MIGRATION AND EFFECTS OF COPPER IN P-TYPE BISMUTH TELLURIDE

OSCAR P. MANLEY

TECHNICAL REPORT 376
SEPTEMBER 1, 1960

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
RESEARCH LABORATORY OF ELECTRONICS
CAMBRIDGE, MASSACHUSETTS
The Research Laboratory of Electronics is an interdepartmental laboratory of the Department of Electrical Engineering and the Department of Physics.

The research reported in this document was made possible in part by support extended the Massachusetts Institute of Technology, Research Laboratory of Electronics, jointly by the U.S. Army (Signal Corps), the U.S. Navy (Office of Naval Research), and the U.S. Air Force (Office of Scientific Research, Air Research and Development Command), under Signal Corps Contract DA36-039-sc-78108, Department of the Army Task 3-99-20-001 and Project 3-99-00-000, and was performed under Office of Naval Research Contract Nonr-1841 (51).
MIGRATION AND EFFECTS OF COPPER IN P-TYPE BISMUTH TELLURIDE

Oscar P. Manley

This report is based partly on a thesis submitted to the Department of Electrical Engineering, M.I.T., June 1960, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Abstract

The effects of copper on p-type Bi$_2$Te$_3$ were studied by examining the changes in resistivity and thermoelectric power induced in samples placed in intimate contact with copper. The experimental results were used to estimate the over-all change in the electrical transport parameters (for example, carrier mobilities, effective masses, etc.) between the limits of no copper present and full compensation. Because of analytical difficulties, it was not possible to determine such changes for intermediate degrees of doping. Furthermore, the data for the regions in which the host lattice was overcompensated indicated that a chemical change was taking place; therefore, any interpretation of the experimental results in terms of simple doping did not seem plausible. Our interpretation of these measurements allowed the activation energy for diffusion of Cu in the direction parallel to the cleavage planes to be measured; the results were found to be in agreement with those reported by others.
# TABLE OF CONTENTS

I. Introduction 1

II. Properties and Structure of Bismuth Telluride 2
   2.1 Interstitial Diffusion in $\text{Bi}_2\text{Te}_3$ 2
   2.2 Electrical Properties of p-type Bismuth Telluride 3
   2.3 Hall-Effect Measurements 3
   2.4 Resistivity Measurements 5
   2.5 Thermoelectric-Power Measurements 5
   2.6 Evaluation of the Sample Properties 5

III. Interaction of Copper with Bismuth Telluride near Room Temperature 8
   3.1 Sample Preparation 8
   3.2 Description of Resistivity and Thermoelectric-Power Measurements 9

IV. Effects of Copper on the Properties of $\text{Bi}_2\text{Te}_3$ 14
   4.1 Activation Energy for the Diffusion of Copper 15
   4.2 Estimation of the Effective Surface Concentration of Copper 18
   4.3 Some Electrical Properties of Highly Doped $\text{Bi}_2\text{Te}_3$ 22
   4.4 Chemical Changes in $\text{Bi}_2\text{Te}_3$ Induced by High Copper Concentration 31

V. Conclusion 34

References 35
I. INTRODUCTION

This report furnishes verification of the fact that copper propagates very rapidly in bismuth telluride at or near room temperature. This propagation has been observed by measuring changes of resistivity and thermoelectric power in rather long crystals of bismuth telluride (Bi$_2$Te$_3$), one end of which was exposed to copper for various lengths of time. The general effects of copper on bismuth telluride are, however, sufficiently complicated to warrant broader discussion.

Because it appeared that relatively simple diffusion took place over a part of the experimental regime, a study of the general theory of diffusion was undertaken. The results of that study are available in a separate technical report (1) and need not be repeated here.

Some of the background of this work, which includes brief considerations of the electrical conduction mechanism in bismuth telluride, as well as the results of preliminary experiments on the interaction of copper with bismuth telluride at higher temperatures, is available elsewhere (2, 3). These two earlier pieces of work set the stage for the present study of diffusion theory, and the rest of the work to be reported here.
II. PROPERTIES AND STRUCTURE OF BISMUTH TELLURIDE

Bismuth telluride ($\text{Bi}_2\text{Te}_3$) has a rhombohedral unit cell with $R3m$ symmetry (4, 5, 6). (See Fig. 1.) There is one molecule per unit cell. The crystallographic properties are:

- $a = 10.47 \text{ Å}$
- $a = 24^\circ 8'$
- 1 Te at 0,0,0
- 2 Bi at ± $u,u,u$
- 2 Te at ± $v,v,v$
- $u = 0.399$
- $v = 0.792$

This material has very marked cleavage planes at right angles to the c-axis of the crystal. The cohesive force between these cleavage planes is so weak that the material laminates very easily. It has been proposed that these weak forces are due to van der Waals bonds. The melting temperature is 585°C and the maximum in the liquidus-solidus curve is on the bismuth-rich side of the stoichiometric composition (7).

![Fig. 1. Structure of $\text{Bi}_2\text{Te}_3$ lattice.](After Harker, Z. Krist. 33, 181, 1934.)

2.1 INTERSTITIAL DIFFUSION IN $\text{Bi}_2\text{Te}_3$

An inspection of Fig. 1 and a glance at the values of the appropriate lattice parameters suggest that in the direction perpendicular to the c-axis the easiest path of diffusion is in the region between the adjacent layers of tellurium$^{(1)}$. We find that in this region there exist interstitial sites that can easily accommodate some foreign ions.
The space in the "box" formed by point abcdefgh in Fig. 2, which is quite large, can easily be further expanded because the box is formed by comparatively weak van der Waals forces. Moreover, the ionic radius of Cu$^+$ is only 0.96 Å. Hence it would be expected that the energy barrier separating the neighboring sites A and A' is quite low.

2.2 ELECTRICAL PROPERTIES OF P-TYPE BISMUTH TELLURIDE

The crystals used for this investigation were prepared by the Czochralski method, which is described elsewhere (12, 22). All of these crystals were very uniform in their electrical properties: the resistivity was found to be approximately 2 mho-cm; and the thermoelectric power, approximately 200 µV/°C.

The measurements described in sections 2.3-2.5 were carried out on a single uncut crystal, approximately 4 inches long, 5.30 mm wide, and 1.66 mm thick. The following properties were measured: (a) Hall effect in the temperature range 77°K-290°K; (b) resistivity in the temperature range 77°K-290°K; and (c) thermoelectric power at room temperature.

2.3 HALL-EFFECT MEASUREMENTS

The crystal was taped to an aluminum block which was provided with a copper-Constantan thermocouple to monitor the temperature of the sample. The electrical connections are indicated in Fig. 3. An ultrasonic soldering iron was used to place beads of low-temperature solder on the edges of the crystal, and very thin nickel wires were used for external connections.

The whole assembly was suspended in a double dewar which, in turn, was placed between the poles of a 6-inch Varian magnet. The outside dewar was filled with liquid nitrogen, and, as the nitrogen evaporated, the temperature varied continuously from 77°K to 290°K.
The Hall voltage was generated by passing 100 ma of direct current through the crystal in the direction parallel to the cleavage planes and by impressing a magnetic field of 7000 gauss in the direction normal to these planes. The output was measured with a K-3 potentiometer. In order to eliminate most of the thermoelectric effects, each value of Hall voltage was based on a set of four measurements: one for each direction of current and magnetic field. The sample temperature was monitored at the beginning and at the end of every set, and the average of the two readings was taken as the temperature appropriate to the Hall voltage based on the set.

Separate ac measurements of the Hall constant, in which a Dauphiné chopper (8) was used, showed that the error in the dc Hall measurements, caused by the Nernst-Ettinghausen effects, was negligible.

The results of our Hall-effect measurements (Fig. 4a) are practically the same as those reported by Drabble (9) for his sample, SBTC/23.

![Hall Effect Measurement](image_a)

![Resistivity Measurement](image_b)

Fig. 4. (a) Hall-effect measurement. (b) Resistivity measurements.
2.4 RESISTIVITY MEASUREMENTS

The dependence of resistivity on temperature was found by measuring the voltage drop across terminals 1 and 2 (Fig. 3) when 10 mA of alternating current at frequency 93.5 cps was passed in the direction parallel to the cleavage planes. To minimize the effects of pickup and noise, a wave analyzer, Type GR726-A, was used as the output meter. The temperature was changed in the same manner as for the Hall-effect measurements.

Since the contact beads were approximately 0.5 mm - 1 mm in diameter, it was difficult to determine by inspection the geometrical factor necessary for obtaining the actual resistivity from the measured V/I ratio. Instead, the resistivity of the crystal was determined at room temperature by the four-point method (see section 3.2). The value obtained was then divided by the V/I ratio for the same temperature to obtain the proper multiplying factor for the rest of the resistivity data.

The temperature dependence of the resistivity follows quite closely a $T^{3/2}$ law (Fig. 4b), from which it may be inferred that the carrier concentration over the temperature range that is of interest is rather constant and the mobility is limited primarily by acoustic-mode lattice scattering.

2.5 THERMOELECTRIC-POWER MEASUREMENTS

The thermoelectric power was measured by the hot-probe method at room temperature only. It was found to vary over the entire length of the crystal from 195 $\mu$V/°C to 210 $\mu$V/°C.

2.6 EVALUATION OF THE SAMPLE PROPERTIES

If we assume conduction by a single charge carrier and acoustic-mode scattering, the thermoelectric power (inclusive of possible degeneracy) is given by

$$\alpha = \frac{k}{e} 2 \left( \frac{F_1(\eta_p)}{F_0(\eta_p)} - \eta_p \right)$$  \hspace{1cm} (1)

where

$$F_\Gamma(\eta) = \int_0^\infty \frac{E^\Gamma[1+\exp(E-\eta)]^{-1}}{1+\exp(E-\eta)} \, dE$$  \hspace{1cm} (2)

and

$$\eta_p \equiv \frac{E_v - E_F}{kT}$$  \hspace{1cm} (3)

Here, $E_v$ is the energy at the top of the valence band, $E_F$ is the Fermi energy, $k$ is Boltzmann's constant, and $T$ is the temperature in °K.

Since the thermoelectric power was found to be limited in range, $195 \mu$V/°C < $\alpha$ < 210 $\mu$V/°C.
<210 \mu V/°C, the position of the Fermi level is required, from Eq. 1, to lie in the range 
\(-0.125 < \eta_p < 0.125\). Thus the use of partially degenerate statistics is definitely 
required in the analysis of subsequent data.

To determine the charge-carrier concentration, it is necessary to interpret the 
Hall-effect data properly. If the six-valley model proposed by Drabble and Wolfe (10) 
for Bi\(_2\)Te\(_3\) is accepted, the Hall coefficient \(\rho_{123}\) that is appropriate to the experimental 
configuration described above is

\[
\rho_{123} = \frac{4u}{p_e(1+u)^2}
\]

(4)

where \(p\) is the hole concentration, and \(u\) is a parameter depending upon the principal 
effective masses of holes and on the angle of inclination of the constant-energy ellipsoids 
to the c-axis of the crystal. An inspection of the Hall-effect data shows that \(\rho_{123}\) 
increases as the temperature increases. This increase is characteristic of p-type 
Bi\(_2\)Te\(_3\), and there is still no adequate explanation for it. It cannot be accounted for 
by assuming a transition from degenerate to nondegenerate statistics because: (a) the 
change observed is too large, and (b) there is no evidence of such a transition (thermo-
electric power at room temperature is not characteristic of a fully degenerate material).

Furthermore, it is quite unlikely that the hole concentration decreases with increasing 
temperature. The only alternative is that the parameter \(u\) is temperature-dependent. 
It is not, at the present time, worth while to present our further speculations on this 
score. It is important, however, that the Hall-coefficient variation tends to flatten at 
temperatures near 77°K. Hence, if it is assumed that all of the acceptors are ionized 
at that temperature - a quite reasonable assumption in view of the narrow gap of 
Bi\(_2\)Te\(_3\) - and if it is also assumed that whatever mechanism causes the Hall coefficient 
to rise with temperature may be neglected at 77°K, the hole concentration can be esti-
mated on the basis of a Hall coefficient \(p_{123}\) at that temperature.

It is necessary to know the value of \(u\). As Drabble and Wolfe have shown, \(u\) may 
be determined from a combination of galvanomagnetic measurements. Since, in the 
present case, the Hall coefficient behaves so much like Drabble's (9) sample, SBTC/23, 
the value of \(u\) that was used in the present analysis was that obtained by him for that 
sample, \(u = 8.416\). Thus

\[
p = 9 \times 10^{18} \text{ cm}^{-3}
\]

(5)

Now, in general,

\[
p = 2 \left(\frac{2\pi m_p^* kT}{\hbar^2}\right)^{3/2} \frac{2}{\sqrt{\pi}} F_{1/2}(\eta_p)
\]

(6)

where \(m_p^*\) is the density-of-states effective mass of a hole, and all of the other symbols 
have their conventional meanings. Substituting in Eq. 6 the values of \(\eta_p\) and \(p\) found
in Eqs. 4 and 5, and taking \( T = 300^\circ K \) (that is, the temperature at which \( \eta_p \) was determined), we find that the effective mass of holes lies in the range \( 0.57 < \frac{m_p}{m_o} < 0.65 \), where \( m_o \) is the rest mass of an electron. Compare this value with \( \frac{m_p}{m_o} = 0.51 \) found by Drabble \((9)\) at \( 77^\circ K \), with the Fermi level inside the valence band \( (\eta_p = 1.8) \). As will be elaborated upon later, it is thought that the effective mass of holes in \( \text{Bi}_2\text{Te}_3 \) increases as the Fermi level moves out of the valence band into the forbidden gap. Hence the effective mass found above is reasonably consistent with other available data.

If the assumption made previously is correct – that the carrier concentration is constant in the temperature range \( 70^\circ K - 300^\circ K \) – then, by using for the Fermi function \( F_{1/2}(x) \) the approximant

\[
F_{1/2}(x) = \frac{\sqrt{\pi}}{2} e^x \left[ 1 + 0.25 e^x \right]^{-1}
\]

it can be shown that the slope of thermoelectric power versus \( \ln T \) is

\[
\frac{d|\alpha|}{d(\ln T)} = 160 \mu\text{V}/^\circ\text{C}
\]

over the temperature range in question. Had classical statistics been used, the slope would have been only \( \frac{3}{2} \frac{k}{e} = 129 \mu\text{V}/^\circ\text{C} \). Experimental data reported by Goldsmid \((11)\) for a wide range of doping show slopes of \( 150 \mu\text{V}/^\circ\text{C} \). The agreement lends support to the basis of our present analysis of the material.
III. INTERACTION OF COPPER WITH BISMUTH TELLURIDE NEAR ROOM TEMPERATURE

3.1 SAMPLE PREPARATION

Samples suitable for a diffusion experiment were prepared in the following manner. A single crystal, grown in the crystal puller, was mounted on a glass plate with the aid of De Kotinsky cement. Sections of the crystal, approximately 1.5-2 inches long, were cut by using a diamond saw. Details of the cutting procedure will be discussed in a subsequent report (12).

After the samples were cut, their electric properties were checked. Thermo-electric power and resistivity were measured for each sample to establish its initial properties. These properties were constant within 5 per cent over the length of each sample, a uniformity that was considered acceptable for subsequent experiments.

The customary procedure at this point would have been to grind and polish the surface on which the diffusing agent is to be deposited, in order to fix clearly the exact location of the diffusion-couple interface and hence to minimize the error in locating the origin from which the diffusion distance is to be measured. It was found that this polishing procedure cannot be followed with Bi$_2$Te$_3$. All attempts to grind and polish the butt end of the samples introduced irreparable damage that extended far into the bulk of the material.

Two phenomena contributed to this damage. First, the individual planes of the crystals are so loosely bound together that they are separated easily by any shear stress applied normally to the planes, as in grinding. The resulting flaring extends several millimeters into the bulk of the sample. Second, Bi$_2$Te$_3$ flows under shear stress and fills up all cracks and voids on the surface to which the stress is applied. The resulting surface is more amorphous than crystalline. Therefore, it is necessary to remove that layer by some process such as etching, which re-exposes the cracks and voids. The final result is usually a rougher, more pock-marked surface than the one at the beginning. Fortunately, in Bi$_2$Te$_3$ the migration of Cu in the direction of the cleavage planes is so rapid that the error in locating the interface caused by surface roughness is negligible. In fact, other factors were found to exist that influenced more seriously the effective location of the diffusion-couple interface. These factors will be discussed in section 4.1 in connection with the determination of the activation energy for diffusion.

Next, the lateral surfaces of the crystal were covered with Picein, which is easily soluble in such organic solvents as benzene. The end face of the crystal which resulted from the cutting operation was left exposed. This exposed surface was etched with dilute aqua regia for a period of between one-half hour and one hour. The Picein coating was found to be impervious to aqua regia, and hence the surface parallel to the cleavage planes, on which future measurements were to be made, was found to be
undamaged by this etching process.

The prepared sample was suspended from a loop of nickel wire, which formed one of the electrodes in a copper electroplating cell. The cell itself consisted of a test tube, 25 mm in diameter, filled with saturated copper sulphate solution. The other electrode was a strip of chemically pure copper. The cell was placed in a constant temperature bath. For sample No. 3 the temperature of the bath was 0°C, that is, the bath was simply ice water. The actual temperature inside the cell was approximately 1°C. For sample No. 8, the temperature of the bath was set at 30°C; in this case, the thermostat consisted of a silicone oil bath maintained at the prescribed temperature by means of electric heaters. Before the plating proper was started, the polarity of the cell was reversed for 1 minute in order to remove from the sample by outplating it any possible oxide layers and dirt.

After the outplating step had been completed, a current of 0.5 ma at 0°C, and 1 ma at 30°C, was used for plating copper onto the end of the bismuth-telluride sample. The plating current was left on during the entire time of the diffusion run; but because of the low resistivity of the sample material, the electric field produced inside it by the plating current was sufficiently small to permit neglecting the transport of copper by the field. Thus, it is felt that experimental conditions for pure diffusion from an infinite source were fulfilled.

At various intervals of time the sample was removed from the cell, the Picein coating was removed from one side with benzene, and resistivity and thermoelectric power measurements (in that order) were made at points along the sample. During the first few intervals of time, only resistivity measurements were made because, initially, the time it took to perform the measurements (15-20 minutes for resistivity measurement alone) was sufficiently long to introduce an appreciable uncertainty into the effective time for diffusion at the temperature of the bath. Toward the end of the run, however, the half-hour interval required to perform both thermoelectric and resistivity measurements along the sample was small compared with the total time of diffusion. Accordingly, after 50 or 75 hours of diffusion, both resistivity and thermoelectric-power measurements were made. The protective coating was, of course, reapplied each time before replacing the sample in the thermostat.

3.2 DESCRIPTION OF RESISTIVITY AND THERMOELECTRIC-POWER MEASUREMENTS

The four-point probe method, which is due to Valdes (13), was used to perform the resistivity measurements. As originally presented by Valdes, this method was applicable to isotropic materials only. However, Gray (14) has shown that in the case of an anisotropic material like bismuth telluride, in which a basal plane exists, Valdes' analysis can be extended to four-point probe measurements in that plane.

The probe assembly shown in Fig. 5 consists of four tungsten wires spaced
approximately 0.3 mm apart. Since this spacing is of the same order of magnitude as the diameter of the wires themselves, and since Valdes' derivation is based on the assumption of hemispherical boundary conditions at the contact points to the material, the tips of the wires were rounded off to ensure the validity of the derivation. Boundary corrections were unnecessary because the crystals were at least 5 mm wide and the measurements were made close to the centers. The arrangement of the auxiliary equipment associated with the four-point probe is shown in Fig. 6, and a block diagram of the equipment is shown in Fig. 7.

For the thermoelectric-power measurement, a hot-point probe (Fig. 8) with an associated temperature-control circuit, which has been described by Nelson (14), was used. The voltage generated by the probe was read with a Keithley microvoltmeter. As Nelson (14) showed, under the experimental conditions applicable to this particular case, the thermoelectric power is simply the voltage generated by the probe divided by
Fig. 6. Equipment associated with the four-point probe.

Fig. 7. Block diagram of equipment for the four-point probe method.
the temperature difference between the tip of the probe and the temperature of the crystal (presumably at room temperature).

During some preliminary experiments we found that if the temperature of the probe was higher than approximately 5°C above ambient, the resulting temperature gradient in the sample near the probe was sufficiently large to actually drive the copper away from the vicinity of the point. As a result of this phenomenon, produced by the rapid diffusion of copper in bismuth telluride, the thermoelectric power was observed to drift during the measurement. In subsequent experiments the temperature of the probe tip was limited to 5°C above ambient.

The resistivity measurements were spaced at distances of 0.025 inch apart. However, when the rate of change of resistivity with distance became rather large this interval was cut down to 0.01 inch; this made it comparatively easy to locate the peak in the resistivity. Thermoelectric-power measurements were usually made
at intervals of 0.025 inch.

It is important to exercise care in using the various probes, to minimize surface damage. In any case, data for each run were taken without backtracking, in order to avoid backlash difficulties and spots with surface damage resulting from preceding runs. Successive runs were taken along slightly displaced lines, again, to avoid spots at which measurements were made previously.
IV. EFFECTS OF COPPER ON THE PROPERTIES OF Bi$_2$Te$_3$

The experiments were conducted on two monocrystalline samples, No. 3 and No. 8. Although they came from different ingots, their initial properties were almost identical. Typical results of the resistivity and thermoelectric-power measurements are shown in Figs. 9 and 10. Before delving into the quantitative aspects of these results, it is worthwhile to discuss some of their qualitative features.

Note that as the distance from the Cu-Bi$_2$Te$_3$ interface decreases, the resistivity first increases, reaches a maximum, and then decreases. This behavior may be explained qualitatively as follows. Although, as noted previously, degenerate statistics must be employed in the present instance, it is expected that a mass-action law for holes and electrons is valid within a very rough approximation. That is, the np product is not expected to vary widely as a function of the position of the Fermi level over the range of interest. Now, copper is a donor in Bi$_2$Te$_3$. Hence increase of copper concentration in p-type Bi$_2$Te$_3$ at first leads to compensation. The electron and hole concentrations decrease because of the mass-action constraint on the np product. Therefore, far from the Cu-Bi$_2$Te$_3$ interface resistivity increases as the donor (copper) concentration increases. As the donor (copper) concentration is increased still more, that is, as the
distance to the Cu-Bi$_2$Te$_3$ interface is further decreased, it is to be expected that the host material would become n-type, and the electron concentration would increase still more. The resistivity (now, n-type) would decrease. Although qualitatively this is precisely what appears to happen, closer analysis of the data will show that far more complicated processes take place as the Cu concentration increases.

Turning now to the results of thermoelectric power measurements (Fig. 10), and starting at a large distance from the source interface, we see that as the donor concentration increases, the thermoelectric power, $\alpha$, at first increases, goes through a relatively flat maximum, decreases rather rapidly, goes through a minimum, and finally appears to increase again. The initial increase in $\alpha$ can be understood if it is remarked that for a two-band conduction model

$$\frac{e}{k} \alpha = A(\eta_p) - \eta_p \frac{\sigma_n}{\sigma} [A(\eta_p) + A(\eta_n) + \epsilon]$$

where

$$A(\eta) = \frac{2F_1(\eta)}{F_0(\eta)}$$

$$\eta_n = \frac{E_F - E_C}{kT}$$

Here, $\sigma_n$ is the electron contribution to the total conductivity; $E_C$ is the energy at the lower edge of the conduction band; $\epsilon = E_G/kT$; and $E_G$ is the width of the forbidden gap. For a p-type material, initially, $\sigma_n = 0$. As donors are introduced into the material, the reduced Fermi energy, $\eta_p$, decreases faster than any of the other terms in Eq. 8. Therefore, $\alpha$ increases initially. Eventually, the effects of the increase in $\sigma_n$ overtake the effects of the motion of the Fermi level away from the valence band. As a result, $\alpha$ begins to decrease. When the pertinent transport parameters are independent of the donor concentration, increasing the latter should drive $\alpha$ through a minimum and then up again, as indeed it does in the present experiment. However, as in the case of resistivity, the analysis of the data indicates the presence of more complicated processes.

4.1 ACTIVATION ENERGY FOR THE DIFFUSION OF COPPER

As we have pointed out, the boundary condition applicable at the Cu-Bi$_2$Te$_3$ interface was that of an infinite source of copper. We also found that for the relevant time interval (approximately 3 days) and for the sample lengths involved (approximately 1 in.), no significant amount of copper ever reached the far ends of the samples. Hence, insofar as the hypothesis of simple diffusion is valid (Here, by simple diffusion we mean, among other things, that $D = D(C)$ and hence that Fick's second law holds.), the required solution of the diffusion equation is that for a semi-infinite rod with an infinite source suddenly applied at the origin. According to Crank (15) this solution is
where \( c \) is the concentration of copper at the point \( x \) at time \( t \), and \( c_o \) is the concentration of copper at the Cu-Bi$_2$Te$_3$ interface. More will be said about \( c_o \) in section 4.2.

Note, now, that \( c \) is a monotonically decreasing function of the variable \( x/\sqrt{t} \). Hence, the propagation in space and time of a fixed concentration \( c_f \) at a constant temperature is such that \( x \) is a linear function of \( \sqrt{t} \). In the present experiment the quantity most readily accessible to measurement is the sheet resistivity in the direction of the cleavage planes, rather than the actual copper concentration. In general, the dependence of the conductivity on impurity concentration is compounded of the variation of charge-carrier concentration and the dependence of mobility on impurity concentration. Unless a precise mathematical description of these dependences is available, it is impossible to unravel directly the impurity concentration from the conductivity data. For Bi$_2$Te$_3$ such a mathematical description does not exist, not because of any gross failure of transport theory but because some of the crucial parameters are not known precisely. To illustrate, witness our uncertainty about the initial acceptor concentration in the sample because of the inexplicable behavior of the Hall effect as a function of temperature.

However, it can be shown (16) that if simple diffusion prevails, then the resistivity \( \rho \) as a function of \( x \) and \( t \) can be expressed as

\[
\rho = \rho \left( \frac{x}{(2Dt)^{1/2}} \right) 
\]

Thus, in order to test the validity of the assumption that simple diffusion takes place, it suffices to plot the displacement of a point of constant resistivity versus \( \sqrt{t} \). If the resulting plot is linear, the assumption of simple diffusion is valid.

Figure 11 shows the correlation between \( x \) and \( \sqrt{t} \) for several constant values of \( \rho \) on the undercompensated side of the impurity distribution in the samples. All of the points fall on straight lines within an excellent approximation. On the other hand, similar sets of points on the overcompensated side of the distribution (Fig. 12) show significant departures from linearity. It will be shown below that the copper concentration at \( \rho = \rho_{\text{max}} \) is of the order of $10^{19}$ atoms/cm$^3$.

Note that all of the straight lines in Fig. 11 pass through a point displaced from the origin. This fact may be explained by assuming that, in spite of all of the care taken in preparing the sample, small cracks, approximately 1 mm in length, were produced during cutting. The "infinite source" of Cu initially consists of the copper ions in the plating solution. As a result of capillary action, the small cracks are filled almost instantaneously with the electrolyte upon immersion. Hence the effective diffusion-couple interface is at the bottom of the cracks, rather than on the surface of the sample.
Similar effects have been observed in sample No. 8. Although samples No. 3 and No. 8 came from different single crystals, their initial properties were very similar. Thus it can be assumed that for a given value of $\rho$, the corresponding concentrations of Cu in the two samples were equal.

From the available data, it is possible to estimate the activation energy (in fact the enthalpy) for the diffusion of Cu in the direction parallel to the cleavage planes. Consider some fixed value of $\rho$, say $\rho_f$.

$$\rho_f = \rho \left( \frac{A_1}{(2D_1)^{1/2}} \right) = \rho \left( \frac{A_2}{(2D_2)^{1/2}} \right)$$

(11)
where $D_1$ and $D_2$ are respectively the diffusion coefficients at temperatures $T_1$ and $T_2$, and $A_1$ and $A_2$ are the corresponding slopes of $x$ versus $\sqrt{t}$. It follows that

$$
\frac{D_1}{D_2} = \left(\frac{A_1}{A_2}\right)^2
$$

(12)

Since $D = D_0 \exp(-\Delta H/kT)$ (for convenience $\Delta H$ will be expressed in $\text{ev}$), it can be shown by using Eq. 12 that

$$
\Delta H = \frac{2k \ln \left(\frac{A_1}{A_2}\right)}{\frac{1}{T_1} - \frac{1}{T_2}}
$$

(13)

The slopes $A_1$ and $A_2$ were found by fitting straight lines to the experimental points $x$ versus $\sqrt{t}$ for fixed values of $\rho$ on samples No. 3 and No. 8, respectively. The fits were made by using the minimum mean-square-error criterion. The temperatures were taken to be $T_1 = 274^\circ\text{K}$, and $T_2 = 303^\circ\text{K}$. The results are summarized in Table I.

<table>
<thead>
<tr>
<th>$\rho$ (mhos·cm)</th>
<th>$\Delta H$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.20 ± 0.01</td>
</tr>
<tr>
<td>4.5</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td>6</td>
<td>0.22 ± 0.01</td>
</tr>
<tr>
<td>7.5</td>
<td>0.22 ± 0.01</td>
</tr>
<tr>
<td>9</td>
<td>0.21 ± 0.01</td>
</tr>
<tr>
<td>$\rho_{\text{max}}$</td>
<td>0.25 ± 0.01</td>
</tr>
</tbody>
</table>

These values are to be compared with the value $\Delta H = 0.21\text{ ev}$ reported by Carlson (17). It appears that for $\rho = \rho_{\text{max}}$ the diffusion activation enthalpy is significantly higher than the enthalpies deduced for $\rho < \rho_{\text{max}}$. We conclude, therefore, that probably at this point the hypothesis of simple diffusion ceases to be valid. However, for the remainder of the analysis of our data we shall assume that $\Delta H = 0.21\text{ ev}$ for $\rho$ ranging up to $\rho = \rho_{\text{max}}$.

4.2 ESTIMATION OF THE EFFECTIVE SURFACE CONCENTRATION OF COPPER

Before continuing with the analysis of the data some formulas that are useful in the discussion of a two-band conduction model will be developed.

The conductivity is given by
\[ \sigma = \epsilon_n \mu_p [p + b n] \]  
(14)

where \( \mu_p \) is the hole mobility, and \( b = \frac{\mu_n}{\mu_p} \) is the ratio of electron-to-hole mobilities.

The condition of electrical neutrality, if we assume that all of the donors \( N_D \) and acceptors \( N_A \) are ionized, is

\[ N_D - N_A = n - p \]
(15)

and the generalized mass-action law applicable to degenerate systems is

\[ np = 4 \left( \frac{2 \pi kT(m_n m_p)^{1/2}}{n^2} \right) F_{1/2}^{1/2}(\eta_p) F_{1/2}^{1/2}(\eta_n) \]
(16)

If for the initial material the donor concentration is negligible, and at room temperature the material is still in the exhaustion range, it follows that

\[ N_A = p_0 \]
(17)

Hereafter, unless otherwise specified, the subscript "o" denotes the prediffusion doping properties of the material. Straightforward algebraic manipulations lead to the following expressions:

\[ \frac{p}{N_A} = \frac{1}{2} \frac{\mu_{p0}}{\mu_p} [1 \pm s] \]
(18)

\[ \frac{n}{N_A} = \frac{1}{2} \frac{\mu_{p0}}{\mu_n} [1 \pm s] \]
(19)

\[ \frac{\epsilon}{k} a = \frac{1}{2} [A(\eta_p) - A(\eta_n) - \epsilon] - \eta_p \pm \frac{\eta_n}{2} [A(\eta_p) + A(\eta_n) + \epsilon] \]
(20)

\[ \frac{N_D}{N_A} = 1 - \frac{\mu_{p0}}{2 \mu_n} [(b-1) \pm (b+1)s] \]
(21)

where the upper sign refers to the properties on the p-type side of the maximum in the resistivity distribution, and the lower sign refers to the n-type side, \( r = \rho / \rho_o \), and \( s \) is given by

\[ s = \left\{ 1 - 4b \left( \frac{\mu_p}{\mu_{p0}} \right)^2 \left( \frac{m_n m_p}{m_{p0}^2} \right)^{3/2} \frac{1}{\left[ F_{1/2}^{1/2}(\eta_p) F_{1/2}^{1/2}(\eta_n) \right]^{1/2}} \right\}^{1/2} \]
(22)

Also note that \( \eta_p + \eta_n = -\epsilon \). The quantity \( s \) in Eq. 22 can be written as

\[ s = \frac{\sigma_p - \sigma_n}{\sigma} \]
(23)
Whence Eq. 20 becomes

\[ a = \phi_1(\eta_p) \pm \frac{\sigma_p - \sigma_n}{\sigma} \phi_2(\eta_p) \]  

(24)

where

\[ \phi_1(\eta_p) = \frac{1}{2} \frac{k}{e} [A(\eta_p) - A(-\eta_p^e - e^e)] - \eta_p \]  

(25)

and

\[ \phi_2(\eta_p) = \frac{1}{2} \frac{k}{e} [A(\eta_p) + A(-\eta_p^e + e^e)] \]  

(26)

Thus

\[ \frac{da}{dr} = \left[ \phi_1' \pm \frac{\sigma_p - \sigma_n}{\sigma} \phi_2' \pm \frac{\sigma_p - \sigma_n}{\sigma_o} \phi_2 \pm r\phi_2 \frac{d}{d\eta_p} \left( \frac{\sigma_p^e - \sigma_n^e}{\sigma_o} \right) \right] \frac{d\eta_p}{dr} \]  

(27)

Now,

\[ \frac{dr}{d\eta_p} \propto \frac{1}{2} \mu_p m_p^{3/2} F_{-1/2}(\eta_p) - \frac{1}{2} \mu_n m_n^{3/2} F_{-1/2}(\eta_n) \]

\[ + F_{1/2}(\eta_p) \frac{d}{d\eta_p} \left( \mu_p m_p^{3/2} \right) + F_{1/2}(\eta_n) \frac{d}{d\eta_p} \left( \mu_n m_n^{3/2} \right) \]  

(28)

Hence, if \( \eta_p \) and \( \eta_n \) are both greater than approximately 2, and the mobilities, as well as the masses of holes and electrons, are not very strongly dependent on the position of the Fermi level,

\[ \frac{dr}{d\eta_p} = 0 \]  

(29)

when \( \sigma_p = \sigma_n \). Therefore, we conclude that the resistivity maximum occurs approximately when the condition \( \sigma_p = \sigma_n \) is satisfied.

In order to evaluate the quantity \( D_0 \) and to proceed with the analysis of the electrical properties of \( \text{Bi}_2\text{Te}_3 \) doped with copper, it is necessary to find the surface concentration of the latter. Ordinarily, this is done by measuring the sheet resistivity in the plane normal to the direction of migration of the diffusing atoms. Such a procedure could not be adopted in the present experiment for a number of reasons. First, because of the poor mechanical properties of \( \text{Bi}_2\text{Te}_3 \) no sample suitable for such measurements could be prepared. Second, lack of precise knowledge of the dependence of the resistivity on the concentration of Cu makes it difficult to obtain a very accurate estimate of this concentration. Third, it is suspected that at large concentrations of Cu significant changes take place in the very structure of the host material (see sec. 4.4). Hence, we can hope to find only an effective surface concentration rather than the true one.

Carlson (17) reports having estimated the equilibrium surface concentration in the cleavage plane. However, for a material as anisotropic as \( \text{Bi}_2\text{Te}_3 \) we would suspect
that the equilibrium surface concentration in the plane normal to the cleavage planes would be significantly different.

In view of the facts mentioned in the preceding discussion, we decided to estimate the surface concentration $c_o$ by an indirect route. Since Carlson's measurements involved an instantaneous point source, his results were independent of the value of $c_o$. It has been established that the experimental data on the diffusion constant reported here result in an activation energy that is in excellent agreement with that of Carlson. We shall assume that the value of $D_o$ reported by him is equally valid, and we shall use it to establish the value of $c_o$.

It is seen from Eq. 21 that as $\rho$ approaches $\rho_o$,

$$\frac{N_D}{N_A} \to 1 - \frac{\mu_{po}}{r\mu_p}$$

It will be shown in section 4.3 that there are grounds for believing that to the first approximation the copper ions act as neutral impurities insofar as the mobility is concerned. Hence, for low copper concentrations, it can be assumed that $\mu_p = \mu_{po}$. Thus

$$\lim_{r \to 1} \frac{N_D}{N_A} = 1 - \frac{1}{r}$$

Assume, now, that, actually, the Cu in $\text{Bi}_2\text{Te}_3$ is singly ionized. Because after the penetration of Cu into p-type $\text{Bi}_2\text{Te}_3$, $\text{Bi}_2\text{Te}_3$ becomes n-type, there is little doubt that Cu acts as the donor. The only question that remains open is the state of ionization of the Cu that is lodged in the host lattice. If it is doubly, rather than singly, ionized, the error in the estimate of $c_o$ is, at most, a factor of 2. As we shall see presently, our value of $c_o$ will not be better than this anyway. To stress this assumption, the effective surface concentration will be denoted hereafter $N_{D_o}$, rather than $c_o$; and $c$ will be represented by $N_{D'}$.

Recall that the conditions under which the diffusion experiment was carried out approximate the diffusion in a semi-infinite rod from an instantaneously applied infinite source.

$$\frac{N_D}{N_{D_o}} = \text{erfc} \left( \frac{x}{(2Dt)^{1/2}} \right)$$

Combining Eqs. 31 and 32, we find that

$$\lim_{r \to 1} \left( 1 - \frac{1}{r} \right) = \frac{N_A}{N_{D_o}} \text{erfc} \left( \frac{x}{(2Dt)^{1/2}} \right)$$

The values of $N_A/N_{D_o}$ for several values of $x$, based on the resistivity measurements for sample No. 3, are presented in Table II. These calculations were based on the constancy of $x/\sqrt{t}$ for fixed values of $r$. The diffusion coefficient is taken to be that
reported by Carlson: \( D = 0.034 \exp\left(-\frac{0.21 \text{ev}}{kT}\right) \text{cm}^2/\text{sec.} \)

<table>
<thead>
<tr>
<th>( r )</th>
<th>( \frac{N_A}{N_D} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.35</td>
<td>( 2.2 \times 10^{-2} &lt; \frac{N_A}{N_D} &lt; 2.9 \times 10^{-2} )</td>
</tr>
<tr>
<td>1.25</td>
<td>( 2.1 \times 10^{-2} &lt; \frac{N_A}{N_D} &lt; 2.8 \times 10^{-2} )</td>
</tr>
<tr>
<td>1.1</td>
<td>( 2.3 \times 10^{-2} &lt; \frac{N_A}{N_D} &lt; 3.7 \times 10^{-2} )</td>
</tr>
<tr>
<td>1.05</td>
<td>( 2.8 \times 10^{-2} &lt; \frac{N_A}{N_D} &lt; 5.5 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

The uncertainty in the value of \( \frac{N_A}{N_D} \) stems from the probable error associated with the minimum mean-square-error calculations of the ratio \( x/\sqrt{t} \). For the purposes of subsequent calculations \( \frac{N_A}{N_D} \) will be taken to be equal to \( 4 \times 10^{-2} \). That estimate is based on the value of \( \frac{N_A}{N_D} \) for \( r = 1.05 \), which is the closest one to \( r = 1 \). Because of the inherent limit of resolution in the resistivity data in this region, it was not possible to get consistent results for \( r < 1.05 \).

On the basis of the initial properties of the samples, it is estimated that \( N_A = 6.9 \times 10^{18} \text{cm}^3 \) (see section 4.3). Hence, the effective surface concentration is \( N_D = 1.5 \times 10^{20} \text{cm}^3 \). This value is to be compared with the conservative estimate of \( 10^{18} - 10^{19} \text{cm}^3 \) which Carlson reported for the equilibrium surface concentration in the direction of the cleavage planes.

4.3 SOME ELECTRICAL PROPERTIES OF HIGHLY DOPED BI\(_2\)TE\(_3\)

When the transport parameters can be assumed to be independent of the impurity concentration, and the material is nondegenerate, it can be shown by combining the expression for the thermoelectric power \( a \) and the resistivity \( \rho \) that the relation between \( a \) and \( \rho \) is given by

\[
\frac{e}{k} a + \frac{1}{2} \ln \left[ b \left( \frac{m_n}{m_p} \right)^{3/2} \right] = \pm \left( 2 + \epsilon + \ln \frac{\rho}{\rho_m} \right) R + \frac{1}{2} [(1-R) \ln(1-R) - (1+R) \ln(1+R)]
\]

(34)

where \( R^2 = 1 - \left( \frac{\rho}{\rho_m} \right)^2 \), and \( 1/\rho_m = 2e(\mu_n \mu_p n_p)^{1/2} \) is the maximum value of the
resistivity $\rho$. Equation 34 is plotted for several values of $\epsilon$ in Fig. 13. By comparing Eq. 34 with the experimental results for $a$ versus $\rho$, shown in Fig. 14, it is seen that it does not apply for any reasonable choice of $\epsilon$.

![Fig. 13](image1.png)

Fig. 13. Thermoelectric power, $a$, versus normalized resistivity, $\rho/\rho_0$, when the transport parameters are independent of doping level.

![Fig. 14](image2.png)

Fig. 14. Thermoelectric power, $a$, versus normalized resistivity, $\rho/\rho_0$, from experimental data. (Sample No. 3.)
Hence, it is believed that all of the important properties of \(\text{Bi}_2\text{Te}_3\), such as mobilities, effective masses, and possibly the forbidden gap width, are to some extent dependent on the impurity concentration.

Since all the above-mentioned properties are interrelated through very complicated expressions, it is impossible to disentangle their explicit variations by using the available experimental results. More independent experiments would be required. However, it also appears from the same equations that, at the resistivity maximum, some properties are derivable from quite simple expressions because of the vanishing of certain terms. Again, as will be shown presently, it seems that for copper concentrations higher than that associated with the resistivity peak, the host material cannot be regarded as \(\text{Bi}_2\text{Te}_3\) simply doped with Cu. Thus, it seems possible, as well as pertinent, to estimate only the total change in the electrical transport properties over the range of doping with copper that carries the sample from initial to maximum resistivity.

As an example, the initial properties of sample No. 3 are summarized in Table III.

Table III. Initial (prediffusion doping) properties of \(\text{Bi}_2\text{Te}_3\) (sample No. 3 at room temperature).

\[
\begin{align*}
\rho_0 &= 2.23 \times 10^{-3} \text{ ohm-cm} \\
\alpha &= 226 \pm 2 \mu\text{v/}^\circ\text{C} \\
\frac{m_{po}}{m_o} &= 0.57 < \eta_{po} < 0.65 \\
-0.35 < \eta_{po} < -0.3 \\
5.4 \times 10^{18}/\text{cm}^3 < N_A = \rho_o < 6.9 \times 10^{18}/\text{cm}^3 \\
405 < \mu_{po} < 515
\end{align*}
\]

For the purpose of numerical calculation the initial effective mass of holes will be taken as \(m_{po} = 0.61m_o\); and the acceptor concentration will be taken as \(N_A = 6.2 \times 10^{18}/\text{cm}^3\). It should be remarked here that the initial value of hole mobility \(\mu_{po}\) is in good agreement with the latest values reported (18). If the assumptions leading to Eq. 31 are granted, near the maximum of resistivity the electron contribution to the conductivity, \(\sigma_n\), is equal to the hole contribution to the conductivity, \(\sigma_p\). Hence

\[
\mu_p m_p^{3/2} F_{1/2}(\eta_p) = \mu_n m_n^{1/2} F_{1/2}(\eta_n)
\]

or

\[
b \left( \frac{m_n}{m_p} \right)^{3/2} \frac{F_{1/2}(\eta_p)}{F_{1/2}(\eta_n)} = F_{1/2}(\eta_p) \]

(36)
Also at that point the thermoelectric power is given by

\[ \frac{e}{k} c = \frac{1}{2} [A(\eta_p) - A(\eta_n) - \epsilon] - \eta_p \]  

(37)

From the experimental results given in Fig. 14,

\[ \frac{e}{k} c \mid \rho = \rho_{\text{max}} = 1 \]  

(38)

If the reduced gap energy, \( \epsilon \), were known, \( \eta_p \) and \( \eta_n \) could be determined from Eq. 37, and hence the ratio \( \frac{F_{1/2}(\eta_p)}{F_{1/2}(\eta_n)} \) could be obtained. However, reported values (11) of \( \epsilon \) lie anywhere between 0.1 ev and 0.2 ev, so that \( \eta_p \) and \( \eta_n \) cannot be determined separately to any degree of accuracy. Fortunately, it is found that within the above-mentioned energy range the required ratio is fairly constant and, within a few per cent, we have

\[ \frac{F_{1/2}(\eta_p)}{F_{1/2}(\eta_n)} = 0.145 \]  

(39)

The donor concentration at the point of full compensation is given by

\[ \frac{N_D}{N_{D_0}} = \text{erfc} \frac{x_m}{(2Dt)^{1/2}} \]  

(40)

and, from Eq. 21,

\[ \frac{N_D}{N_A} = 1 - \frac{\mu_p}{2r_{\text{max}}} \left( \frac{1}{\mu_p} - \frac{1}{\mu_n} \right) \]  

(41)

where \( x_m \) is the position, \( r_{\text{max}} \) of the resistivity maximum at time \( t \). Using the previously established values of \( x/(2Dt)^{1/2} \) and \( N_{D_0} \), the donor (copper) concentration at full compensation is found to be

\[ N_D = 2 \times 10^{19} / \text{cm}^3 \]  

(42)

With \( r_{\text{max}} = 5.75 \), it is found that

\[ \frac{1}{\mu_n} - \frac{1}{\mu_p} = \frac{2r_{\text{max}}}{\mu_p} \left( \frac{N_D}{N_A} - 1 \right) = \frac{26.3}{\mu_p} \]  

(43)

From Eqs. 36, 39, and 43, it follows that

\[ 1 - 0.145 \left( \frac{\mu_p}{\mu_n} \right)^{3/2} = 26.3 \frac{\mu_n}{\mu_p} \]  

(44)

whence
\[
\left( \frac{\mu_n}{\mu_p} \right)^{3/2} > 0.145
\]  \hspace{1cm} (45)

and also
\[
b = \frac{\mu_n}{\mu_p} < 1
\]  \hspace{1cm} (46)

Since after using Eqs. 36, 39, 41 and 43, we have
\[
\frac{1}{0.145} \left( \frac{\mu_n}{\mu_p} \right)^{3/2} - 1 = 26.3 \frac{\mu_p}{\mu_{po}}
\]  \hspace{1cm} (47)

it follows that
\[
0.145 \left[ 26.3 \frac{\mu_p}{\mu_{po}} + 1 \right] = \left( \frac{\mu_n}{\mu_p} \right)^{3/2} = \frac{0.145}{1 - 26.3 \frac{\mu_n}{\mu_{po}}}
\]  \hspace{1cm} (48)

Using Eq. 46, we find that
\[
\frac{1}{1 - 26.3 \frac{\mu_n}{\mu_{po}}} < \frac{1}{1 - 26.3 \frac{\mu_p}{\mu_{po}}}
\]

and
\[
1 + 26.3 \frac{\mu_n}{\mu_{po}} > 1 + 26.3 \frac{\mu_p}{\mu_{po}}
\]

Thus
\[
0.145 \left[ 1 + 26.3 \frac{\mu_n}{\mu_{po}} \right] < \left( \frac{\mu_n}{\mu_p} \right)^{3/2} < 0.145 \left( 1 - 26.3 \frac{\mu_p}{\mu_{po}} \right)^{-1}
\]  \hspace{1cm} (49)

and by using Eqs. 36 and 49, we find
\[
\left( 1 + 26.3 \frac{\mu_n}{\mu_{po}} \right)^{-1} > b > 1 - 26.3 \frac{\mu_p}{\mu_{po}}
\]  \hspace{1cm} (50)

By some further algebraic manipulations and remembering that \( b = \frac{\mu_n}{\mu_p} \), inequality 50 yields
\[
26.3 \frac{\mu_n}{\mu_{po}} < b < \left( 1 + 26.3 \frac{\mu_n}{\mu_{po}} \right)^{-1}
\]

and therefore
It can also be shown that the inequality 50 yields

\[
\frac{\mu_n}{\mu_{po}} < \frac{\sqrt{5} - 1}{2} \left( \frac{N_D}{N_A} - 1 \right) \frac{1}{2r_{max}} = 0.023
\]  

and

\[
\frac{\mu_p}{\mu_{po}} < 0.038
\]  

From Eq. 18, it follows that when \( s = 0 \) the electron concentration is

\[
\frac{\mu}{N_A} = \frac{\mu_{po}}{2r_{max} \mu_n}
\]  

Hence, using Eq. 52, we have

\[
\frac{\mu}{N_A} > \frac{N_D}{N_A} - 1
\]

or \( n > 2.3 \times 10^{19} / \text{cm}^3 \).

Similarly, \( p > 1.4 \times 10^{19} / \text{cm}^3 \). Furthermore, applying the neutrality condition leads to

\[
2p > n > p
\]  

Now, at the point of full compensation,

\[
\frac{p}{n} = b
\]  

Therefore from Eqs. 55 and 56, \( \frac{1}{2} < b < 1 \), and

\[
0.145 > \left( \frac{m_n}{m_p} \right)^{3/2} > 0.29
\]

Furthermore, applying the neutrality condition leads to two additional conditions that are of interest:

\[
\left( \frac{m_p}{m_{po}} \right)^{3/2} > 2.3
\]

and

\[
\left( \frac{m_n}{m_{po}} \right)^{3/2} > 0.54
\]
For ease of reference some of the properties of the compensated sample are summarized in Table IV. Some of the inequalities are presented graphically in Figs. 15-19. The shaded areas indicate the regions in which the inequalities are satisfied.

Table IV. Properties of fully compensated p-type Bi₂Te₃ (sample No. 3 at room temperature).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( r_{\text{max}} )</td>
<td>5.75</td>
</tr>
<tr>
<td>( \frac{\mu_p}{\mu_{po}} )</td>
<td>&lt; 0.038</td>
</tr>
<tr>
<td>( \frac{\mu_n}{\mu_{po}} )</td>
<td>&lt; 0.024</td>
</tr>
<tr>
<td>( \frac{m_p}{m_o} )</td>
<td>&gt; 1.1</td>
</tr>
<tr>
<td>( \frac{m_n}{m_o} )</td>
<td>&gt; 0.4</td>
</tr>
<tr>
<td>( n )</td>
<td>&gt; ( p )</td>
</tr>
<tr>
<td>( 0.145 &lt; \left( \frac{m_n}{m_p} \right)^{3/2} &lt; 0.29 )</td>
<td></td>
</tr>
<tr>
<td>( n &gt; 2.3 \times 10^{19}/\text{cm}^3 )</td>
<td></td>
</tr>
<tr>
<td>( p &gt; 1.4 \times 10^{19}/\text{cm}^3 )</td>
<td></td>
</tr>
</tbody>
</table>

The implications of some of the properties listed in Table IV will now be discussed. In this connection it should first be noted that the static dielectric constant \( \kappa_o \) is very large, probably of the order of \( 10^3 \). The following evidence is offered to sustain this contention. First, in spite of the heavy doping levels achievable in Bi₂Te₃, no evidence of ionized impurity scattering has ever been reported. Second, even in the infrared region, 8 \( \mu \)-11 \( \mu \), index of refraction measurements (19) indicate a corresponding \( \kappa \sim 10^2 \). Third, the present measurements of the activation energy for diffusion involved Cu concentrations that were one to two orders of magnitude higher than those of Carlson (the average spacing between Cu ions is approximately 10 lattice parameters). Yet, the activation energy is practically the same as that found by Carlson. This suggests a very weak Coulomb interaction between adjacent Cu ions - another evidence of a very high dielectric constant.

With the preceding discussion in mind, it can be shown that with a simple hydrogenic model for the ionized impurities assumed, the Bohr radius is approximately 50 \( \text{Å} \), or more. The dimensions of a unit cell of Bi₂Te₃ in the direction of the
Fig. 15. Region of possible values of $\mu_p$ deduced from experimental data.

Fig. 16. Region of possible values of $\mu_n$ deduced from experimental data.

Fig. 17. Region of possible values of $b = \mu_n / \mu_p$ deduced from experimental data.
Fig. 18. Region of possible values of $m_p$ deduced from experimental data.

cleavage planes are approximately 5 Å. Therefore, in that direction there may exist a large degree of overlapping of the hole wave functions. Thus the phenomenon of impurity banding is plausible. In general, the curvature of the impurity band close to the valence band is smaller than that of the valence band itself. Therefore, after compensating the holes in the valence band, with conduction in the impurity band persisting, the effective mass of holes will appear larger. This perhaps explains the observed fact that the effective mass of holes more than doubles by the time full compensation is achieved.

Fig. 19. Region of possible values of $m_n/m_p$ deduced from experimental data.
The estimated effective mass of electrons found in the compensated region is consistent with one of the values reported by Drabble (20), \( m_n = 0.46 m_o \). Here, even though impurity banding may occur near the conduction band, it seems that the predominant contribution to electronic conductivity is from the conduction band itself. It should be pointed out, however, that values of \( m_n \) as high as 3.2 \( m_o \) have been reported by Goldsmid (11); this suggests the possible existence of an impurity band near the conduction band.

Finally, a note is in order on the remarkable decrease with doping of the mobilities. Even though, because of the large dielectric constant, ionized impurity scattering is not observable in \( \text{Bi}_2\text{Te}_3 \), the chances are that the interstitial Cu ions introduce deformations of the lattice in their immediate neighborhood. Such deformations may be regarded to a first approximation as neutral impurities. If that is so, the hole mobility in the compensated region is given by

\[
\frac{1}{\mu_p} = \frac{1}{\mu_{po}} + \frac{1}{\mu_{pl}}
\]

(57)

where \( \mu_{pl} \) is given by Erginsoy's (21) formula for neutral impurity scattering:

\[
\mu_{pl} = \frac{e^2 m_p}{20 \hbar^3 N_{N} \kappa_o}
\]

in which \( N_{N} \) is the density of neutral scattering centers. Hence, within an order of magnitude,

\[ N_{N} \kappa_o \sim 10^{22} \]

This result is consistent with the estimated values of \( N_{N} \sim 10^{19} \) and \( \kappa_o \sim 10^{3} \). It should be noted that the preceding discussion is in no way a proof, but merely a consistency argument to demonstrate the plausibility of the explanation offered for the large decrease in the mobilities. One could ask at this point, Why is it that in the initial material with \( 10^{18} - 10^{19} \) impurities/cm\(^3\) no neutral impurity scattering is observed? (See the temperature dependence in Fig. 4b.) At the present time, the answer is believed to rest upon the fact that substitutional impurities do not deform the lattice to the extent that interstitial impurities do. To verify or contradict this contention, further work in this area is necessary.

4.4 CHEMICAL CHANGES IN Bi\(_2\)Te\(_3\) INDUCED BY HIGH COPPER CONCENTRATION

As we have hinted in the preceding sections, for concentrations of Cu in excess of \( 10^{19} / \text{cm}^3 \), we can no longer maintain the model of \( \text{Bi}_2\text{Te}_3 \) doped with Cu. In fact, there appears to be some experimental evidence that if the concentration of Cu is sufficiently high, a chemical reaction with the host lattice takes place. This evidence will now be presented.
An attempt was made to convert Bi$_2$Te$_3$ from p-type into n-type by allowing copper to diffuse until the sample was saturated. It was found that during the first few hours fairly good n-type characteristics were obtained. However, after a day or so at room temperature the thermoelectric power, for example, dropped from approximately $-150 \, \mu V/^\circ C$ to nearly zero. Moreover, the electrical properties were no longer uniform over the length of the sample, but instead developed a patchy character.

It was also found that after a couple of days at room temperature, the copper cap formed by electroplating one of the ends of the sample would fall off of its own accord. At 100$^\circ$C the cap would usually fall off in a few hours.

Furthermore, it was established that prolonged electroplating of copper (four days, or more) at room temperature resulted in a flaring out of the end of the sample which was exposed to copper, followed by the copper cap falling off.

All of these observations can be explained if it is assumed that, even at low temperatures, Cu reacts with Bi$_2$Te$_3$ if the former is present in sufficiently large quantities. Thus, for instance, the falling off of the copper caps can be understood by assuming that, say, Cu$_2$Te forms at the Cu-Bi$_2$Te$_3$ interface. Since Cu$_2$Te does not appear to be a good bonding agent between Cu and Bi$_2$Te$_3$, the copper cap simply falls off. Moreover, the volume of a molecule of Cu$_2$Te is much larger than the interstitial spaces in Bi$_2$Te$_3$ in which Cu atoms are presumably lodged. Thus, if Cu$_2$Te is formed, the cleavage planes would be separated, and the flaring described above results.

There are some noticeable effects in the data presented in the preceding sections which could be explained by assuming a chemical reaction between Cu and the host lattice. One of these is the apparent departure from simple diffusion on the overcompensated side of the samples in which diffusion experiments were conducted (see Fig. 12). The second effect, by far more striking, is seen in the graph of $\rho/\rho_0$ versus $p/P_0$ (see Fig. 14). Here, on the undercompensated side of the sample (right-hand side of the graph) there is excellent agreement between the two sets of data, taken approximately 24 hours apart. On the other hand, on the overcompensated side the two sets of data disagree seriously. It appears that after approximately 24 hours exposure to a heavy concentration of Cu at 0$^\circ$C the sample properties change significantly. Finally, it should be mentioned that a structure developed in the tail end of the resistivity versus distance plots for sample No. 8 (see Manley (22)). No such structure was observed in sample No. 3. However, it should be recalled that experiments on sample No. 8 were carried out at 30$^\circ$C.

In order to determine what the effects of the electrolyte are on Bi$_2$Te$_3$ at higher temperatures, a sample of single-crystal Bi$_2$Te$_3$ was immersed in concentrated copper sulphate and maintained at 100$^\circ$C for approximately 12 hours. At the end of that period, the crystal was found to have cleaved, and triangular pits were discovered on the cleavage planes (see Fig. 20). Figure 20 shows that the equilateral triangles are oriented one way on one side of the cleavage, and the other way on the other side. Furthermore, comparison with the Laue patterns for the two sides shows that the triangular
Fig. 20. Etch pits in the cleavage planes of $\text{Bi}_2\text{Te}_3$ and the corresponding Laue patterns.

Etch pits have the same orientation as the principal zone axes parallel to the c-axis of the crystal. A glance at the structure of $\text{Bi}_2\text{Te}_3$ (Fig. 1) reveals that the tellurium atoms in the cleavage planes are arranged on the vertices of equilateral triangles with the threefold axes of rotation passing through the center of every triangle. Moreover, the triangular lattices across the cleavage planes are rotated 60° with respect to each other.

Therefore, if, by some process, triangular etch-pits are formed on one side of a cleavage plane by consecutive removal of tellurium atoms from that side, then the same process will result in triangular pits rotated 60° on the other side of the same cleavage plane. This is precisely what has been observed. If it is true that the pits were caused by copper located in the cleavage-plane interstices reacting with the nearest-neighbor tellurium atoms, then presumably this is what happened: Large quantities of copper entered along the dislocation line revealed by the dense line of triangles. Copper telluride formed, and the force resulting from the large volume of $\text{Cu}_2\text{Te}$ molecules disrupted the crystal.
V. CONCLUSION

The work summarized in this report points out the reasons why copper contacts used in a bismuth-telluride thermocouple in time degrade the performance of the device. First, copper diffuses very rapidly into the elements of the device. Second, p-type Bi$_2$Te$_3$ is compensated by copper acting as a donor impurity. Third, at sufficiently high copper concentrations, there occurs a chemical reaction with the host material, even at relatively low temperatures.
References


4. A. D. Harker, The crystal structure of the mineral tetradymite Bi$_2$STe$_2$, Z. Krist. 89, 175 (1934).


