.

For Te-doped Bi-Sb alloys, $R_{21}$ is given by equation (2-21):

$$R_{21} = -\frac{4}{Ne} \cdot \frac{\mu_i \mu_1}{(\mu_1 + \mu_2)^2}$$

(2-21)

Since $\mu_2 << \mu_1$, equation (2-21) can be reduced to

$$R_{21} \approx -\frac{4}{Ne} \frac{\mu_i}{\mu_1}$$

(2-21-a)

Equation (2-21-a) indicates that $R_{21}$ not only depends on $1/Ne$, but also depends on the mobility ratio $\mu_1/\mu_1$. The present results indicate that $R_{21}$ approaches zero for Te-doped Bi-Sb alloys between 80 and $300^\circ\text{K}$.

IV.3 Electron Mobilities: $\mu_1$ and $\mu_3$

It was shown in section (II.2) that the product $R_{31} S_{11}$ for Te-doped Bi-Sb alloys is approximately equal to $\mu_1$. 
And the product $R_{23} \sigma_{33}$ is approximately equal to $\mu_3$

$$R_{23} \sigma_{33} \approx \mu_3 \quad (2-17)$$

Fig. 4.3-b shows the variation of the electron mobilities with temperature between 80 and 300$^\circ$K. The results indicate that the electron mobility decreases with increasing percentage of Sb atoms. Jain (4) concluded from his resistivity data that the mobilities should be lower for the alloys than the pure bismuth. The present work confirms his results for the undoped Bi-Sb alloys. The temperature dependence of the mobility can be expressed by $\mu = C T^{-y}$. It is found that for pure bismuth $y = 2.4$, for Te-doped Bi$_{95}$Sb$_5$ $y = 2.2$, and $y = 1.53$ for Te-doped Bi$_{88}$Sb$_{12}$. The results are also in agreement with Jain's observations on bismuth and undoped Bi-Sb alloys; he obtained smaller values for $y$ for the alloys than for the bismuth in the mobility law $\mu = C T^{-y}$.

Variation of the Hall mobilities $R_{31} \leq_{11}$ and $R_{32} \leq_{33}$ for Sn-doped Bi-Sb alloys with temperature is shown in Fig.4.3-a. These Hall mobilities should be very close to the electron mobilities as shown in section (II.2). The experimental results are compared with pure bismuth. It is interesting to note that the mobilities of both Sn-doped Bi-Sb alloys vary with $T^{-2.5}$, while for pure bismuth the mobility varies with $T^{-2.4}$. It is also found that these mobilities decrease with increasing percentage of Sb in the alloys.
Fig. 4.3-a Hall mobility versus T (°K)
Fig. 4.3-b Electron Mobility versus T (°K)
The temperature dependence of electron mobilities for Te-doped Bi-Sb alloys varies from $T^{-1.5}$ to $T^{-2.2}$. This indicates that acoustic lattice scattering is predominant for these alloys in the temperature range 80°K to 300°K. Impurity scattering and alloy scattering might be more important for temperatures below 80°K.

IV.4 Nernst Coefficient

It was pointed out, in section (II.5), that the Nernst coefficient for Te-doped Bi-Sb alloys depends on the type of scattering and the mobility of electrons. The experimental results can be explained in terms of equation (2-31):

\[ Q_{ij} = (\frac{K}{e}) \cdot r \cdot \lambda \cdot \mu_j \]  

(2-31)

Fig. 4.4-a shows the variation of Nernst coefficients $Q_{31}$ and $Q_{23}$ with temperature between 80°K and 300°K, for Te-doped Bi$_{88}$Sb$_{12}$ alloy. The results show that both $Q_{31}$ and $Q_{23}$ are negative in the temperature range 80°K to 300°K. This indicates that the acoustic lattice scattering is predominant between 80°K and 300°K. This observation is in excellent agreement with the results of mobility data shown in section (IV.3) for Te-doped Bi-Sb alloys.

It is possible to calculate the Nernst coefficient for single-type carriers from equation (2-31) as long as one knows the mobility data of the carriers, the scattering parameter, and the degree of degeneracy. In order to fit the experimental results for Te-doped
Fig. 4.4-a  Nernst coefficient versus temperature (°K)
Te doped Bi$_{88}$Sb$_{12}$  (H = 500 gauss)

Fig. 4.4-b  Nernst coefficient versus temperature (°K)
Te doped Bi$_{95}$Sb$_{5}$  (H = 500 gauss)
\[ \nabla T \parallel 1, H \parallel 2 \]
Bi$_{89}$Sb$_{12}$ alloy, it is reasonable to assume the acoustic lattice scattering ($\lambda = \frac{1}{2}$) for this alloy and to use the mobility data shown in Fig.4.3-b. It is found that for $r = 0.7$, the calculated value fits the experimental result quite well. From this result, it is concluded that the Te-doped Bi$_{88}$Sb$_{12}$ alloy is partially degenerate. Similar calculation for the Te-doped Bi$_{95}$Sb$_5$ alloy is shown in Fig.4.4-b, which is also compared with the experimental data for this alloy. It is found that the Nernst coefficient for Te-doped Bi-Sb alloys decreases with increasing temperature just as the mobility does. The Nernst coefficient for Te-doped Bi$_{95}$Sb$_5$ is larger than that of the Te-doped Bi$_{88}$Sb$_{12}$ alloy. This result can be attributed to the higher electron mobilities in the former.

Fig.4.4-d to Fig.4.4-f show the variation of the Nernst coefficient with magnetic fields, for the Te-doped Bi-Sb alloys. The results show that the Nernst field increases with magnetic field and reaches maximum at a certain field strength and approaches zero at the high fields limit. The vanishing of the Nernst coefficient at the high fields is due to the fact that the relaxation time of charge carriers becomes energy independent at high fields (i.e. $\tau = \tau_0$ and $\lambda = 0$). Thus, $Q_{ij}$ in (2-31) is zero when $\lambda = 0$. It is also seen from Fig.4.4-c that the Nernst coefficient is small near room temperature because these alloys become highly degenerate near room temperature.

The quantitative behavior of the Nernst coefficient for Sn-doped Bi-Sb alloys is even more involved. As mentioned in section (II.5),
the magnitude of the Nernst coefficient for Sn-doped Bi-Sb alloys is the sum of two terms (see equation (2-36)): one is the single carrier term, and the other is the bipolar term. The experimental results can only be explained qualitatively.

The variation of the Nernst field with temperature for Sn-doped Bi$_{95}$Sb$_5$ alloy between 80 and 300°K is shown in Fig. 4.4-g. At 80°K, the Nernst coefficient is positive. This means that the bipolar term is more dominant than the single carrier term (since the former is positive and the later is negative). For temperature higher than 260°K, the Nernst coefficient becomes negative, which indicates that the bipolar term is smaller than the single carrier term. This effect can be explained by examining equation (2-36). Since $N > P$ for Sn-doped Bi-Sb alloys near room temperature, it turns out that the bipolar term becomes very small near room temperature and is comparable with the single carrier term. At high magnetic fields, the bipolar term is important (it does not decrease with magnetic field) and the single carrier term tends to vanish. Thus, the Nernst coefficient is positive and large in magnitude at high magnetic fields. Fig. 4.4-h and Fig. 4.4-i show the temperature dependence of the Nernst coefficient for the Sn-doped Bi$_{88}$Sb$_{12}$ alloy between 80 and 300°K. These curves show similar characteristics when compared to the Sn-doped Bi$_{95}$Sb$_5$ alloy.

The variation of the Nernst coefficient with magnetic field for Sn-doped Bi-Sb alloys is shown in Fig. 4.4-j to Fig. 4.4-m.
Fig. 4.4-c  Nernst field versus temperature (°K)
Fig. 4.4-d  Nernst field versus H (Kilogauss)
Te doped Bi$_{95}$Sb$_5$
VT // 1, H // 2

Fig. 4.4-e  Nernst field versus H (Kilogauss)
VT // 3, H // 1
Te doped Bi$_{88}$Sb$_{12}$
Fig. 4.4-f  Nernst field versus H (Kilogauss)

Te doped Bi$_{88}$Sb$_{12}$

VT // l, H //2
Fig. 4.4-g  Nernst field versus temperature (°K)

Sn doped Bi$_{95}$Sb$_{5}$

νT // 1, H // 2
Fig. 4.4-h  Nernst field versus temperature (°K)
Sn doped Bi$_{88}$Sb$_{12}$
VT // 3, H // 1
Fig. 4.4-1 Nernst field versus temperature (°K)

Sn doped Bi$_{86}$Sb$_{12}$

VT // 1, H // 2
Fig. 4.4-j  Nernst field versus H (Kilogauss)

Sn doped Bi$_{95}$Sb$_5$

VT // 1, H // 2
Fig. 4.4-k  Nernst field versus H (Kilogauss)
**Fig. 4.4-1** Nernst field versus H (Kilogauss)

Sn doped B\textsubscript{18}Sb\textsubscript{12}

VT // 1, H // 2
Fig. 4.4-m  Nernst field versus $H$ (Kilogauss)
Sn doped Bi$_{88}$Sb$_{12}$
\( \nabla T // 3, H // 1 \)
It is seen that all the Nernst coefficients are negative at very low field, and change to positive value at high magnetic fields. From the experimental results, it is found that the Nernst coefficient is larger for pure bismuth and decreases in magnitude for Bi-Sb alloys with an increasing percentage of antimony in these alloys.

Some of the low-field Nernst coefficients for Bi-Sb alloys at 80°C are listed in Table III for comparison.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Nernst coefficient (cm²/sec.°K)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Bi₉₃.₇Sb₆.₃</td>
<td>Q₁ = 1.14, Q₂ = 1.17</td>
<td>Calculated by Goldsmid(13)</td>
</tr>
<tr>
<td>Sn-doped Bi₉₅Sb₅</td>
<td>Q₁ = 1.1, Q₂ = 0.25</td>
<td>Present result (experiment)</td>
</tr>
<tr>
<td>Sn-doped Bi₈₈Sb₁₂</td>
<td>Q₁ = -0.92, Q₂ = -1.12</td>
<td>&quot;</td>
</tr>
<tr>
<td>Te-doped Bi₉₅Sb₅</td>
<td>Q₁ = -2.4</td>
<td>&quot;</td>
</tr>
<tr>
<td>Te-doped Bi₈₈Sb₁₂</td>
<td>Q₁ = -0.2, Q₂ = -0.3</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

IV.5 Seebeck Coefficient:

The variation of the Seebeck coefficient measured parallel to the binary axis for the Sn-doped and Te-doped Bi-Sb alloys is shown in Fig. 4.5-a. In Sn-doped Bi-Sb alloys, the Seebeck coefficient is negative and decreases with increasing temperature. This result can be explained qualitatively in terms of equation (2-26);
\[
\alpha_i = \frac{-\alpha_e + \left(\frac{\sigma_i}{\sigma_e}\right) \alpha_h}{1 + \frac{\delta_i}{\sigma_e}} ,
\]

(2-26)

where \(\alpha_e\) and \(\alpha_h\) are the partial Seebeck coefficients of the electrons and holes which are isotropic in most cases, and \(\sigma_{e_1}\) and \(\sigma_{h_1}\) are the partial conductivities which are anisotropic for bismuth.

In bismuth, the partial Seebeck coefficients, \(\alpha_e\) and \(\alpha_h\), are comparable in magnitude, and the conductivity ratio \(\sigma_{e_1}/\sigma_{h_1}\) is larger than unity. It must also be the case in these Sn-doped Bi-Sb alloys. Therefore, the total Seebeck coefficient is negative and almost as large in magnitude as \(\alpha_e\). The conductivity ratio \(\sigma_e/\sigma_h\) is larger at low temperatures than near room temperature. This is why \(\alpha_i\) decreases with temperature for Sn-doped Bi-Sb alloys. In the Sn-doped Bi-Sb alloys, the Seebeck coefficients measured parallel to the trigonal axis and parallel to the binary axis are almost the same between 80 and 300\(^\circ\)K within experimental error.

Fig. 4.5-a shows the variation of the Seebeck coefficient with temperature for Te-doped Bi-Sb alloys. Since these alloys are N-type materials, they can be interpreted in terms of equation (2-24). The results are compared to the results obtained by Brown and Silverman (8) for Te-doped Bi\(^{85}\)Sb\(^{15}\) alloy. As shown in table IV, the Seebeck coefficients at 80 and 300\(^\circ\)K for bismuth and Bi-Sb alloys are compared with the present work for the Sn-doped and Te-doped Bi-Sb alloys.
Table IV Seebeck Coefficient (μV/°C)

<table>
<thead>
<tr>
<th>Materials</th>
<th>80°K</th>
<th>300°K</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth (1)</td>
<td>$\alpha_1 = -43$, $\alpha_\parallel = -92$</td>
<td>$\alpha_1 = -51$, $\alpha_\parallel = -102$</td>
<td>Gallo et al.</td>
</tr>
<tr>
<td>Bi-Sb(12%) (31)</td>
<td>$\alpha_1 = -125$, $\alpha_\parallel = -160$</td>
<td>$\alpha_1 = -85$, $\alpha_\parallel = -110$</td>
<td>Smith et al.</td>
</tr>
<tr>
<td>Bi-Sb(5%) (31)</td>
<td>$\alpha_\parallel = -101$</td>
<td>$\alpha_\parallel = -102$</td>
<td></td>
</tr>
<tr>
<td>Sn-doped Bi$_{95}$Sb$_5$</td>
<td>$\alpha_1 = -130$</td>
<td>$\alpha_1 = -94$</td>
<td>$\pm 10 \mu V$ (present results)</td>
</tr>
<tr>
<td>Sn-doped Bi$<em>{88}$Sb$</em>{12}$</td>
<td>$\alpha_1 \approx \alpha_\parallel = -115$</td>
<td>$\alpha_1 \approx \alpha_\parallel = -83$</td>
<td></td>
</tr>
<tr>
<td>Te-doped Bi$_{95}$Sb$_5$</td>
<td>$\alpha_\parallel \approx \alpha_1 = -47$</td>
<td>$\alpha_1 = -54$</td>
<td></td>
</tr>
<tr>
<td>Te-doped Bi$<em>{88}$Sb$</em>{12}$</td>
<td>$\alpha_\parallel \approx \alpha_1 = -64$</td>
<td>$\alpha_1 = -72$</td>
<td></td>
</tr>
</tbody>
</table>

Remark: // denotes $\nabla_T$ // trigonal, \perp denotes $\nabla_T \perp$ trigonal.

IV.6 Electron Fermi Energy and Effective Mass in Te-doped Bi-Sb Alloys

The electron Fermi energy for Te-doped Bi-Sb alloys can be found in the following way. Assuming the conduction bands are parabolic with ellipsoidal energy surfaces, and that the energy dependence of the relaxation time is $E^\lambda$, then (2-24) can be rewritten as follows:

$$
\alpha_e = -\left[ \frac{(5/2+\lambda) F_3/2+\lambda(\eta)}{(3/2+\lambda) F_{1+\lambda}(\eta)} - \eta \right] \tag{2-24}
$$

For intravalley acoustic lattice scattering which is assumed in this calculation, $\lambda$ is $-\frac{1}{2}$. Thus, (2-24) reduced to:

$$
\alpha_e = -\left[ \frac{5}{2} \frac{F_3(\eta)}{F_0(\eta)} - \eta \right] \tag{2-24.a}
$$
\( \alpha (\mu V/\circ C) \)

\( \nabla T // \text{binary} \)

- Sn doped Bi\textsubscript{95}Sb\textsubscript{5}
- Sn doped Bi\textsubscript{88}Sb\textsubscript{12}

- Te doped Bi\textsubscript{95}Sb\textsubscript{5}
- Te doped Bi\textsubscript{88}Sb\textsubscript{12}
- Te doped Bi\textsubscript{89}Sb\textsubscript{15} (Brown & Silverman)

Fig. 4-5-a  Seebeck coefficient versus T (\( ^\circ K \))
Fig 4.5-b  Seebeck coefficient versus reduced Fermi energy
Fig. 4.5-c  Electron Fermi energy versus temperature (°K)
Fig. 4.5-b shows the variation of the Seebeck coefficient with reduced Fermi energy \( \eta \) calculated from equation (2-24-a). Using (2-24-a) and the Seebeck coefficient shown in Fig. 4.5-a, the variation of Fermi energy with temperatures is shown in Fig. 4.5-c, for Te-doped Bi-Sb alloys. These results are compared with the result for bismuth obtained by Gallo et al. (1).

The total number of electrons per unit volume \( N \) can be obtained from the Hall coefficient data for Te-doped Bi-Sb alloys (as shown in Fig. 4.2-e and Fig. 4.2-f). With the assumption that the conduction bands are parabolic, the total number of electrons per unit volume is given by (17) as follows:

\[
N = B (4\pi/\hbar^3)(2m^*kT)^{3/2}P_2(\eta)
\]

(4-1)

where \( m^* = (m_1m_2m_3)^{1/3} \) is the density of states effective mass per ellipsoid for the electrons; \( B \) is the number of ellipsoids.

The density of states effective mass per ellipsoid that is determined by the present work depends on whether a 3 or 6 ellipsoids model is assumed. It can be seen from Table V that the effective mass of electrons for Te-doped Bi-Sb alloys is slightly different from that of bismuth measured by other methods. (see Table I)

From the present results (Table V), it appears that the electron density of states effective mass depends slightly on temperatures between 80 and 300°K. Because of the divergence of the other results for bismuth, it is impossible to choose between 3 or 6 ellipsoids from the present results.
Table V  Electron Density of States Effective Mass
in unit of $m_0$

<table>
<thead>
<tr>
<th>Materials</th>
<th>80°K</th>
<th>300°K</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 ellipsoids</td>
<td>6 ellipsoids</td>
</tr>
<tr>
<td>Bismuth (1)</td>
<td>0.054</td>
<td>0.034</td>
</tr>
<tr>
<td>Te-doped Bi$_{95}$Sb$_5$</td>
<td>0.06</td>
<td>0.038</td>
</tr>
<tr>
<td>Te-doped Bi$<em>{88}$Sb$</em>{12}$</td>
<td>0.162</td>
<td>0.103</td>
</tr>
</tbody>
</table>

IV.7  Magneto-Seebeck Coefficient

It was pointed out in section (II.4) that the Seebeck coefficient for an extrinsic material increases with magnetic field and saturates at the high-field limit. Fig.4.7-a and Fig.4.7-b show the variation of the Seebeck coefficient with magnetic field for Te-doped Bi-Sb alloy. The results indicate that the Seebeck coefficient increases with magnetic field for temperatures between 80 and 300°K. This shows that these alloys are N-type extrinsic materials. The Seebeck coefficient at high fields can be expressed by equation (2-24), with $\lambda = 0$, ($\gamma = \gamma_e$) (14)

$$\alpha_e = - (\frac{e}{2}) \left[ \frac{5}{3} \frac{F_{\mu}(\eta)}{F_{\gamma}(\eta)} - \eta \right]$$  \hspace{1cm} (2-24-a)

The computed Seebeck coefficient for Te-doped Bi$_{88}$Sb$_{12}$ alloy using
expression (2-24-a) is plotted against temperature as shown in
Fig.4.7-c. The computed curve is compared with the experimental
curve at 10 kilogauss and indicates good agreement. (Fig.4.7-c)

The Magneto-Seebeck effect for Sn-doped Bi-Sb alloys is much
more complicated as indicated in section (II.4). Fig.4.7-d and
Fig.4.7-e show the variation of the Seebeck coefficient with magnetic
field between 80 and 300°C, for Sn-doped Bi-Sb alloys. At low
temperatures, the Seebeck coefficient increases with magnetic field
and saturates at a certain field strength. As the magnetic field is
further increased, the Seebeck coefficient decreases and changes
from negative to positive value at a high-field limit. This phenomenon
can be explained qualitatively in terms of equation (2-26-a).

\[ \alpha(H) = \frac{-\alpha_e + b(H)\alpha_h}{(1 + b(H))} \]  \hspace{1cm} (2-26-a)

where \( b(H) = \sigma_h/\sigma_e \) is the hole and electron conductivity ratio
and is function of the magnetic field.

As mentioned previously, \( \alpha_e \) and \( \alpha_h \) are comparable in magnitude,
and \( b(H) \) is in general smaller than unity at low magnetic fields.
Hence \( \alpha(H) \) is always negative for Sn-doped Bi-Sb alloys at low fields.
The partial Seebeck coefficients \( \alpha_e \) and \( \alpha_h \) increase with magnetic
field and saturate at the high-field limit. Therefore, \( \alpha(H) \) will also
increase with magnetic field and saturates at a certain field strength.
However, as the magnetic field is increased, the electron conductivity,
**Fig. 4.7-a**  Seebeck coefficient versus $H$ (Kilogauss)
Te doped Bi$_{95}$Sb$_{5}$
VT // 1, H // 2

**Fig. 4.7-b**  Seebeck coefficient versus $H$ (Kilogauss)
Te doped Bi$_{85}$Sb$_{12}$
VT // 1, H // 2
Fig. 4.7-c Magneto-Seebeck coefficient versus $T^{(\circ K)}$

( $H = 10$ kilogauss)
Fig. 4.7-d  Seebeck coefficient versus H (Kilo gauss)
Sn doped Bi$_{88}$Sb$_{12}$
$\gamma T // 1, H // 2$
Fig. 4.7-e  Seebeck coefficient versus H (Kilogauss)
Sn doped Bi$_{95}$Sb$_5$
$\nu T$ // 1, $H$ // 2
$\sigma_e$, falls much faster than that of the hole conductivity, $\sigma_h$, because the electron mobility is higher than the hole mobility. It turns out that $b(H)$ increases with the magnetic field and becomes greater than unity at high magnetic fields. Thus, the Seebeck coefficient changes sign at the high-field limit. (Fig.4.7-e)

The above results on the Magneto-Seebeck effect for Sn-doped Bi-Sb alloys indicate that the phenomenon is similar to that in bismuth and Bi-Sb alloys.

IV.8 Band Models for Sn-doped and Te-doped Bi-Sb alloys

The presence of the heavy-hole band in bismuth has been suggested by a number of authors. (e.g. Jain (4)) Recent work by Jain et al. (28) at 20.4 °K suggests that the heavy holes do not have any influence at this or lower temperatures; but Gallo et al. (1) state that a heavy -hole band become important on going from 300 K to 300 K. The present work on Sn-doped and Te-doped Bi-Sb alloys are in agreement with this viewpoint.

Fig.4.8-a shows the band models proposed by Jain (4) for pure bismuth and Bi-Sb alloys. It is interesting to note that the optical band gap ($E_o$) between light-electron and light-hole bands is fixed, while the light-electron band overlaps with the heavy-hole band for bismuth and splits apart with an increased doping of antimony.
pure bismuth       Bi-Sb alloy (5%)       Bi-Sb alloy (12%)

Fig. 4.8-a Band models for bismuth and Bi-Sb alloys

$C_L$ and $V_L$ denote light-electron band and light-hole band, respectively, and $V_H$ denotes heavy-hole band.

Hall coefficient measurements on Sn-doped Bi-Sb alloys indicate that antimony atoms (10$^{18}$/cc) introduce a small amount of acceptor levels (or free holes) at 80$^\circ$K and have no obvious effects at higher temperatures. From the results of the present work, it is found that most of the transport properties for Sn-doped Bi-Sb alloys are analogous to that of undoped Bi-Sb alloys. However, resistivity measurements on Sn-doped Bi-Sb alloys indicate that the band gap between light-electron and light-hole bands for Sn-doped Bi-Sb alloys is larger than that of undoped Bi-Sb alloys (see Fig. 4.1-a and Fig. 4.1-b). The proposed band-model for Sn-doped Bi-Sb alloys is shown in Fig. 4.8-b.

Sn-doped Bi$_{95}$Sb$_5$       Sn-doped Bi$_{88}$Sb$_{12}$

Fig. 4.8-b Band models for Sn-doped Bi-Sb alloys
Resistivity measurements on the Te-doped Bi-Sb alloys indicate that these alloys are semimetal between 80 and 300°K, while the Seebeck coefficient measurements on these alloys show that the bands are overlapping. It is, therefore, reasonable to assume that the band model of these alloys are similar to that of bismuth proposed by Jain (4) except more overlapping between light-electron and heavy-hole bands. Fig. 4.3-c shows the proposed band models for the Te-doped Bi-Sb alloys.

\[ \text{Te-doped Bi}_{0.95}\text{Sb}_{0.05} \]

\[ \text{Te-doped Bi}_{0.88}\text{Sb}_{0.12} \]

**Fig. 4.3-c** Bands model for the Te-doped Bi-Sb alloys

The postulation of the existence of the heavy-hole band for these doped alloys are based on the fact that the electron concentrations for both Te-doped and Sn-doped Bi-Sb alloys are much higher than that of holes and the transport properties of Sn-doped Bi-Sb alloys are governed by the electrons near room temperatures. This is because at high temperatures some of the electrons jump from the heavy-hole band to the light-electron band through thermal excitation and leave some of the heavy holes in the heavy-hole band. These heavy holes are so heavy and sluggish that they do not contribute to the transport process. Goldsmid (13) has explained the negative value of the Nernst coefficient for Bi-Sb alloy near room temperature as a result of the heavy-hole band. The present results on Sn-doped Bi-Sb alloys are in agreement with his viewpoint.
CHAPTER V

THERMOELECTRIC AND THERMOMAGNETIC

ENERGY CONVERSION

V.1 Thermoelectric Refrigeration

The maximum temperature difference $\Delta T_{\text{max}}$ which can be achieved with a simple thermoelectric couple is approximately (18,19)

$$\Delta T_{\text{max}} = \frac{1}{2} Z T_c^2$$  \hspace{1cm} (5-1)

where $T_c$ is the absolute temperature of the cold junction. The figure of merit of the couple, $Z$, is defined as:

$$Z = \frac{(\alpha_P - \alpha_N)^2}{\left((\kappa_P \rho_P)^{1/2} + (\kappa_N \rho_N)^{1/2}\right)^2}$$  \hspace{1cm} (5-2)

where $N$ and $P$ refer to the two arms of the thermocouple as shown in Fig. 5.1-a. The $Z$ for a couple is, in general, intermediate between the figure of merit of the $P$ and $N$ materials themselves.

The best materials which have been available for thermoelectric refrigeration are alloys of Bismuth telluride (with Bismuth selenide and antimony telluride), with properties similar to the curves shown in Fig. 5.1-b. The maximum temperature difference which can be achieved with these materials is shown in Fig. 5.1-c. It drops very fast as the heat sink temperature is lowered. It has been shown by Smith et al. (h) that a properly oriented (//3) specimen of $\text{Bi}_{95-\text{Sb}}_{5}$
has a higher N-type Figure of merit than any known Bi$_2$Te$_3$ alloy below 220°K. It could therefore be combined with a p-type Bi$_2$Te$_3$ alloy to provide a higher Z below this temperature.

Fig. 5.1-a Single-stage Thermoelectric refrigerator

![Diagram of single-stage thermoelectric refrigerator]

Fig. 5.1-b Figure of merit versus T(°K)
Fig. 5.1-c Maximum temperature difference
versus heat sink temperature (°K)

- N-branch: Bi$_{95}$Sb$_5$, P-branch: Bi$_2$Te$_3$
- N- and P-branch: Bi$_2$Te$_3$

In the design of an optimum cooling couple, the dimensions of the two arms should be matched as follows: (18, 19)

\[ \frac{A_P L_N}{A_N L_P} = \left( \frac{k_P}{k_N} \frac{\rho_N}{\rho_P} \right)^{\frac{1}{2}} \]  \hspace{1cm} (5-3)

Where A and L are the area and length of the individual arms, and k and \( \rho \) are the thermal conductivity and resistivity, respectively.

Smith et al. (31) pointed out that if one took equal arm lengths of N-type Bi$_{95}$Sb$_5$ and P-type Bi$_2$Te$_3$, both materials radically differing in temperature dependence, one would find \( \frac{A_P}{A_N} = 3.2 \) at 200°K and \( \frac{A_P}{A_N} = 1.9 \) at 100°K. The volume and mass of the semimetal required in such a couple is therefore smaller than that of the semiconductor if both arms are of equal length. It may also be
possible to use shorter semimetallic arms, with a further reduction in size and weight, since the contact resistance achieved with direct soldering appears to be negligibly small.

The full advantage of the high Z and small dimensions of the semimetallic thermoelements would be realized if a comparable P-type material were available. However, even in combination with available semiconductors, the Bi-Sb alloys should find immediate application in low temperatures or multistage thermoelectric refrigerators.(20)

V.2 Thermomagnetic Refrigeration

Following the significant advances in thermoelectric refrigeration and generation during recent years, attention has also been directed to thermomagnetic cooling at low temperatures. Fig.5.2-a shows a thermomagnetic cooling device. The Ettingshausen figure of merit $Z_E$ is defined by:

$$
Z_E = \frac{(QH)^2 \sigma}{k_L}
$$

(5-4)

where $Q$ is the Nernst coefficient

$H$ is the magnetic field intensity

$\sigma$ is the electrical conductivity

$k_L$ is the lattice thermal conductivity

Delves (21) has shown that the Ettingshausen figure of merit $Z_E$ (which has much the same significance for thermomagnetic devices as has the more familiar figure of merit $Z$ for thermoelectric devices)
can be quite large for an intrinsic semiconductor or semimetal. He concluded that the material should have an energy gap less than kT, a low lattice thermal conductivity $k_L$, and high mobilities for both electrons and holes. If, as usual, the electron mobility is higher than the hole mobility, the value of $Z_E$ is controlled primarily by the latter; finding a material with sufficiently large hole mobility seems to present the greatest problem.

Among the elements and compounds whose relevant properties are known at the present time, the one which comes nearest to satisfying all the requirements is the semimetal bismuth. Some improvement might be expected for alloys of bismuth with antimony in which $k_L$ should be lower than bismuth. In fact, promising results for Bi–Sb alloys have been reported by Weaver et al. (22)

The Ettingshausen figure of merit for bismuth and Bi–Sb alloys obtained by other authors are compared with the present result for Sn-doped Bi$_{95}$Sb$_5$ as shown in Table VI.

### Table VI Ettingshausen Figure of Merit

<table>
<thead>
<tr>
<th>Materials</th>
<th>80°C</th>
<th>300°C</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth</td>
<td>$2.1 \times 10^{-3} / ^\circ K$</td>
<td>$2.9 \times 10^{-3} / ^\circ K$</td>
<td>calculated by Goldsmid (13)</td>
</tr>
<tr>
<td>Bi$_{95}$Sb$_5$</td>
<td>$5 \times 10^{-3} / ^\circ K$</td>
<td></td>
<td>experiment, by Smith et al. (22)</td>
</tr>
<tr>
<td>Sn-doped Bi$_{95}$Sb$_5$</td>
<td>$2.6 \times 10^{-3} / ^\circ K$</td>
<td></td>
<td>present result*</td>
</tr>
</tbody>
</table>

* Calculated value, with $H = 10$ kilogauss and $k/\sigma = 2.5 \times 10^{-6} \ V^2/ ^\circ K$
The most thorough investigation of the Bi-Sb alloys as thermomagnetic materials has been undertaken by Kooi and his colleagues. (23) They attained a maximum temperature difference of $T_{\text{max}} = 54^\circ\text{K}$, using an exponentially shaped Bi$_{97}$-Sb$_3$ specimen with $T_\alpha = 156^\circ\text{K}$ for $H_Z = 15\text{KG}$ and for a shape ratio of the width at the hot and cold faces was 13:1

![Diagram of thermomagnetic refrigerator](image)

Fig. 5.2-a Thermomagnetic Refrigerator (Infinite stages)

V.3 Comparisons between Thermoelectric and Thermomagnetic Refrigerators

The Nernst Ettingshausen figure of merit is given by (5-4). It is important to realize that the bipolar Nernst coefficient remains almost constant however high the magnetic field, while the single carrier term in Nernst coefficient tends to zero in high magnetic field (see Equation (2-35)). Thus, in an intrinsic conductor or semimetal with equal mobilities for the two types of carrier(14),

$$Z_E = \frac{(GH)^2\sigma(H)}{kT(H)} \approx \frac{\sigma(0)(\alpha_H - \alpha_c)^2}{4k_L}$$

(5-4-a)
Equation (5-4-a) allows a direct comparison to be made between the thermomagnetic refrigerator and the hypothetical thermoelectric refrigerator in which only one type of carriers contribute to the transport processes.

The thermomagnetic refrigerator has the following advantages:

1. Only one type of material is required. (an exponential shape of specimen as shown in Fig.5.2-a represents infinite stages)

2. $S(0)$ is the sum of the conductivity in the two bands (valence band and conduction band) and should therefore be greater than the conductivity in the thermoelectric devices.

3. The thermal conductivity contains only the lattice component, whereas in the thermoelectric refrigerator there is an electronic component too.

4. If $\lambda$ is negative, the partial Seebeck coefficients $\alpha_\omega$ and $\alpha_\lambda$ are increased while applying a magnetic field. Thus, $(\alpha_\omega - \alpha_\lambda)^2/4$ should be greater than the Seebeck coefficient for the thermoelectric refrigerator.

However, there are some disadvantages for the thermomagnetic refrigerator. These include:

1. A rather high magnetic field is required in order to obtain a higher figure of merit.

2. The mobility of the charge carriers decreases with temperature, and it is for this reason that the thermomagnetic refrigerator will probably find its applications only at rather low temperature.
V.4 Application of Sn-doped Bi$_{95}$Sb$_5$ alloy to Thermoelectric and Thermomagnetic Refrigeration:

It has been shown in section (IV.3) that the band gap for Sn-doped Bi-Sb alloys should be larger than the undoped Bi-Sb alloys. This can also be seen from the large Seebeck coefficient for the Sn-doped Bi$_{95}$Sb$_5$ as shown in Fig.4.5-a. The large Seebeck coefficient for Sn-doped Bi$_{95}$Sb$_5$ implies that this alloy might have a higher figure of merit than the undoped Bi-Sb alloys provided that the ratio $\kappa/k$ remains unchanged as for the undoped Bi$_{95}$Sb$_5$ alloy.

The values of $k/\sigma$ (Wiedermann-Franz ratio) for the undoped Bi$_{95}$Sb$_5$ obtained by Smith et al. (31) are given below:

\[
\begin{align*}
    k/\sigma &= 2.5 \times 10^{-6} / \Omega \cdot K & \text{at } 80^0K \\
    k/\sigma &= 6.4 \times 10^{-6} / \Omega \cdot K & \text{at } 300^0K
\end{align*}
\]

If the values of $k/\sigma$ for Sn-doped Bi$_{95}$Sb$_5$ remain unchanged as for the undoped Bi$_{95}$Sb$_5$, then, from the measured Seebeck coefficient and the values of $k/\sigma$ listed above, the figure of merit for Sn-doped Bi$_{95}$Sb$_5$ can be obtained from equation (5-5):

\[
    Z = \sigma^2 \kappa / \kappa (5-5)
\]

The computed figure of merit for Sn-doped Bi$_{95}$Sb$_5$ is listed in Table VII for comparison.

<table>
<thead>
<tr>
<th>Materials</th>
<th>80$^0$K</th>
<th>300$^0$K</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped Bi$_{95}$Sb$_5$</td>
<td>$4.5 \times 10^{-3} / \Omega \cdot K$</td>
<td>$1.8 \times 10^{-3} / \Omega \cdot K$</td>
<td>experiment, by Smith et al. (31)</td>
</tr>
<tr>
<td>Sn-doped Bi$_{95}$Sb$_5$</td>
<td>$6.76 \times 10^{-3}$</td>
<td>$1.26 \times 10^{-3}$</td>
<td>present result</td>
</tr>
</tbody>
</table>
CONCLUSIONS

Several conclusions can be drawn from the study of the transport properties of the Sn-doped and Te-doped Bi-Sb alloys between 80 and 300°K:

(1) Resistivity measurements on the Te-doped Bi-Sb alloys indicate that these alloys behave as semimetal between 80 and 300°K; the Sn-doped Bi-Sb alloys behave as semiconductors for temperatures below 135°K in the 80 to 300°K temperature range. These alloys are highly anisotropic; the resistivity ratio for Sn-doped Bi_{88}Sb_{12} is \( \rho_{33}/\rho_{11} \approx 2.5 \), and equal to 1.7 for Te-doped Bi_{88}Sb_{12} alloy.

(2) Hall effect measurements on the Te-doped Bi-Sb alloys indicate that these alloys are N-type extrinsic materials. The present results at 80°K indicate that each tellurium atom adds one free electron to these alloys, while the results obtained by Brown & Silverman (8) at 20.4°K indicate that two Te atoms add one free electron to the Bi_{85}Sb_{15} alloy. Hall effect measurements on the Sn-doped Bi-Sb alloys indicate that these alloys are N-type materials. It seems that the tin atoms do introduce a certain amount of free holes at 80°K. No obvious effects are observed at 300°K, since electron concentrations are higher than that of holes at 300°K.

(3) From resistivity and Hall effect measurements, electron mobilities are obtained between 80 and 300°K, for Te-doped and Sn-doped
Bi-Sb alloys. The present results are compared with the previous results for bismuth. (4) It is concluded that the electron mobility for these doped Bi-Sb alloys decreases with increasing percentage of antimony in these alloys; this effect is more obvious at 80 than at 300°K. The electron mobility $\mu$ is proportional to $T^{-1.5}$ for Te-doped Bi-Sb alloys near room temperature, and is proportional to $T^{-2.5}$ for Sn-doped Bi-Sb alloys between 80 and 300°K. The results indicate that acoustic lattice scattering is predominant between 80 and 300°K.

(4) The Nernst coefficient for Te-doped Bi-Sb alloys is negative and small between 80 and 300°K. From the results, it is concluded that these alloys are partially degenerate and the acoustic lattice scattering is dominant between 80 and 300°K which is consistent with conclusion (3). The Nernst coefficient for Sn-doped Bi-Sb alloys shows anomalous behavior between 80 and 300°K; it is large and positive at 80°K, and is negative and small at 300°K. Goldsmid (5) has explained the negative sign in the Nernst coefficient for $\text{Bi}_{93.7}\text{Sb}_{6.3}$ alloy at 300°K by postulating a heavy-hole band. The present conclusion is in agreement with his viewpoint.

(5) The Seebeck coefficient measurements on the Te-doped Bi-Sb alloys indicate that the electron Fermi energy increases with increasing temperature between 80 and 300°K. The results also indicate that bands are overlapping (since Fermi energy is positive). The Fermi
energy increases rapidly near room temperatures. Gallo et al. (1) have explained this anomalous behavior by postulating a heavy-hole band. The present conclusion also agree with this viewpoint.

(6) Band models similar to that of Jain's (4) are proposed for Te-doped and Sn-doped Bi-Sb alloys. Presumably, the Te-doped Bi-Sb alloy has the bismuth-like band model proposed by Jain (4) except more overlapping between light-electron and heavy-hole bands; the Sn-doped Bi-Sb alloy has the undoped Bi-Sb alloy-like band model proposed by Jain (4) except the larger band gap between light-electron and heavy-hole bands.

(7) A larger Seebeck coefficient is obtained for Sn-doped Bi$_{95}$Sb$_5$ alloy below 150 oK in the temperature range of 80 to 300 oK, when compared with the undoped Bi$_{95}$Sb$_5$ alloy. A higher figure of merit for this alloy at 80 oK is obtained as compared to the undoped Bi-Sb alloys. This is beneficial for thermoelectric refrigeration.
REFERENCES

(7) H. J. Goldsmid, Phil. Mag. 8, 1225 (1963).
(17) R. W. Ure, Jr., "Thermoelectricity—Science and Engineering",
( Interscience Publisher, Inc. N. Y. 1960 ).

(18) H. J. Goldsmid, "Application of Thermoelectric",
( John Wiley & Sons, Inc. N. Y. 1960 ).

(19) A. F. Ioffe, "Semiconductor Thermoelements and Thermoelectric

(20) Uenohara and R. Wolfe, IRE Trans. on Electron Devices E D-8,
521 (1961).


495 (1962).

(23) C. F. Kooi, R. B. Horst, K. F. Cuff and S. R. Hawkins,


(31) G. E. Smith R. Wolfe, J. Appl. Phys. 33, 841 (1962); R. Wolfe
and G. E. Smith, Appl. Phys. Letters 1,5 , (1962); R. Wolfe,

(32) A. C. Beer, "Galvanomagnetic Effects in Semiconductors ",