DETERMINATION OF RESISTIVITY AND HALL COEFFICIENT OF SEMICONDUCTING MATERIALS BETWEEN 80°K AND 375°K

By R. C. Ruff
Propulsion and Vehicle Engineering Laboratory

NASA

George C. Marshall
Space Flight Center
Huntsville, Alabama

TECHNICAL MEMORANDUM X-53763

DETERMINATION OF RESISTIVITY AND HALL COEFFICIENT
OF SEMICONDUCTING MATERIALS BETWEEN 80°K and 375°K

By R. C. Ruff

George C. Marshall Space Flight Center
Huntsville, Alabama

ABSTRACT

An apparatus for determining the resistivity and Hall coefficient of materials between 80 and 375° Kelvin is described. The apparatus is capable of determining resistivity over a range from approximately 3×10^{-6} ohm-cm to 10^5 ohm-cm and Hall coefficient from 0.2 cm^3/coulomb to 10^{10} cm^3/coulomb with an absolute error less than 5 percent. An introduction to the resistivity and Hall effect is presented with special emphasis on certain other basic solid state properties which can be calculated from the resistivity and Hall coefficient data according to the "band theory" of semiconductors. The results from resistivity and Hall coefficient determinations on a specimen of silver-antimony-iron-telluride ($AgSb_{0.8}Fe_{0.2}Te_2$) thermoelectric material are presented along with the charge carrier concentration and the Hall mobility which are quantities derived from the measured values. The results from resistivity determinations on a series of eight experimental electrical brush materials are presented.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

NASA-GEORGE C. MARSHALL SPACE FLIGHT CENTER

TECHNICAL MEMORANDUM X-53763

DETERMINATION OF RESISTIVITY AND HALL COEFFICIENT
OF SEMICONDUCTING MATERIALS BETWEEN 80°K AND 375°K

By

R. C. Ruff

PROPULSION AND VEHICLE ENGINEERING LABORATORY
RESEARCH AND DEVELOPMENT OPERATIONS

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

TECHNICAL MEMORANDUM X-53763

DETERMINATION OF RESISTIVITY AND HALL COEFFICIENT
OF SEMICONDUCTING MATERIALS BETWEEN 80°K AND 375°K

SUMMARY

An apparatus for determining the resistivity and Hall coefficient of materials between 80 and 375°K is described. This apparatus provides basic electrical information on materials in support of developmental programs for thermoelectric and electrical brush materials for use in vacuum. The apparatus uses mechanical pressure contacts to sense the required voltage differences and uses two synchronous mechanical choppers to reduce thermal gradients due to Peltier heating and to remove the d.c. contribution from thermoelectric voltages. The apparatus is capable of determining resistivity over a range from approximately 3×10^{-6} ohm-cm to 10^5 ohm-cm and the Hall coefficient from 0.2 cm^3/coulomb to 10^{10} cm^3/coulomb with an absolute error less than 5 percent.

An introduction to the "band theory" of semiconductors is presented with special emphasis on the following basic solid state properties which can be calculated from a knowledge of the temperature dependence of the resistivity and Hall coefficient: the charge carrier type, the charge carrier concentration, the Hall mobility, the band gap energy, and the impurity activation energy.

The results from resistivity and Hall coefficient determinations on a specimen of silver-antimony-iron-telluride ($AgSb_{0.8}Fe_{0.2}Te_2$) thermoelectric material were used to calculate values of the charge carrier concentration and the Hall mobility for this material. The results from resistivity determinations on a high resistivity electrical brush specimen of molybdenum disulfide-silver ($[MoS_2]_{85}Ag_{15}$) which exhibited semiconducting properties were used to calculate the activation energy of the impurity centers. The results from resistivity determinations also were compared with the resistivity of pure silver to establish the effect of composition on resistivity.

INTRODUCTION

A need exists for a method to accurately determine the resistivity and Hall coefficient of selected materials as a function of temperature over a wide range of values.

The importance of the resistivity and the Hall coefficient lies in the significant information about the electronic structure of the material which can be calculated directly with these properties. The polarity of the Hall coefficient identifies the majority carrier while the magnitude of the Hall coefficient yields the electronic charge carrier density. The resistivity, in conjunction with the Hall coefficient, yields information on the electronic charge carrier mobility. If the Hall coefficient is measured in the temperature range in which a semiconductor exhibits extrinsic conduction (i.e., the only available charge carriers are those which are provided by impurity atoms), the atomic impurity concentration can be calculated. The energy band gap of a semiconductor can be calculated from a knowledge of the temperature dependence of the resistivity.

The measurement of the Hall effect affords the only simple method of calculating the impurity concentration. Although the Hall effect will not yield information on specific types of impurities, it can be especially useful as a method of analyzing the effectiveness of the various techniques used in purifying raw materials in preparation for further studies.

In order to have a method of obtaining this information whenever needed, an apparatus was designed and built to measure the Hall and resistivity voltages in the temperature range from 80°K to 350°K. Since many of the materials to be studied will have a large thermo-electric figure of merit, the electronic measuring circuit was designed to utilize two synchronous mechanical choppers for the purpose of reversing the current leads and the voltage measuring leads with a frequency of 37.5 hertz to eliminate the temperature differential which would build up under prolonged direct current exposure, thus, adding a thermoelectric voltage component to the resistivity or Hall voltage. The apparatus was designed to measure resistivities of materials over the range from that approaching the best metallic conductors (3×10^{-6} ohm-cm) to the upper range of the useful high resistivity semiconductors (10^5 ohm-cm). The apparatus also is capable of measuring the Hall effect in materials over the range of impurity concentrations from below 10^{10} impurities/cm^3 to approximately 10^{19} impurities/cm^3.

ELECTRICAL CONDUCTION PROCESSES IN SEMICONDUCTORS

Band Theory

Although the classical free electron theory is sufficient to describe the resistivity and Hall effect of most metals, the electronic transport properties of semiconductors can be described only by using the energy band theory of solids. A complete justification for the band theory and a theoretical derivation of the equations describing the

2

electronic properties are beyond the scope of this report but may be found in Reference 1.

The foundation of the band theory is the model used to describe the electron energy bands in a solid. The energy bands of a very pure semiconductor are shown in Figure 1.

The semiconductor is characterized by two bands of allowable electron energies called the valence band and the conduction band separated by a band of energy levels forbidden to the electron. The semiconductor is further characterized by the fact that at absolute zero temperature, the valence band is completely full of electrons and the conduction band is empty. This distinguishes a semiconductor from a metal because the valence band of a metal is only partially full at the absolute zero of temperature.

The width of the forbidden band is designated as the energy gap, E_g, and varies for the known semiconductors from about 0.01 electron volt (ev) for mercury telluride to 5.3 ev for diamond. Table 1 is a partial list of band gap values for typical semiconductors as compiled in Reference 2. The difference between an insulator and a semiconductor is one of definition only because an insulator is simply a semiconductor with a very large forbidden band as can be seen for diamond. Another definition which is useful in the derivation of the temperature dependence of the resistivity is the Fermi level designated as the Fermi energy E_F when measured from the top of the valence band. The Fermi level is defined as that level where there is a 50 percent probability of an energy state being occupied. For example, the Fermi level of a pure semiconductor at the absolute zero of temperature can be found by noting that there is zero probability of finding an electron at the bottom of the conduction band, and 100 percent probability of finding an electron at the top of the valence band. Therefore, assuming a linear change of probability across the forbidden band, the Fermi energy is exactly 50 percent of the energy gap.

It should be mentioned that at the absolute zero of temperature a pure semiconductor would be a perfect electrical insulator. This is true because conduction involves the process of transferring kinetic energy to an electron by the application of an electric field. However, this is impossible, because there is no vacant energy state in the valence band to which an electron could be transferred and no electron is allowed to raise its energy into the forbidden gap.

The properties of the pure semiconductor begin to change as the temperature is increased above the absolute zero of temperature. As the temperature is raised, it becomes possible for individual electrons in the valence band to instantaneously absorb sufficient energy from collisions with phonons (thermal vibrations) to raise their energy to

one of the unoccupied energy states in the conduction band. Once an electron is in the conduction band, it is free to contribute to conduction because of the availability of the continuum of energy states into which it can move under the influence of an electric field. This process of lifting an electron into the conduction band further aids conduction by virtue of the vacant state (hole) which is left in the valence band. When an electron jumps into this hole, under the influence of an applied electric field, a new hole is created. As this process is repeated, the effect is the same as if a positive charge was transported through the semiconductor. In fact, the process reacts to electric and magnetic fields exactly as a current of positive charges.

A term which occurs in practically all equations dealing with conduction in a semiconductor is the effective mass of the charge carriers designated as M_e or M_h for electrons or holes, respectively. A free electron acting under the influence of an electric field will accelerate with a value depending on its mass. An electron and a hole in a semiconductor also will accelerate but with values depending on the effective masses which are usually different from the mass of a free electron. In the derivation of the complete band theory, the effective masses are found to be related to the energy band structure by a differential equation.

Since the effective masses cannot be determined by resistivity or Hall measurements, they will be treated as added constants and will not be discussed further.

Intrinsic Conduction

The discussion thus far has dealt only with pure semiconductors. The statements all apply to intrinsic conduction which must be distinguished from extrinsic or impurity conduction. The intrinsic temperature range is defined as that temperature range in which the electrical properties of a semiconductor are not essentially modified by impurities.

As shown by quantum mechanics, the fact that electrons are indistinguishable means that they will obey Fermi-Dirac statistics. The Fermi-Dirac distribution function is:

$$f(E) = \frac{1}{\exp\left[(E-E_F)/kT\right] + 1}, \tag{1}$$

where E is the energy of any given energy level measured from the top of the valence band, k is Boltsmann's constant, and T is the temperature in degrees Kelvin. The distribution function gives the probability of finding the energy level E occupied at a temperature T if there is an allowable electron state at that energy. This explains the source of the definition of the Fermi level since:

4

$$f\ (E_F) = \frac{1}{e^0 + 1} = 1/2 = 50\ \%\ . \qquad (2)$$

Combining the distribution function with the density of electron energy states in the conduction band [1] gives the number of electrons N_e in the connection band as:

$$N_e = 2\ (2\pi\ M_e\ kT/h^2)^{3/2}\ \exp[(E_F - E_g)/kT], \qquad (3)$$

where M_e is the effective mass of the electrons in the conduction band. Similarly the number of holes N_h in the valence band is:

$$N_h = 2\ (2\pi\ M_h kT/h^2)^{3/2}\ \exp(-E_F/kT), \qquad (4)$$

where M_h is the effective mass of the holes in the valence band.

A useful equilibrium relation is obtained by multiplying N_e and N_h, yielding,

$$N_e N_h = np = 4(2\pi\ kT/h^2)^3\ (M_e M_h)^{3/2} \exp(-E_g/kT). \qquad (5)$$

The notation $n = N_e$ and $p = N_h$ is introduced to conform to the current practice in the field. It should be noted that the product np is a constant for a given material at a given temperature. This means, for example, that if an impurity is added to the material to increase n, then p must decrease to keep the product constant. This will be true as long as one assumption remains true. That assumption is that the distance of the Fermi level E_F from the edge of both the conduction band and the valence band should be large in comparison to kT.

In an intrinsic semiconductor it can be shown that n = p because the thermal excitation of an electron from the valence band leaves a hole. This fact can be used to calculate E_F by setting equations (3) and (4) equal, yielding,

$$E_F = 1/2\ E_g + 3/4\ kT\ \log\ (M_h/M_e). \qquad (6)$$

This equation clearly shows that the Fermi energy is not a fixed energy in the semiconductor; it is only a reference level which changes with temperature. For most practical purposes, however, the ratio M_h/M_e is sufficiently close to one to drop the second term and the Fermi level is assumed to be at the middle of the band gap for intrinsic material.

The conductivity σ which is the reciprocal of the resistivity ρ is defined for a semiconductor [3] as:

$$\sigma = |e|\ (n\mu_e + p\mu_h), \qquad (7)$$

where μ_e and μ_h are the mobilities (drift velocity/electric field) for electrons and holes, respectively. By convention, both the electron and the hole mobilities are taken to be positive, even though the drift velocities are in opposite directions. As mentioned before, in the intrinsic temperature range, n and p are equal. Letting the subscript i denote intrinsic, the number of electrons or holes is:

$$n_i = p_i = \sqrt{np} = 2(2\pi kT/h^2)^{3/2} (M_e M_h)^{3/4} \exp(-E_g/2kT). \qquad (8)$$

Therefore, the intrinsic conductivity is:

$$\sigma_i = 2|e|(2\pi kT/h^2)^{3/2} (M_e M_h)^{3/4} \exp(E_g/2kT)(\mu e + \mu h). \qquad (9)$$

Furthermore, it can be assumed that for intrinsic semiconductors, the mobilities are limited by lattice scattering effects rather than by impurity or ionic scattering. The equation giving the electron mobility of a semiconductor for which lattice scattering predominates [3] as:

$$\mu_e = \frac{(8\pi)^{1/2} h^4 C_{11}}{(2\pi)^4 \, 3E_1^2 M_e^{5/2} (kT)^{3/2}} = \text{const. } T^{-3/2}, \qquad (10)$$

where h is Planck's constant, C_{11} is the average longitudinal elastic constant, and E_1 is the shift of the edge of the conduction band per unit dilation. The hole mobility is identical except for the interchange of hole effective mass M_h for M_e.

Combining equations (9) and (10) and lumping together all the constants, the conductivity is given by:

$$\sigma_i = A \exp(-E_g/2kT), \qquad (11)$$

where the resultant constant is A. Therefore, it can be seen that the energy band gap can be found by plotting log σ_i or log ρ_i versus reciprocal temperature and measuring the slope of the resulting straight line. The width of the band gap will then be:

$$E_g = -2k\Delta \ln \sigma_i / \Delta (1/T)$$

or

$$E_g = + 4.61 \; k\Delta \log_{10} \rho_i / \Delta (1/T). \qquad (12)$$

For other types of scattering mechanisms, i.e., ionic, impurity, and imperfection, equation (12) is still true to a first order approximation. The reason for the close correspondence is that for any type of scattering the mobility is dependent on temperature only as a simple power law. The temperature dependence of the conductivity in equation (9) is, therefore,

still dominated by the exponential dependence of the carrier concentrations
and equation (11) follows to a first approximation.

Extrinsic Conduction

Corresponding to the definition for intrinsic conduction, extrinsic
conduction is defined as that conduction which occurs in a temperature
range in which the charge transport mechanisms are dominated by im-
purities, i.e., foreign atoms. In order to be truly useful the energy
band diagram of the model assumed for the band theory should also be
capable of explaining the changes in charge transport mechanisms found
to occur when impurity atoms are added to a semiconductor. It has been
shown that, in fact, the band diagram does very clearly depict the
reasons for the differences.

Most useful extrinsic semiconductors are produced by adding to the
basic semiconductor a very small amount of an element which has a valence
different by one from one of the elements of the basic semiconductor.
These "doping" atoms will usually go into the crystal lattice sub-
stitutionally and enter into the same chemical bond as the displaced
atom. However, as mentioned, the doping atom will have either one more
or one less electron than the displaced atom. If the doping atom has
one extra electron, it is called a "donor atom." If the doping atom has
one less electron, it is called an "acceptor," because it will tend to
accept an electron from the surrounding lattice to fill its incomplete
chemical bond.

As shown in the literature [4], these "donor" and "acceptor"
atoms add extra allowable energy states which are positioned in the
previously completely forbidden energy gap. The extra donor energy
states tend to lie in a range from 0.01 ev to 0.05 ev below the conduction
band while the acceptor states lie from 0.01 ev to 0.05 ev above the
valence band.

These extra energy states, due to impurity atoms, are shown dia-
grammatically in Figure 2. The impurity levels are purposefully shown
broken to indicate that they are local levels only and that they do not
form a conduction band of their own, at least not for most moderate
doping concentrations.

In the same manner as explained for intrinsic conduction, electrons
can be thermally excited to the conduction band from the donor levels
or raised into an acceptor level from the valence band leaving a hole,
since the thermal excitation energy needed from the lattice is of the
same order of magnitude as the average room temperature phonon energy
(kT = 0.026 ev for T = 300°K).

The impurity levels are essentially all ionized at room temperature and are contributing one charge carrier per impurity atom to conduction.

Useful doped semiconductors for most purposes are doped with the concentration of one type of impurity far in excess of the other type. Material with an excess of donors is called n-type because conduction is by negative electrons while material with excess acceptors is called p-type because of positive hole conduction.

All moderately doped semiconductors will exhibit intrinsic conduction at sufficiently high temperatures. This means that at high temperatures, the number of charge carriers contributed by impurity levels (the concentration of which is fixed) is negligible with respect to the number of electron-hole pairs excited between the valence band and the conduction band. However, as the temperature is decreased, the conduction goes through a transition region where the concentrations are comparable and finally the extrinsic temperature region is reached where the concentration of charge carriers is constant and equal to the doping concentration. At still lower temperatures the charge carrier concentration again decreases because the average phonon energy is too low to keep all the impurity levels excited.

Therefore, in the same manner as that for finding the band gap E_g for intrinsic material, the donor activation energy E_d can be found by measuring the slope of a graph of $\log \rho$ versus reciprocal temperature. The equation satisfied by E_d [5], is:

$$\log_{10} \rho = 0.217\ E_d/kT + \text{constant}. \qquad (13)$$

The acceptor activation energy E_a can be found by the same method.

Figure 3 is a graph of resistivity versus reciprocal temperature for n- and p-type indium antimonide (InSb) [2] which portrays clearly the intrinsic region, the extrinsic region, and the extrinsic slope region, and illustrates the wide range of values which may be encountered.

Since extrinsic conduction has only one type of charge carrier, the conductivity can be written simply as:

$$\sigma_{ex} = Ne\mu . \qquad (14)$$

Therefore, if the conductivity and the charge carrier density N are known, the mobility can be calculated. Similarly, if the mobility and the conductivity can be measured, then the charge carrier density can be calculated.

8

Hall Effect

The Hall effect was discovered by E. H. Hall in 1879 during an investigation of the nature of the force acting on a conductor carrying a current in a magnetic field. Hall found that when a conductor is placed in a magnetic field perpendicular to the direction of current flow, a voltage is developed across the conductor in the direction perpendicular to both the current and the magnetic field. This voltage is called the Hall voltage.

From electromagnetic theory the Lorentz equation for the force on a charge carrier is given in vector notation as:

$$\vec{F} = q \ (\vec{E} + \vec{V} \times \vec{B}) \ , \qquad (15)$$

where the charge q would be negative for an electron, V is the charge carrier velocity, and B is the magnetic field. The usual testing apparatus will be arranged so that all three vectors will be at right angles as shown in Figure 4. The reason for this arrangement is the simplification which results from being able to write the Lorentz equation in scalar form. If the directions of the applied fields are measured in a right hand coordinate system as shown in Figure 4, the Hall coefficient R is defined by the equation,

$$R = E_y / j_x B_z = \frac{V_H d}{BI} \ , \qquad (16)$$

where j_x is the total current density in the x direction, V_H is the Hall voltage measured across terminals C and D, d is the depth of the specimen in the shape of a rectangular plate, and I is the externally measured current. As derived in Appendix A for the general case of a conductor with both electron and hole charge carriers, the Hall coefficient is:

$$R = \frac{-(n \mu_n^{\ 2} - p \mu_p^{\ 2})}{e \ (n \mu_n + p \mu_p)^2} \ , \qquad (17)$$

where n and p are the electron and hole concentrations, respectively, and μ_n and μ_p are the electron and hole Hall mobilities, respectively. The Hall mobility is distinguished from the actual spatial drift mobility because of differences in the scattering mechanisms for lattice, ionic, or imperfection scattering. However, as shown in Reference 6, the two mobilities are at most different by a factor of two and further the two Hall mobility always approaches the value of the drift mobility at high magnetic fields.

It can be seen from equation (17) that for extrinsic conduction, the Hall coefficient is:

$$R = \pm 1/Ne, \tag{18}$$

where N is the charge carrier concentration, and a positive coefficient signifies hole conduction in p-type material while a negative coefficient signifies electron conduction in n-type material.

MEASUREMENT OF ELECTRICAL RESISTIVITY AND HALL COEFFICIENT

Units

The system of units which has become accepted in the semiconductor field is the so-called "practical" system. The units used are the centimeter, gram, second system for mechanical measurements, the volt, coulomb, ampere system for electrical measurements, and the gauss for magnetic measurements. These units are listed in Table II along with the values of the physical constants mentioned in this report when measured in practical units.

One fact which must be remembered, however, is that the gauss, which is the electromagnetic unit for the magnetic induction B, is not compatible with the electrostatic units. Therefore, in any equation involving both the electrostatic units and the electromagnetic units the following conversion must be made:

$$B_{pract.} = B_{emu} \times 10^{-8} = \text{gauss} \times 10^{-8}. \tag{19}$$

Resistivity

The resistivity of a material is defined as the ratio of the electric field E to the current density j in the direction of the electric field:

$$\rho = E/j \text{ ohm-cm}. \tag{20}$$

The electric field E is restricted to values small enough that Ohm's law is obeyed, i.e., that the resistivity ρ is not a function of E.

For convenience in measuring the resistivity, specimens usually are in the form of rectangular plates, as shown in Figure 4. If the width of the plate is w and the depth d, equation (20) becomes

$$\rho = (V_r/L)/(I/wd)$$

10

or,

$$\rho = \frac{V_r \cdot wd}{IL} \quad \text{ohm-cm}, \tag{21}$$

where V_r is the voltage drop between contacts A and B a distance L apart and I is the total current passed through the plate. As seen in Figure 4, low resistivity contacts should be attached to the end faces to insure uniform current flow down the length of the specimen.

The voltage probe connections A and B are often a problem because they must be of as low resistance as possible and yet small compared with the size of the specimens to avoid disturbing the uniformity of the current flow. A common solution has been to shape or cut the specimens with side-arms where potential leads are to be placed. Enlarged areas are then provided at the ends of the side-arms where a relatively large area contact can be made without disturbing the main body of the specimen.

A more convenient method and the one adopted for the apparatus described in this report is to use spring-loaded pressure contacts.

Hall Coefficient

The Hall coefficient is usually measured on the same specimen for which resistivity measurements are made because all that is needed are two additional Hall voltage probes such as C and D in Figure 4. For a specimen of this shape, the Hall coefficient R was defined by equation (16) to be:

$$R = V_H \, d/IB \quad cm^3/coulomb, \tag{22}$$

where V_H is the Hall voltage measured between contacts C and D. As mentioned earlier, the magnetic induction B is usually measured in gauss which is the electromagnetic unit. Using this unit for B, equation (16) becomes

$$R = dV_H \times 10^8/IB_{emu} \quad cm^3/coulomb. \tag{23}$$

Derived Quantities

As explained earlier, in the extrinsic temperature range, the Hall coefficient is essentially constant. The majority charge carrier is determined directly from the polarity of the Hall coefficient as shown by equation (18). The majority charge carriers are holes if R is positive and electrons if R is negative. Rewriting equation (18) the charge carrier

11

concentration is:

$$N = (Re)^{-1} \text{ carriers/cm}^3. \tag{24}$$

If the Hall coefficient is constant as a function of temperature, it can be assumed that all doping levels are activated and equation (23) has the further meaning of:

$$N = (Re)^{-1} \text{ doping atoms/cm}^3. \tag{25}$$

The Hall mobility μ_H of the majority charge carrier also can be calculated in the extrinsic temperature range by combining equations (14) and (18) to yield:

$$\mu_H = |R|\rho \quad \text{cm}^2/\text{volt-sec.} \tag{26}$$

The temperature variation of the Hall mobility calculated from equation (26) will yield information on the predominant scattering mechanism[6].

In the intrinsic temperature range, the energy band gap E_g can be calculated from a plot of $\log \rho$ versus reciprocal temperature as given by equation (12). After computing the constants, equation (12) reduces to

$$E_g = 0.3969 \; \Delta\log_{10}\rho \; / \; \Delta(10^3/T) \text{ ev.} \tag{27}$$

The intrinsic mobility of both types of carriers can be calculated from a detailed knowledge of the resistivity and Hall coefficient through the use of an involved method which is explained fully in Reference 2.

EXPERIMENTAL APPARATUS

Specimen Holder

The design of the specimen holder presented certain difficulties. A severe size limitation was imposed by the magnet to be used for the Hall effect measurements. The magnet available for these measurements has a pole gap of only 1.83 cm. In order to leave sufficient room for the specimen chamber walls plus a gap for thermal isolation, the maximum size for the specimen holder was 1.27 cm in diameter.

The specimen holder utilizes pressure contacts in a manner similar to that described in Reference 7. A simplified diagram of the specimen holder is shown in Figure 5. The body of the specimen holder was machined from a 1.27 cm diameter Teflon rod. The specimen is in the shape of a rectangular plate and is placed between the two current carrying contacts which have large flat faces to facilitate a

12

uniform current flow in the specimen. In order to compensate for specimens of varying lengths, the lower contact has three fixed positions while the top contact is spring loaded by a miniature coil spring contained in a hole drilled in the Teflon.

The two resistivity and two Hall voltage probes make contact with the specimen by means of pressure exerted by the adjustable tensioning screws. The voltage probes were fabricated from beryllium copper to insure spring action at low temperatures.

It can be seen that the two resistivity probes are on opposite sides of the sample. Although this is not the same arrangement as that shown in Figure 4 which was used to derive the resistivity equations, it is an equivalent arrangement as long as the current flows uniformly down the specimen and as long as no magnetic field is applied.

The electrical connections to the voltage probes and current contacts were made by attaching No. 28 B&S gauge copper wires with a solder designed to produce relatively low thermal emfs in contact with copper.

The temperature sensor used is a copper-constantan thermocouple. The thermocouple junction is bonded directly to the specimen.

The apparatus can be used with specimens having dimensions in the following ranges. The length must be between 1.45 and 2.10 cm. The width should be between 0.30 and 0.70 cm for the most accurate measurements. The depth can be no greater than 0.50 cm.

A photograph of the assembled specimen holder with a specimen in place is shown in Figure 6.

Specimen Chamber

The specimen chamber was designed to fit into the 1.83 cm pole gap of the magnet to be used for these studies. A diagram of the specimen chamber is shown in Figure 7.

The cylindrical wall of the specimen chamber was a section of 1.91 cm outside diameter copper tubing. The section of the tubing which fits between the magnet pole faces was machined to the required 1.83 cm diameter. The base of the specimen chamber was machined from a 1.91 cm diameter copper bar. A mating surface approximately 2.54 cm long was machined to fit snugly inside the copper tubing. Rose's alloy solder was used to bond these surfaces for a vacuum tight seal.

To provide support and guidance for the specimen holder, a projection on the base was formed by machining the copper bar. This projection is in the shape of a dovetail the outer edge of which corresponds to a 1.27 cm diameter concentric with the tube walls. The specimen holder, which also has a diameter of 1.27 cm, has a slot machined down the rear portion which mates with the dovetail. In addition to providing support and centering of the specimen holder, this projection promotes isothermal conditions by providing a high thermal conductivity path for the length of the specimen holder.

Temperature control is accomplished for the specimen chamber by balancing the heat input from heater wires on the outside of the copper base and the heat lost down a rod attached to the copper base and immersed in liquid nitrogen. For the specimen to reach liquid nitrogen temperature, the specimen chamber itself must be immersed in the liquid nitrogen to a level above the specimen. This is because of the high thermal conductivity of the copper tubing. When the specimen has reached liquid nitrogen temperature, the liquid level is dropped just far enough to allow the specimen to be placed in the magnet and the measurements are taken before the temperature begins to change.

At the top of the specimen chamber is an enlarged volume with an O-ring seal to the top plate. The enlarged volume contains the electrical leads. The top plate contains the electrical feedthrough and the vacuum or controlled atmosphere inlet.

Figure 8 is a photograph of the specimen chamber installed in the magnet.

Electrical Circuit

The design of the circuitry to determine the Hall coefficient and the resistivity was a compromise between two conflicting requirements. The first requirement was that the apparatus had to measure the widest possible range of parameters because it is known that the electronic conduction properties of semiconductors vary over a range covering many orders of magnitude. The second requirement was that the operation be kept simple and the measurements as routine as possible.

The first requirement was satisfied by combining a direct current source which supplies a highly regulated current in steps covering five orders of magnitude, with a d. c. indicating amplifier covering six orders of magnitude of voltage measurement. The second requirement was satisfied by utilizing a two-channel strip chart recorder. One channel displays the output of the indicating amplifier while the second channel simultaneously displays the temperature. In addition, the second channel

produces a calibrated output which is transmitted to a temperature programming and control unit. The programming unit can be adjusted to vary the specimen temperature in any preset pattern that might be required. By using this system the operator needs only to lower the specimen temperature to a specified point, usually liquid nitrogen temperature, and place the system in the automatic mode of operation. The measured variable will then be displayed along with the specimen temperature, and the specimen temperature will automatically be varied over a predetermined range.

The electrical circuit for the Hall coefficient and resistivity measuring apparatus is shown in Figure 9. The specimen current is supplied from a highly regulated d.c. power supply set at 20 volts. The current can be varied in decade steps and is calibrated before each test by final adjustment of the potentiometers as indicated by the electrometer. The current to the specimen can be reversed or directed through a mechanical d.c. chopper by proper manipulation of function switch one. Either the resistivity voltage between contacts 3 and 4, or Hall voltage between contacts 5 and 6, can be selected by function switch two to go to the second set of contacts on the mechanical chopper. The chopper synchronously reverses the current and the voltage measuring leads at 37.5 hertz. In this manner, the resistivity or Hall voltage, both of which reverse polarity when the current reverses, can be distinguished from d.c. thermoelectric voltages arising from thermal gradients and the Peltier effect. The contacts of the current carrying section of the chopper are adjusted to make-before-break to prevent arcing while the voltage measuring contacts are adjusted to break-before-make which allows transients to dissipate before the amplifier is connected to the voltage leads. The third function switch selects the forward, reverse, or chopped voltage from either the resistivity or Hall leads which is amplified and displayed by channel number one of the two-pen strip chart recorder. The output of the temperature measuring thermocouple is displayed by channel number two. The amplified output from channel number two is compared against an E.M.F. produced by the temperature programming unit by the current adjusting type (C.A.T.) control unit. The C.A.T. unit then makes any appropriate change in the power output to the specimen chamber heater from the magnetic amplifier which might be necessary to keep the specimen temperature at the programmed value.

The magnetic field for the Hall coefficient measurements is produced by an electromagnet with 10.16 cm diameter pole pieces with 1.83 cm gap spacing. The magnitude of the field is taken from a field versus supplied current calibration curve supplied by the manufacturer.

Figure 10 is a photograph of the complete assembly.

Capabilities and Accuracy

The capabilities of this apparatus are defined by the available ranges in current, magnetic field, and voltage measurement. The possible currents range in decade steps from one microampere to 100 milliamperes. The magnetic field can be varied with reasonable accuracy between 500 gauss and ten kilogauss. The indicating amplifier is capable of measuring d.c. voltages from 10 microvolts full-scale in an eleven-step 1,3,10 sequence.

Utilizing the above values, it is possible to measure the resistivity ρ and Hall coefficient R between the following values:

$$3 \times 10^{-6} \text{ ohm-cm} < \rho < 10^5 \text{ ohm-cm}$$

and

$$0.2 \text{ cm}^3/\text{coul} < R < 10^{10} \text{ cm}^3/\text{coul} .$$

An accurate estimate for the probable error in measurements of a parameter which depends on the measurement of several independent variables is to take the square root of the sum of the squares of the errors of the individual variables [8]. By using the accuracy values stated by the manufacturers of the individual instruments, it is calculated that the error associated with either the resistivity or the Hall coefficient is less than 5 percent.

EXPERIMENTAL RESULTS

To qualify the apparatus, resistivity and Hall coefficient measurements were made on a specimen of silver-antimony-iron-telluride ($AgSb_{0.8}Fe_{0.2}Te_2$) for which the properties were known [9]. In Figure 11, the experimental results of the resistivity and the Hall coefficient measurements are compared with the known results. The experimental values vary from the known values by a maximum of 10 percent. However, this difference should not be assigned, á priori, to apparatus error since there could have been variations in the preparation of the two specimens. Also, the apparatus used to measure the specimen used as a standard is reported to have had a possible error of 3.7 percent.

Using the results shown in Figure 11 for the specimen $AgSb_{0.8}Fe_{0.2}Te_2$, the charge carrier concentration and the Hall mobility were calculated using equations 23 and 25, respectively, and are shown plotted as a function of reciprocal temperature in Figure 12.

16

Resistivity versus temperature measurements were made on several specimens of experimental electrical brush materials being developed for use in a vacuum environment. One of the brush specimens of molybdenum disulfide-silver $(MoS_2)_{85}Ag_{15}$ (designated as A-168) had definite semiconductor characteristics as shown in Figure 13, a plot of the log(resistivity) versus reciprocal temperature. The specimen was evaluated as originally fabricated and after heating for six hours at 457° Kelvin. As shown in Table 1, MoS_2 has an energy gap of 1.45 ev. Therefore, the exponential dependence of the resistivity on temperature of specimen A-168 must be due to thermal activation of silver donor levels in the MoS_2 forbidden band. Using equation (13) the calculated donor activation energy E_d is 0.033 ev before and 0.032 ev after heating.

Figure 14 shows the results of resistivity measurements on eight brush materials which show metallic conduction, i.e., the resistivity increases with increasing temperature. Also shown in Figure 14, for comparison purposes, is the resistivity of pure silver [10]. It can be seen that reducing the silver content in the molybdenum disulfide brushes, in general, increases the resistivity. The exception is brush A-162 which has the same silver content as brush C-16. The addition of 3 percent copper to A-162, however, has increased the resistivity by two orders of magnitude. The low resistivity specimen C-16 had the same composition as specimen A-168 in Figure 13. The differences between specimens A-168 and C-16 have not been explained fully but are attributed to different temperatures used in the fabrication process.

CONCLUSIONS

(1)   The apparatus has been shown to be capable of displaying the resistivity and Hall coefficient over a temperature range between 80°K and 375°K with very little operator attention.

(2)   The absolute error associated with either the resistivity or the Hall coefficient measurement will be less than 5 percent.

(3)   The apparatus can be used for measuring resistivity values between 3×10^{-6} and 10^5 ohm-cm and Hall coefficient values between 0.2 and 10^{10} cm^3/coulomb.

(4)   The data provided by the apparatus are sufficient to enable calculation of the charge carrier type, the charge carrier mobility of extrinsic semiconductors, and the band gap of intrinsic conductors.

APPENDIX

If a magnetic field

$$\vec{B} = (0,0,-B_z) \tag{A-1}$$

and an electric field

$$\vec{E} = (-E_x, 0,0) \tag{A-2}$$

are applied to a conductor, the Lorentz force on a charged particle with a charge of q in a conventional right-hand coordinate system is defined as

$$\vec{F} = q(\vec{E} + E_H + \vec{V} \times \vec{B}) \tag{A-3}$$

where E_H is called the Hall field, and $\vec{V}$ is that velocity due to the electric field $\vec{E}$. Since $\vec{B}$ and $\vec{E}$ each have only one component, Equation A-3 readily reduces to the scalar equation

$$F_y = q(E_H + V_x B_z), \tag{A-4}$$

where E_H is in the y direction.

The velocity V_x can be rewritten by using the definition for the mobility μ

$$V_x = \pm \mu \ (-E_x), \tag{A-5}$$

where the positive sign is used if q is positive i.e., a hole, and the negative sign if q is an electron. The force on an electron (n-type conduction) is, therefore,

$$F_y^n = -e(E_H + \mu_n E_x B_z) \tag{A-6}$$

and the force on a hole (p-type conduction) is

$$F_y^p = + e(E_H - \mu_p E_x B_z), \tag{A-7}$$

where e is the magnitude of the charge on a single electron. The electron current density in the y direction j_y^n due to the force on the electron in the y direction is defined as

$$j_y^n = \sigma_n F_y^n / e = ne \mu_n F_y^n / e \tag{A-8}$$

$$= n \mu_n F_y^n,$$

18

where σ_n is the conductivity of the electrons and n is the electron density. Similarly, the hole current density in the y direction is

$$j_y^{\,p} = p \, \mu_p \, F_y^{\,p}, \qquad\qquad \text{A-9}$$

where p is the hole density. Substituting into Equation A-8 and A-9 the values for the forces from Equations A-6 and A-7, the electron current becomes

$$j_y^{\,n} = -\, ne \, \mu_n \, E_H - ne \mu_n^{\,2} E_x B_z \qquad\qquad \text{A-10}$$

and the hole current becomes

$$j_y^{\,p} = pe \, \mu_p \, E_H - pe \, \mu_p^{\,2} E_x B_z \, . \qquad\qquad \text{A-11}$$

Once current has been established in the conductor due to E and equilibrium has been reached, the net current flow in the y direction must be zero, i.e.,

$$j_y^{\,p} - j_y^{\,n} = 0 \, . \qquad\qquad \text{A-12}$$

Substituting into Equation A-12, the solution for the Hall field E_H is

$$E_H = \frac{(-ne\,\mu_n^{\,2} + pe\,\mu_p^{\,2})\, E_x B_z}{ne\,\mu_n + pe\,\mu_p} \, . \qquad\qquad \text{A-13}$$

The Hall coefficient R is defined as

$$R = E_H / j_x B_z \, , \qquad\qquad \text{A-14}$$

where j_x is the total measured current density defined as

$$j_x = (\sigma_n + \sigma_p)\, E_x \qquad\qquad \text{A-15}$$

$$\quad = (ne\,\mu_n + pe\mu_p)\, E_x \, .$$

Substituting Equations A-12 and A-14 into A-13, the Hall coefficient is

$$R = \frac{(-n\,\mu_n^{\,2} + p\,\mu_p^{\,2})}{e(n\mu_n + p\,\mu_p)^2} \qquad\qquad \text{A-16}$$

when both electrons and holes are present.

TABLE I

ENERGY GAP VALUES FOR REPRESENTATIVE SEMICONDUCTORS*

Semiconductor	Energy Gap Eg (ev)
Diamond	5.3
Si	1.21
Ge	0.785
Sn (grey)	0.08
Te	0.33
Si (hexagonal)	3.0
(zinc blend)	1.9
AlSb	1.6
GaP	2.4
GaAs	1.6
GaSb	0.8
InP	1.3
InAs	0.45
InSb	0.250
CdS	2.4
HgTe	0.01
PbS	0.39
PbSe	0.27
PbTe	0.33
Bi_2Te_3	0.2
MoS_2	1.45
MgO	7.4
ZnO	3.2
CdO	2.3
Cu_2O	2.0
TiO_2	3.0

* [2]

20

TABLE II

THE UNITS USED IN THE "PRACTICAL" SYSTEM AND A LIST OF
PHYSICAL CONSTANTS EXPRESSED IN "PRACTICAL" UNITS

PRACTICAL UNITS

QUANTITY	UNIT
Length	Centimeter
Mass	Gram
Time	Second
Force	Dyne
Work	Erg
Charge	Coulomb
Potential Difference	Volt
Current	Ampere
Electric Field	Volt/Centimeter
Magnetic Field	Gauss

PHYSICAL CONSTANTS

Absolute Zero	$0°K = -273.2°C$
Boltzmann Constant	$k = 1.380 \times 10^{-16}$ erg/deg.
Charge on Electron	$e = 1.602 \times 10^{-19}$ coulomb
Energy of Electron Volt	$1 \text{ ev} = 1.602 \times 10^{-12}$ erg
Mass of Electron	$m = 9.108 \times 10^{-28}$ gram
Planck's Constant	$h = 6.624 \times 10^{-27}$ erg-sec.

VACANT
CONDUCTION BAND

THERMALLY ACTIVATED
ELECTRONS

FORBIDDEN
BAND

E_g

FERMI LEVEL

E_F

FILLED
VALENCE BAND

HOLES
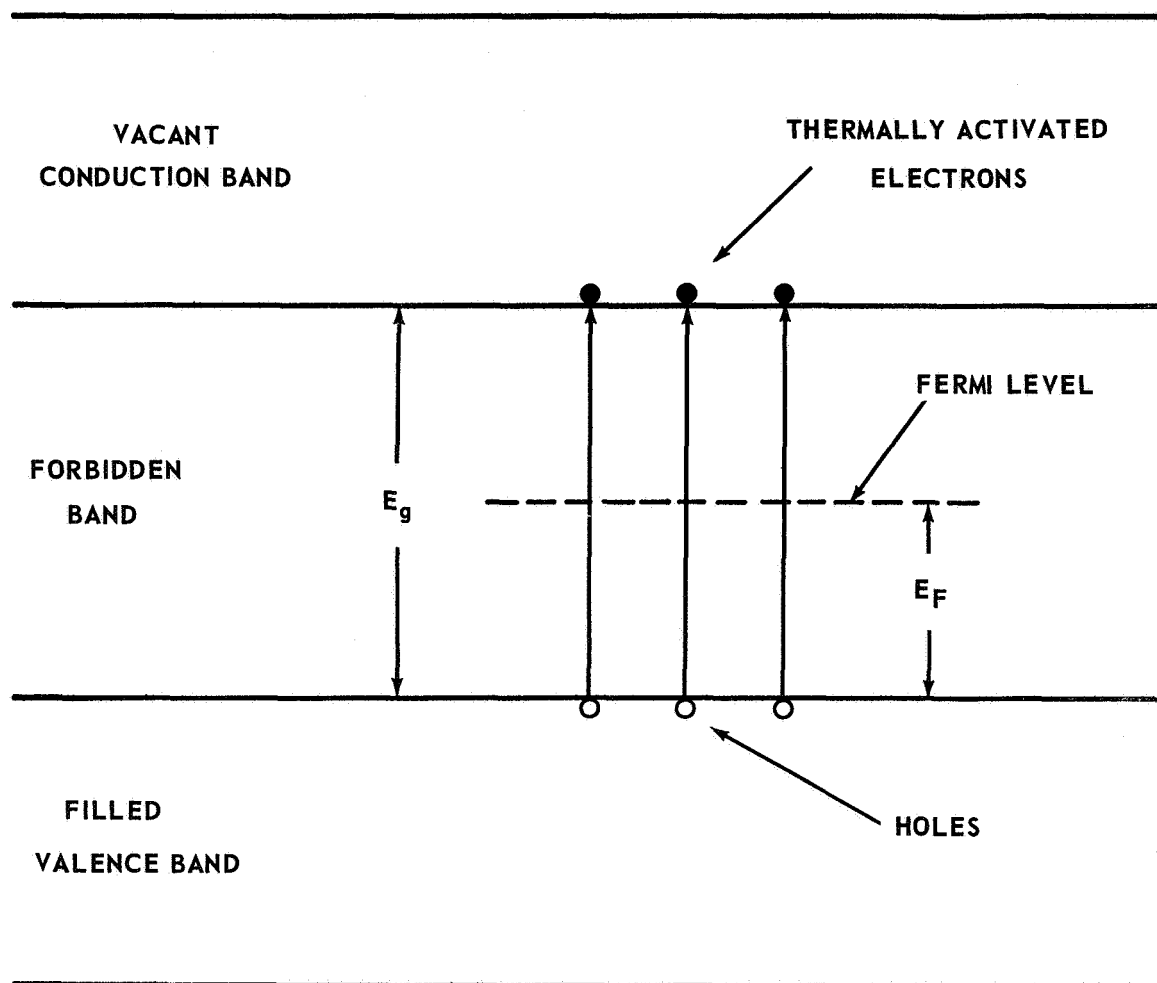
FIGURE 1. -- ENERGY BAND DIAGRAM OF AN
IMPURITY-FREE SEMICONDUCTOR

22

● ELECTRONS
O HOLES

CONDUCTION BAND

DONOR LEVELS

FORBIDDEN
BAND

ACCEPTOR LEVELS

VALENCE BAND
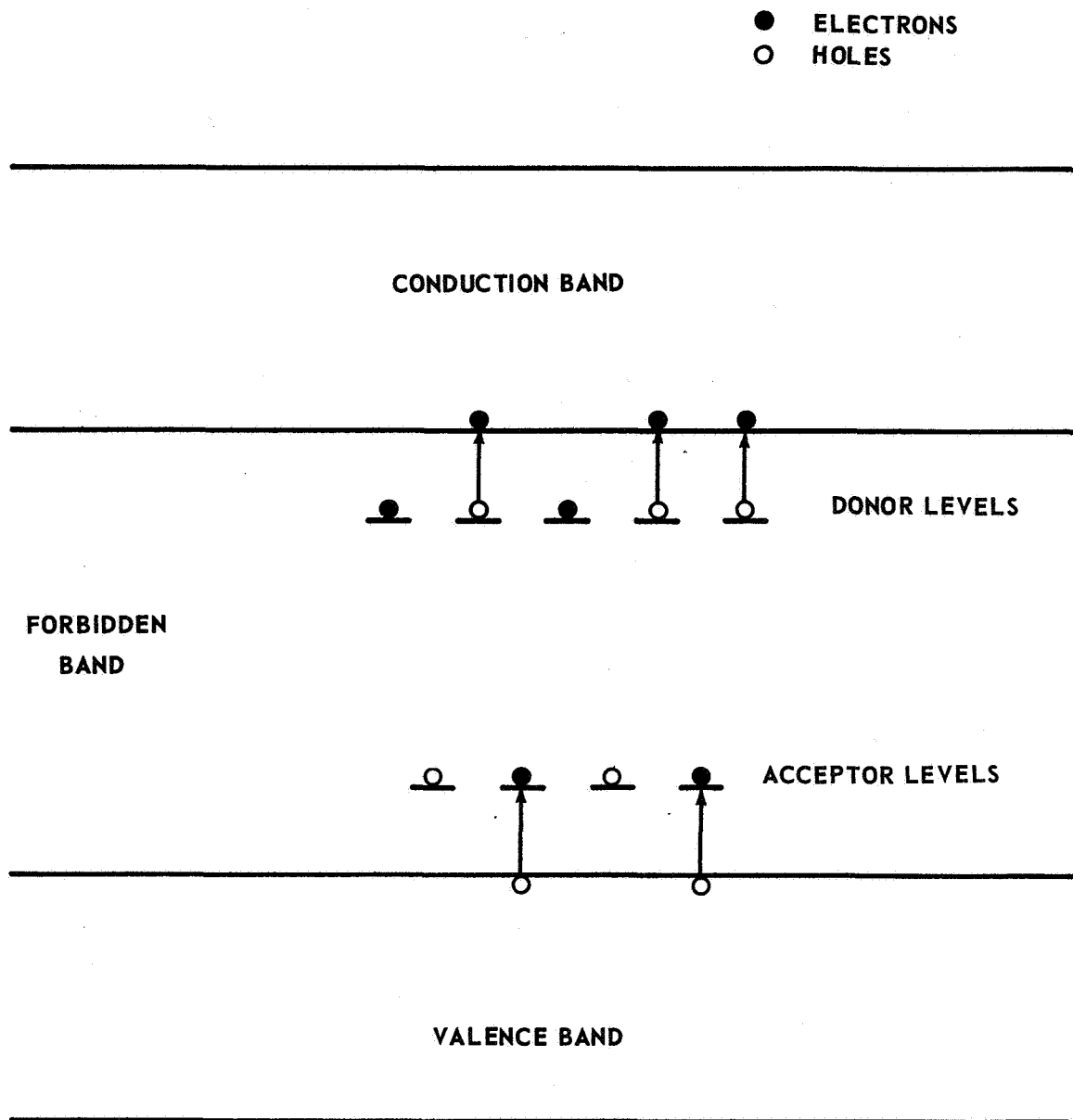
FIGURE 2. – ENERGY BAND DIAGRAM OF AN
EXTRINSIC SEMICONDUCTOR

23
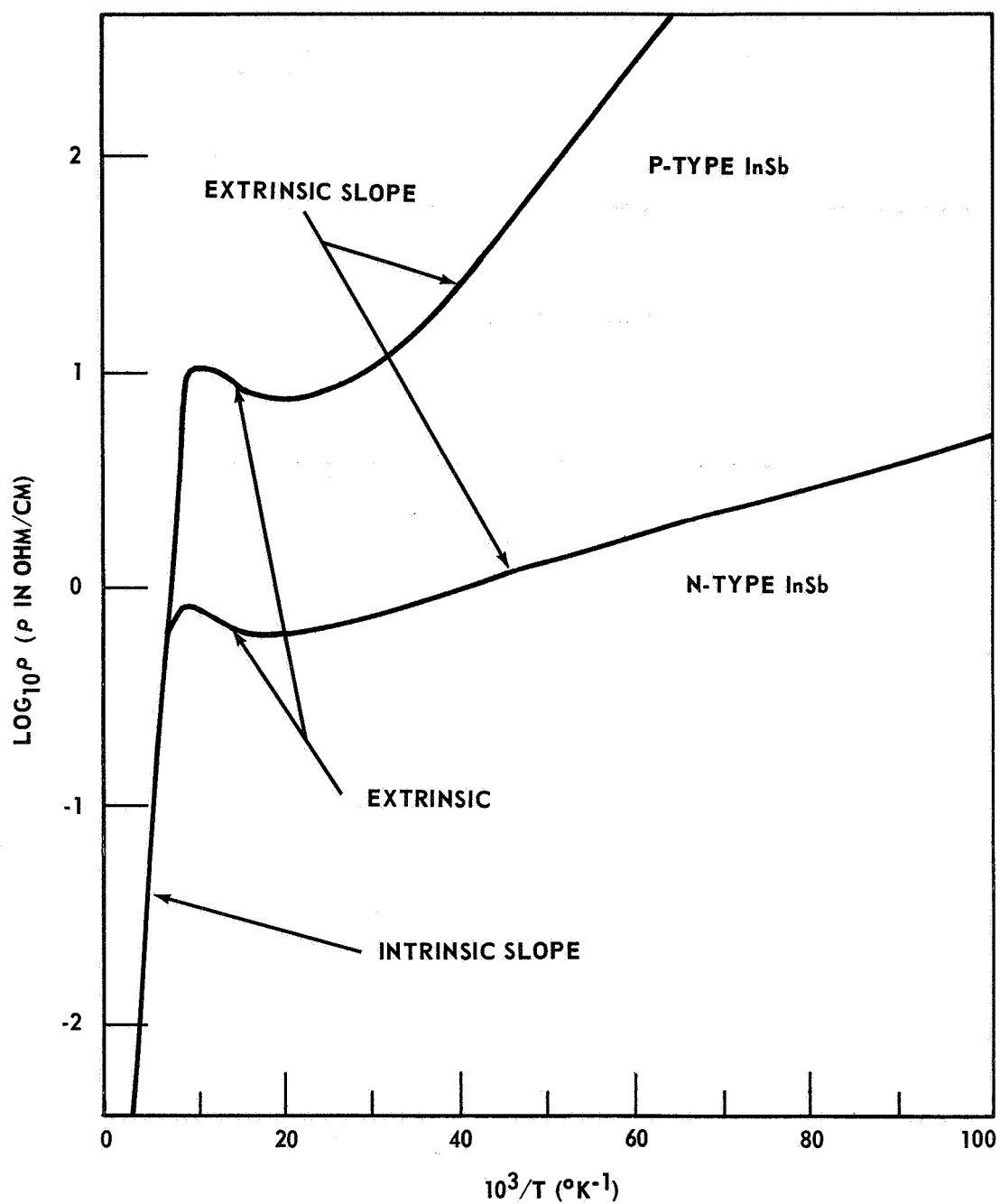
FIGURE 3. — RESISTIVITY VS. RECIPROCAL TEMPERATURE OF
N- AND P-TYPE InSb (REF. 2) ILLUSTRATING
THE WIDE RANGE OF VALUES WHICH
MAY BE ENCOUNTERED
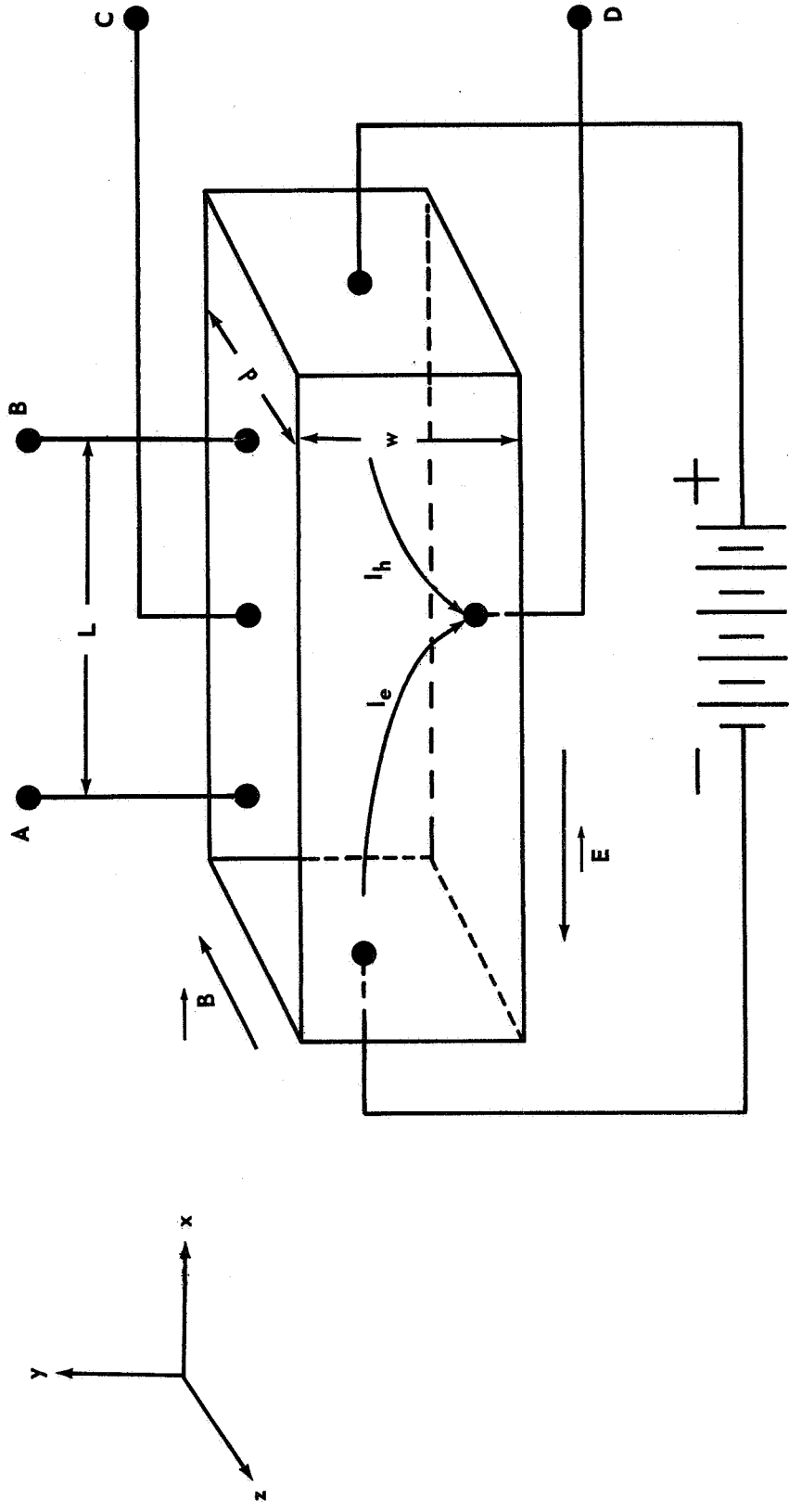
FIGURE 4. - TYPICAL ARRANGEMENT FOR MEASURING RESISTIVITY AND HALL COEFFICIENT

MAGNETIC FIELD INTO PAPER   A – B RESISTIVITY CONTACTS
                               C – D HALL CONTACTS

COIL SPRING

BERYLLIUM COPPER
LEAF SPRING

CURRENT CONTACTS

A

D

C

SAMPLE

B

TENSIONING SCREWS

THERMOCOUPLE LEADS
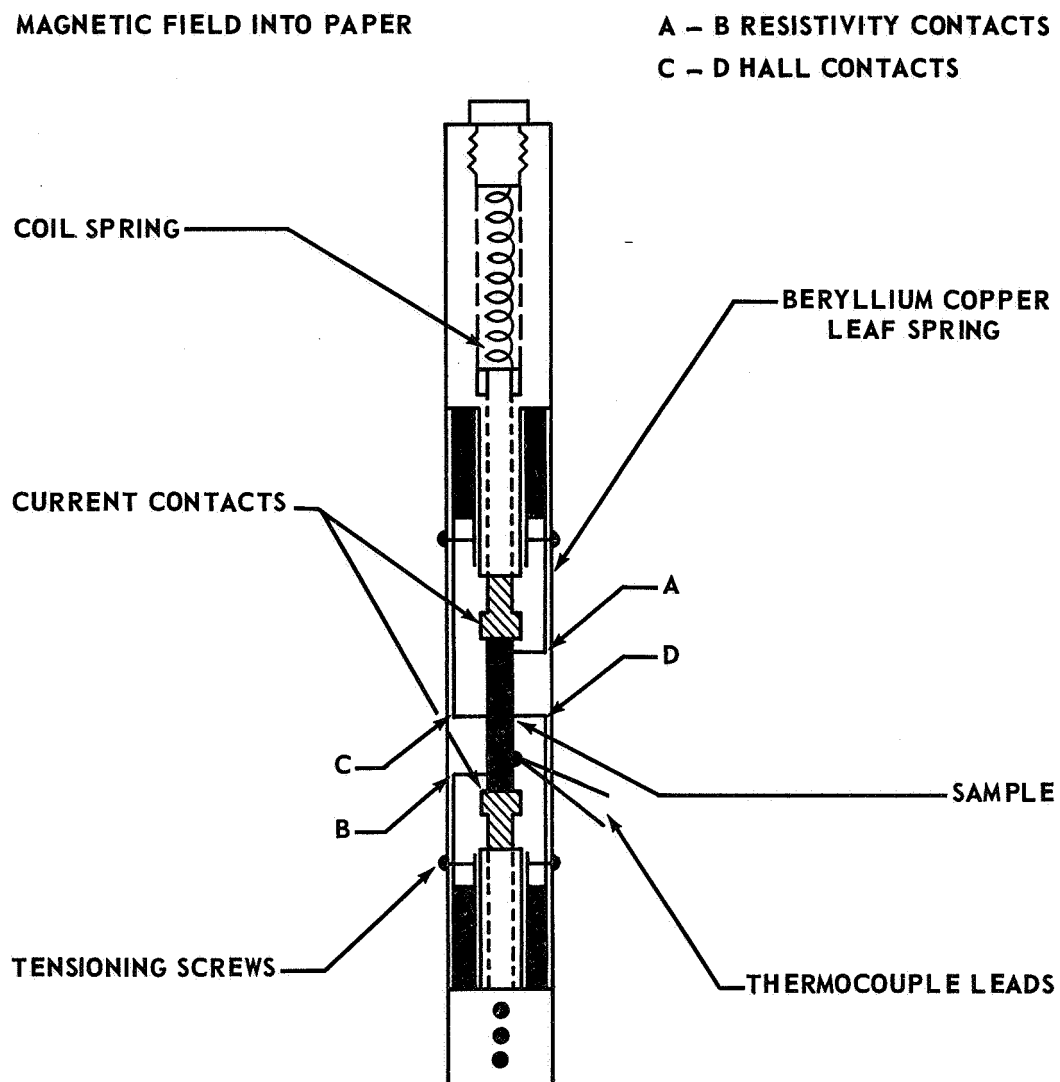
FIGURE 5. - SIMPLIFIED DIAGRAM OF THE SPECIMEN HOLDER FOR MEASURING
RESISTIVITY AND HALL COEFFICIENT

26
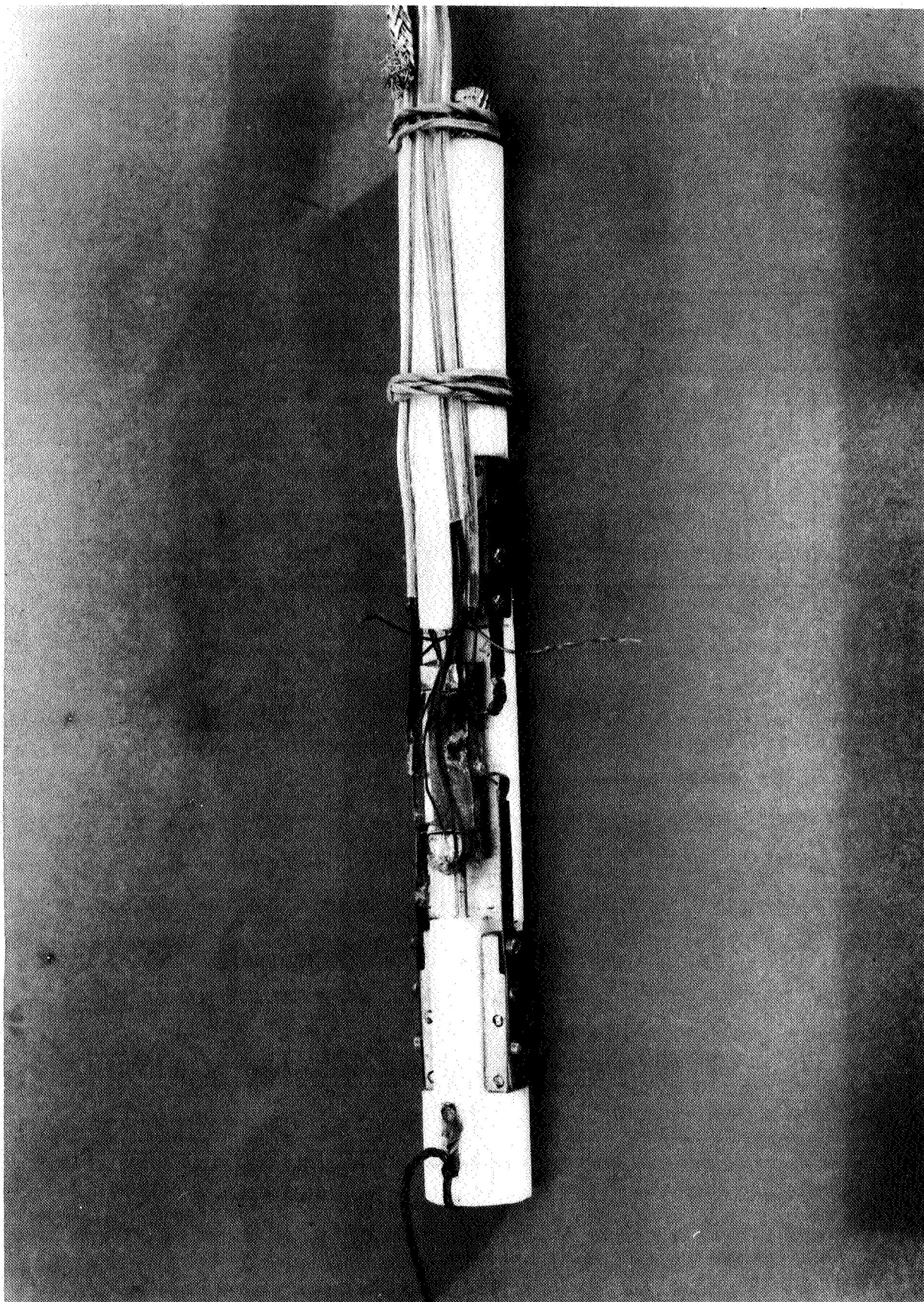
FIGURE 6. PHOTOGRAPH OF ASSEMBLED SPECIMEN HOLDER WITH SPECIMEN IN PLACE

EVACUATION PORT

CONAX FEEDTHRU

COPPER TUBING

DOVETAIL

HEATER

COPPER ROD

LOW TEMP. HEAT SINK
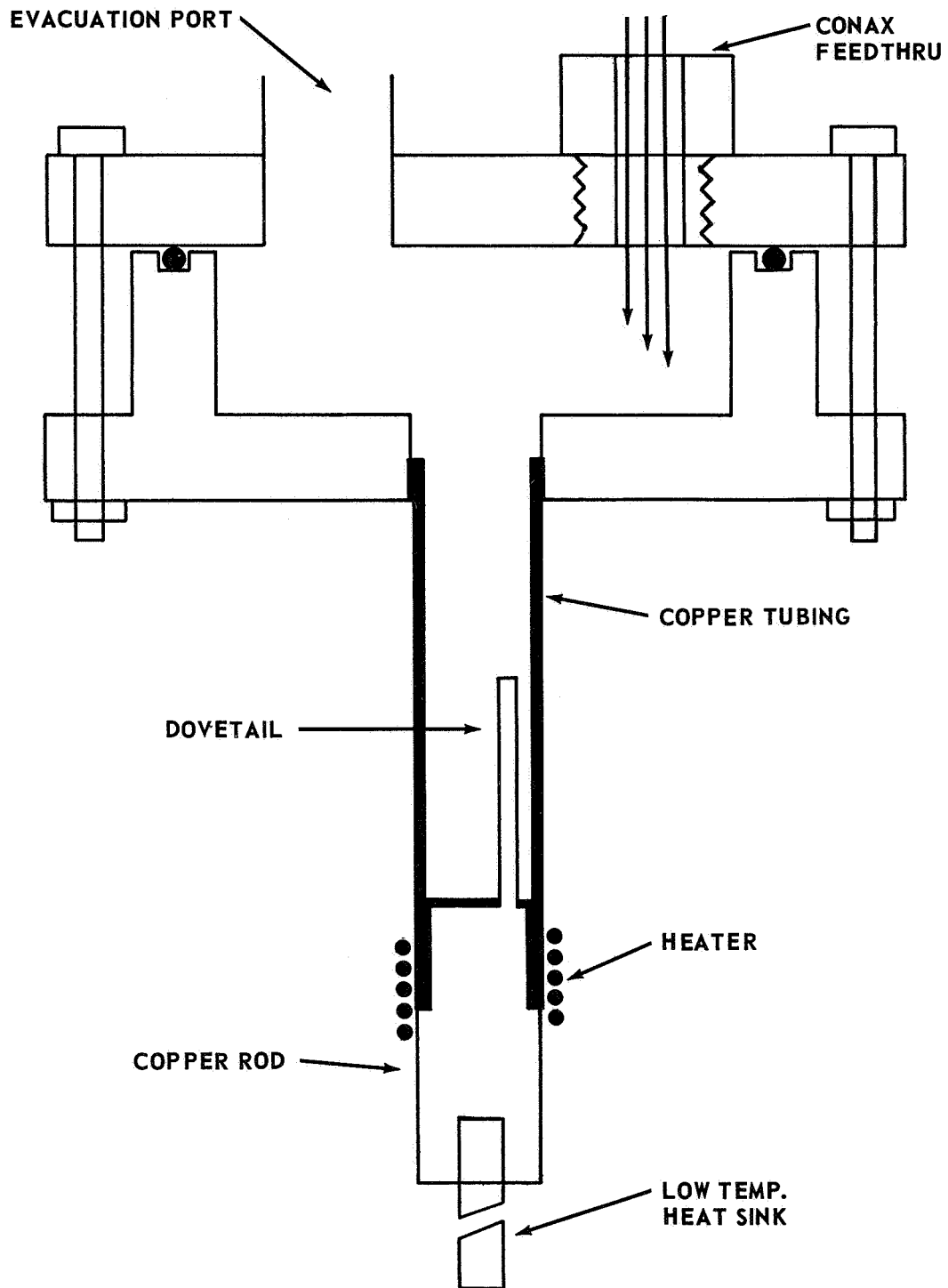
FIGURE 7. - DIAGRAM OF THE SPECIMEN CHAMBER

28
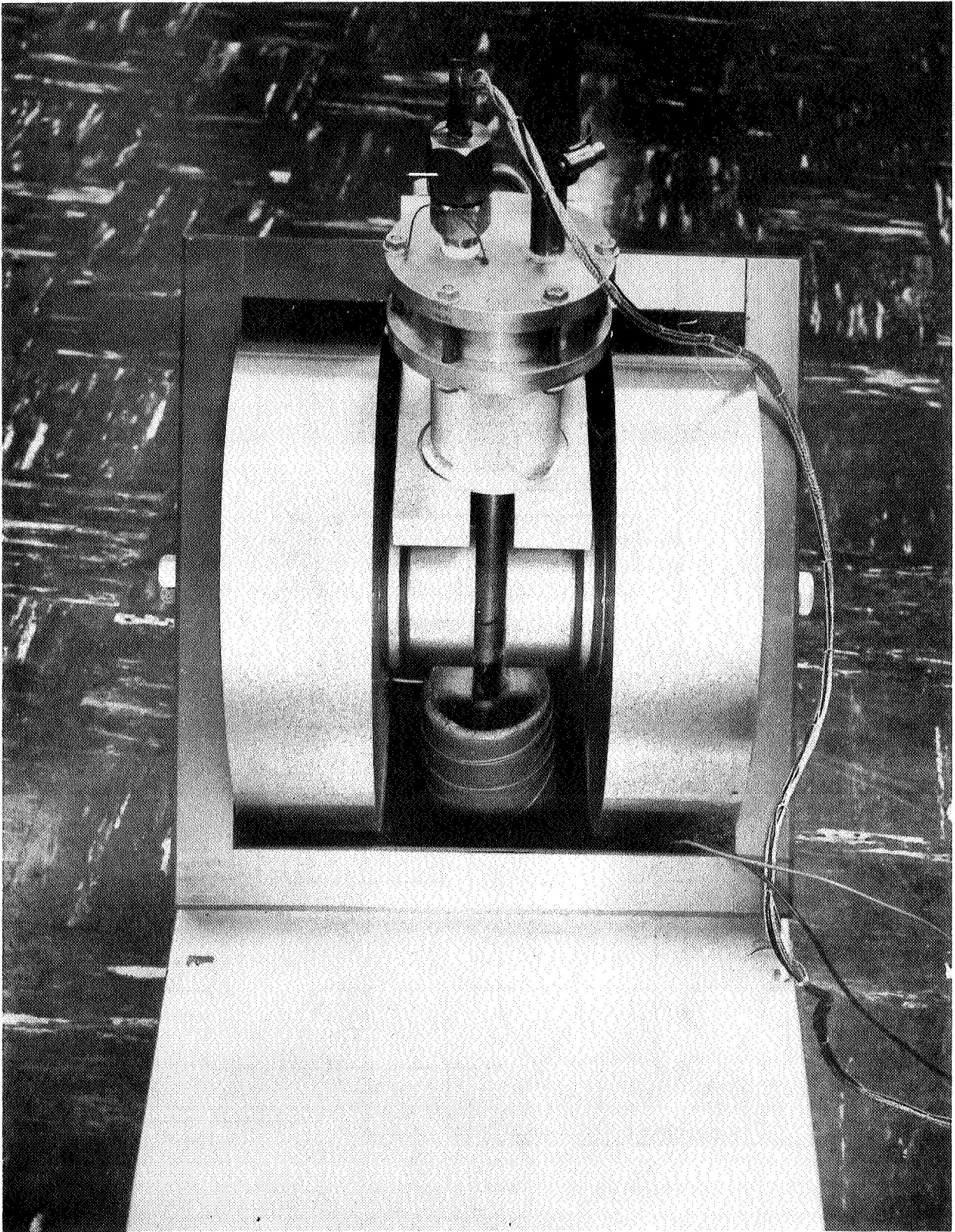
FIGURE 8. PHOTOGRAPH OF SPECIMEN CHAMBER INSTALLED IN MAGNET
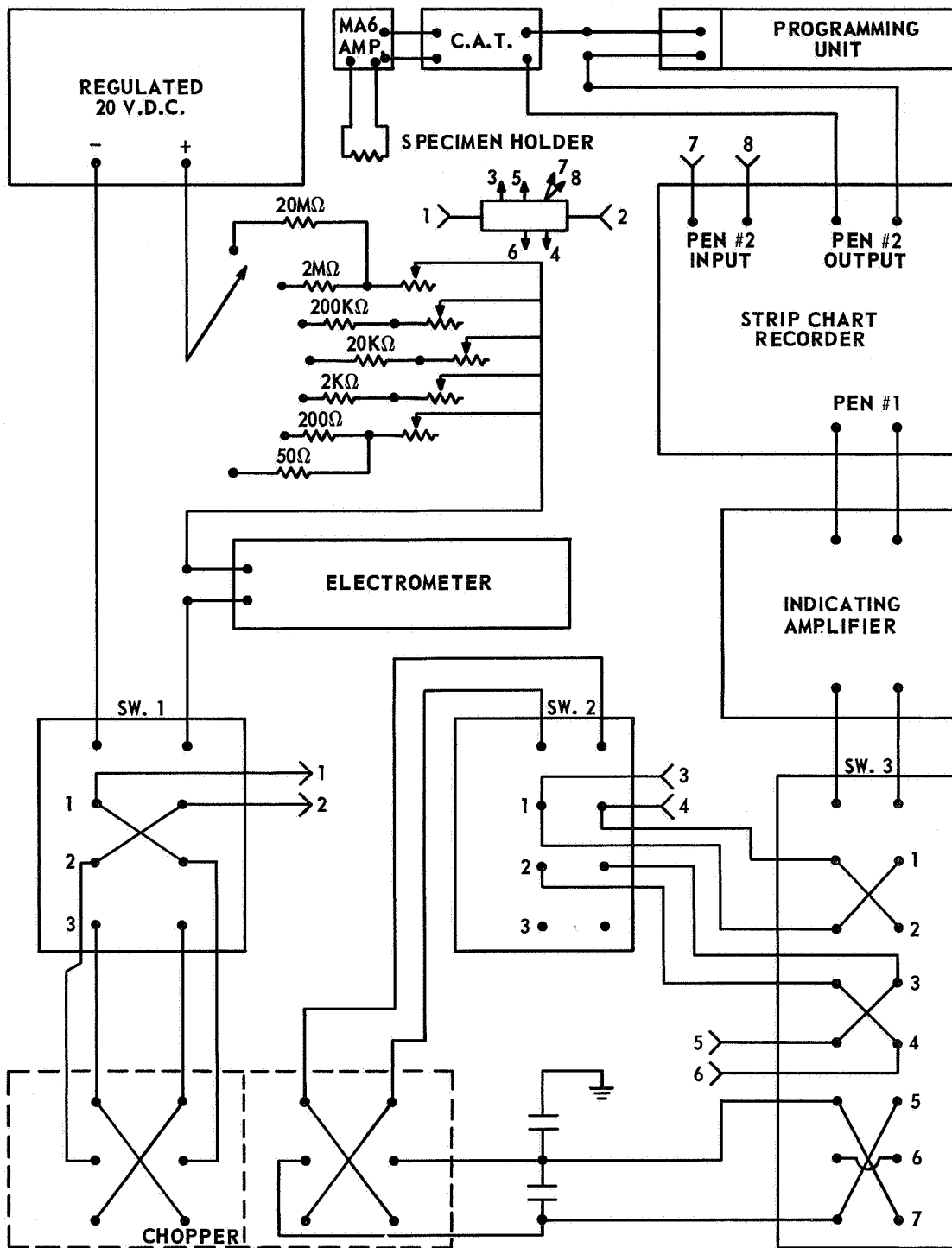
FIGURE 9. - ELECTRICAL CURRENT FOR RESISTIVITY AND HALL
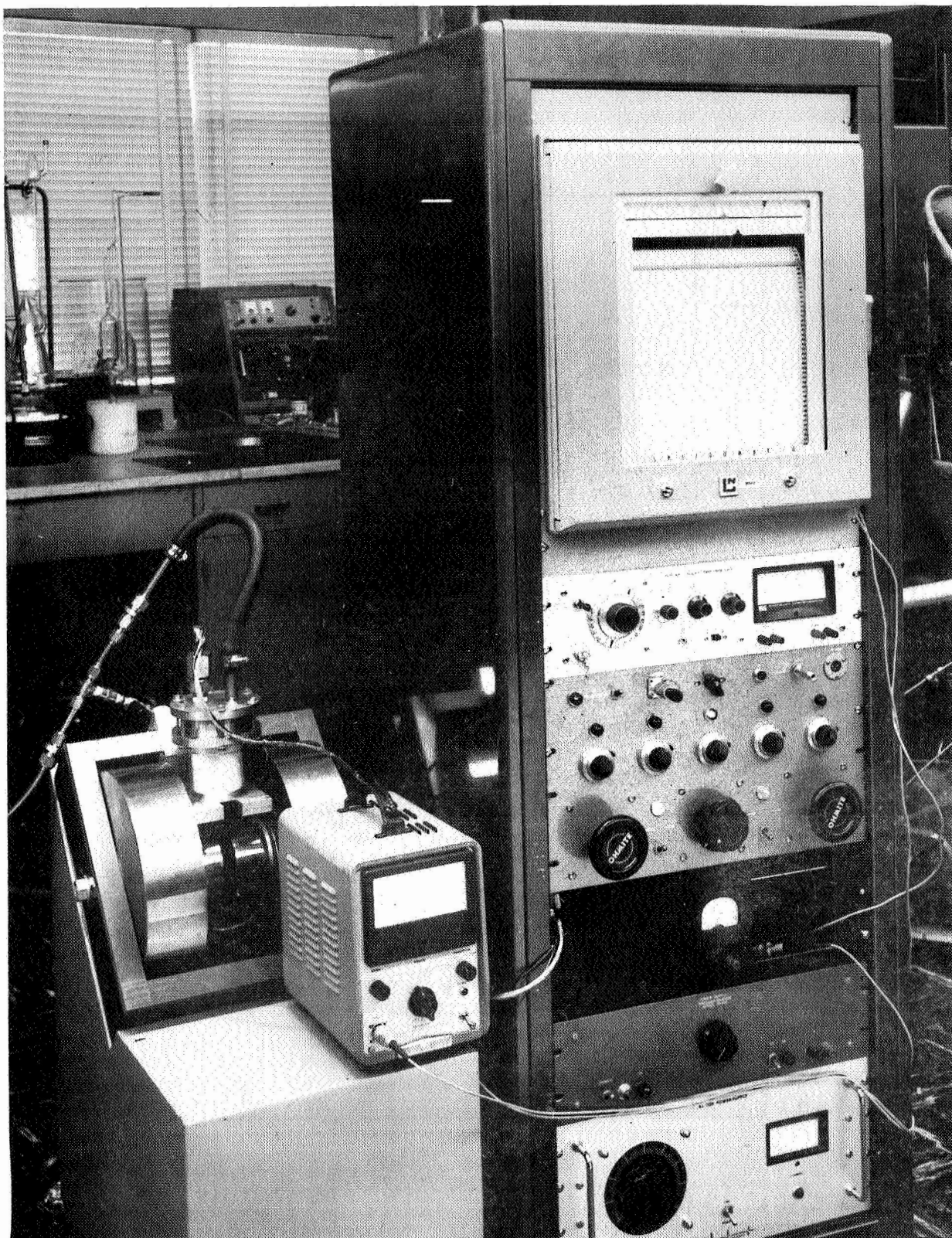COEFFICIENT MEASURING APPARATUS

FIGURE 10. A PHOTOGRAPH OF THE RESISTIVITY AND
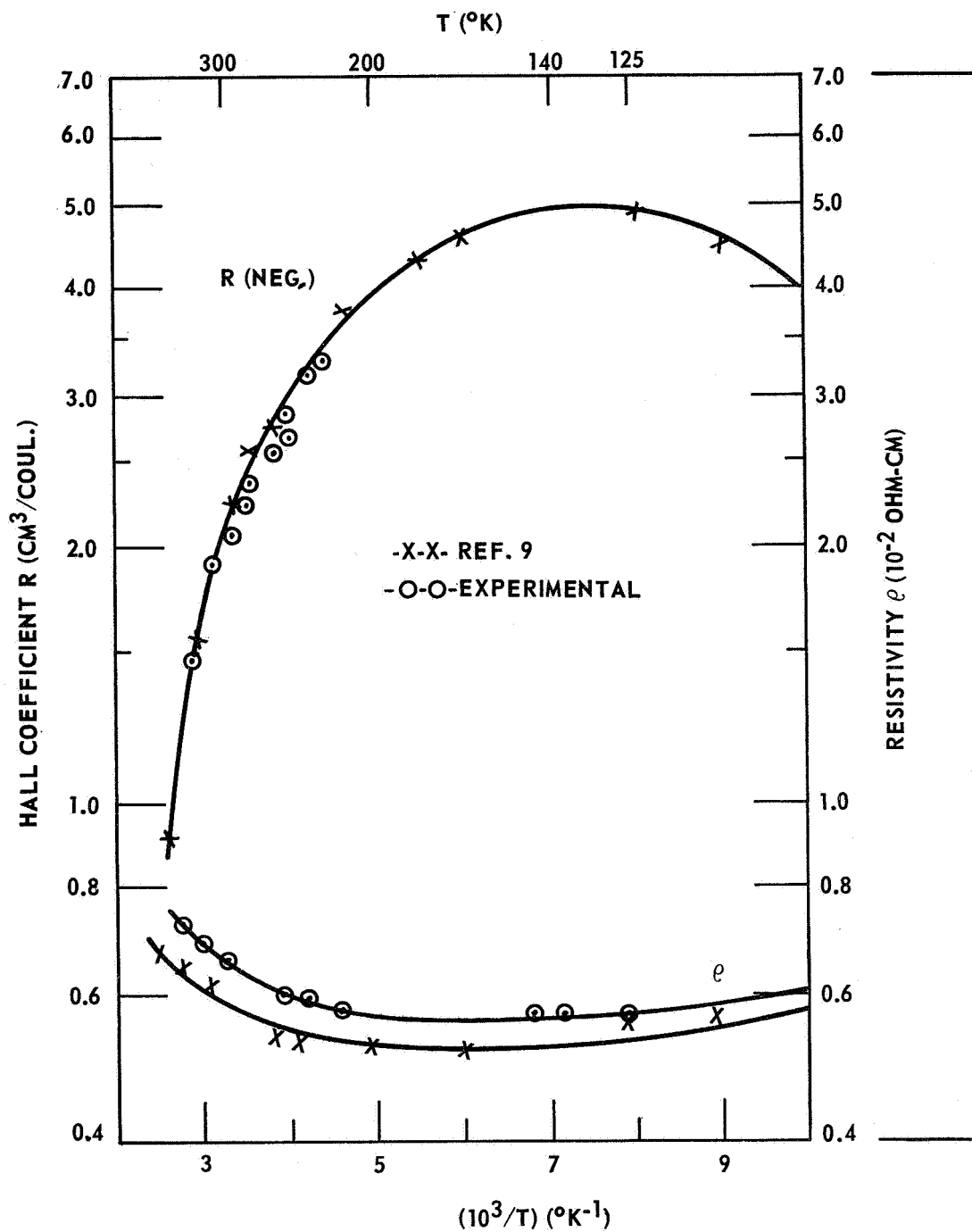HALL COEFFICIENT MEASURING APPARATUS

FIGURE 11. - RESISTIVITY AND HALL COEFFICIENT OF A SPECIMEN
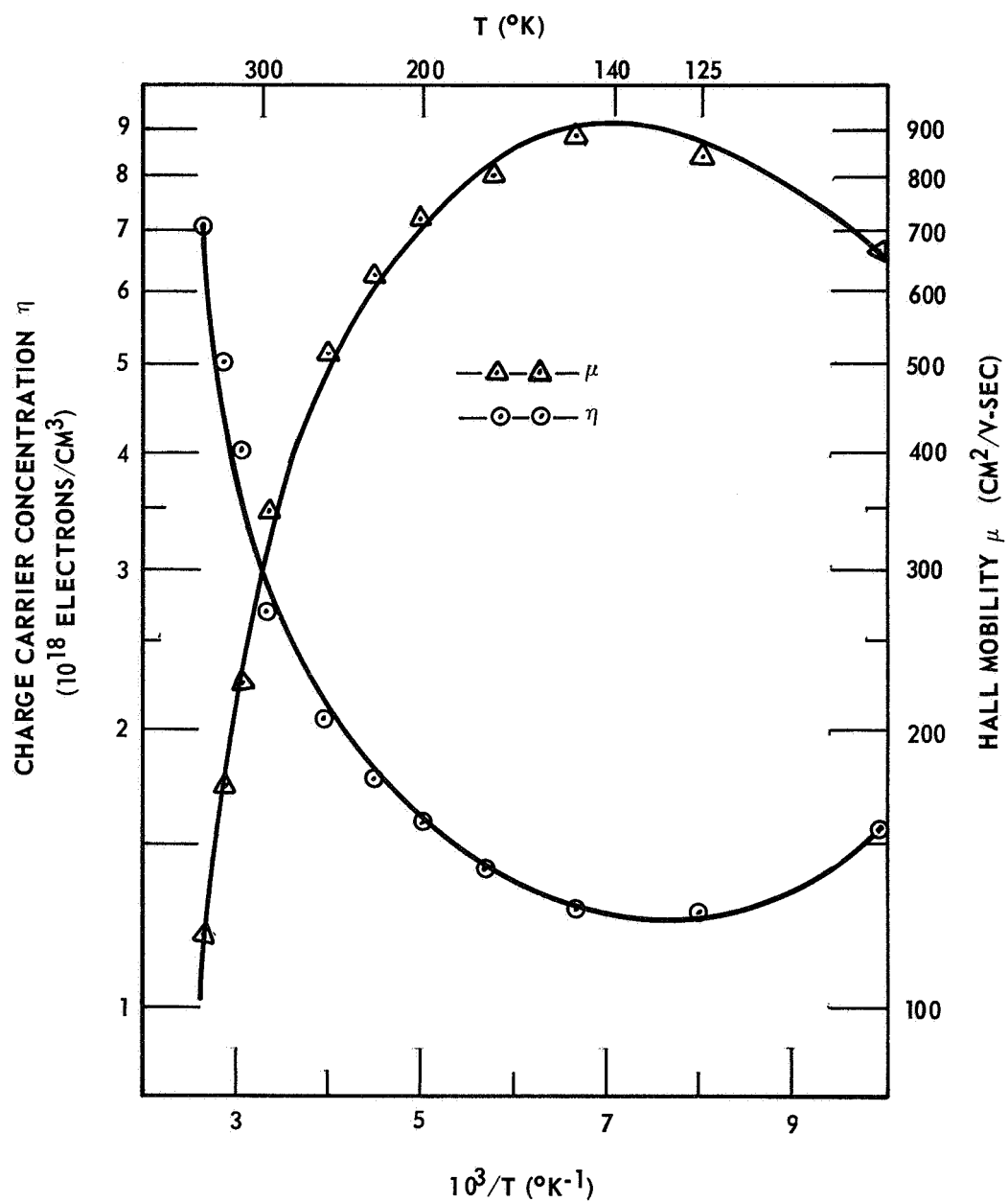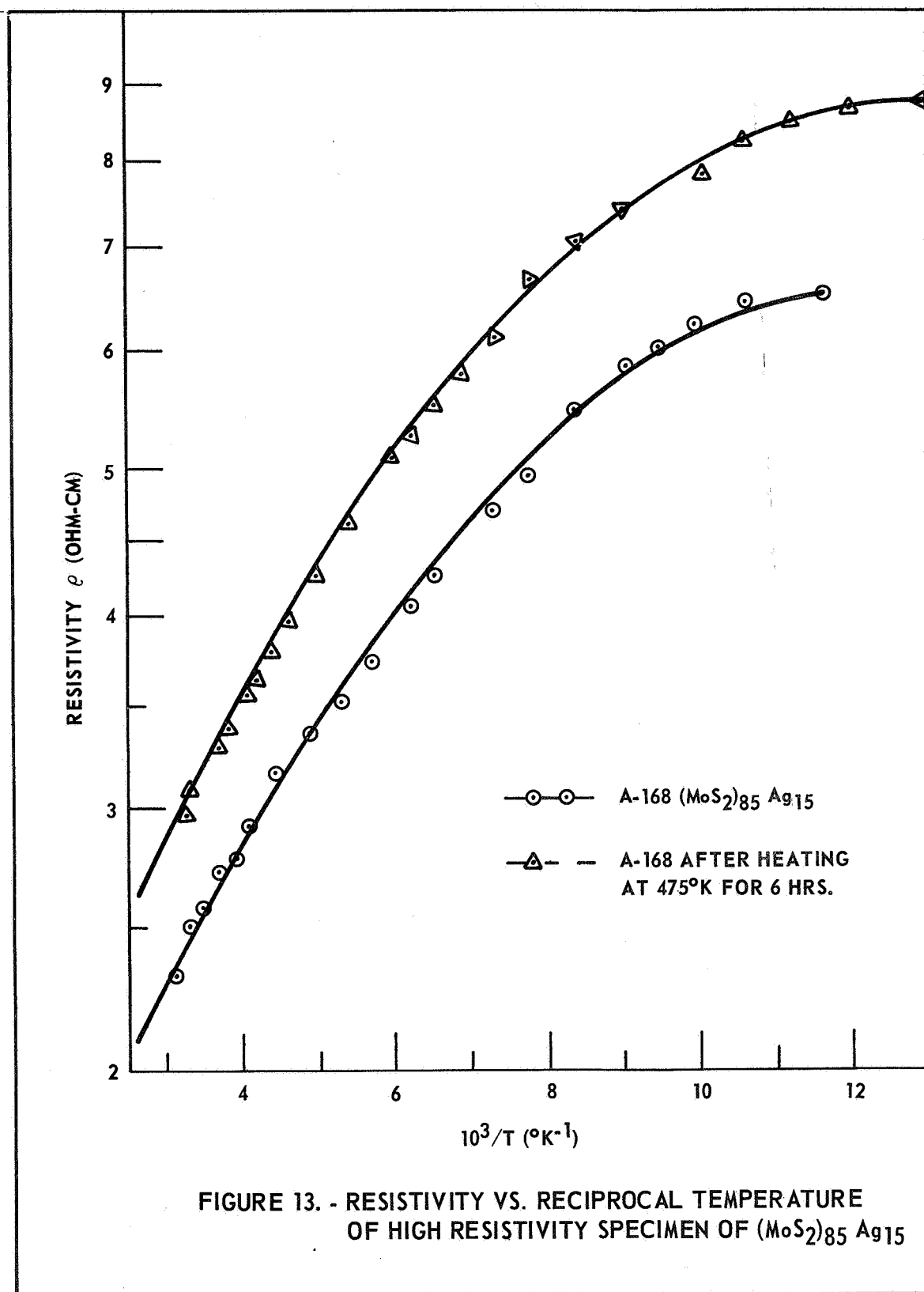OF $Ag\ Sb_{0.8}\ Fe_{0.2}\ Te_2$

FIGURE 12. - CHARGE CARRIER CONCENTRATION AND HALL MOBILITY
FOR $AgSb_{0.8} Fe_{0.2} Te_2$

FIGURE 13. - RESISTIVITY VS. RECIPROCAL TEMPERATURE
OF HIGH RESISTIVITY SPECIMEN OF $(MoS_2)_{85}$ Ag_{15}
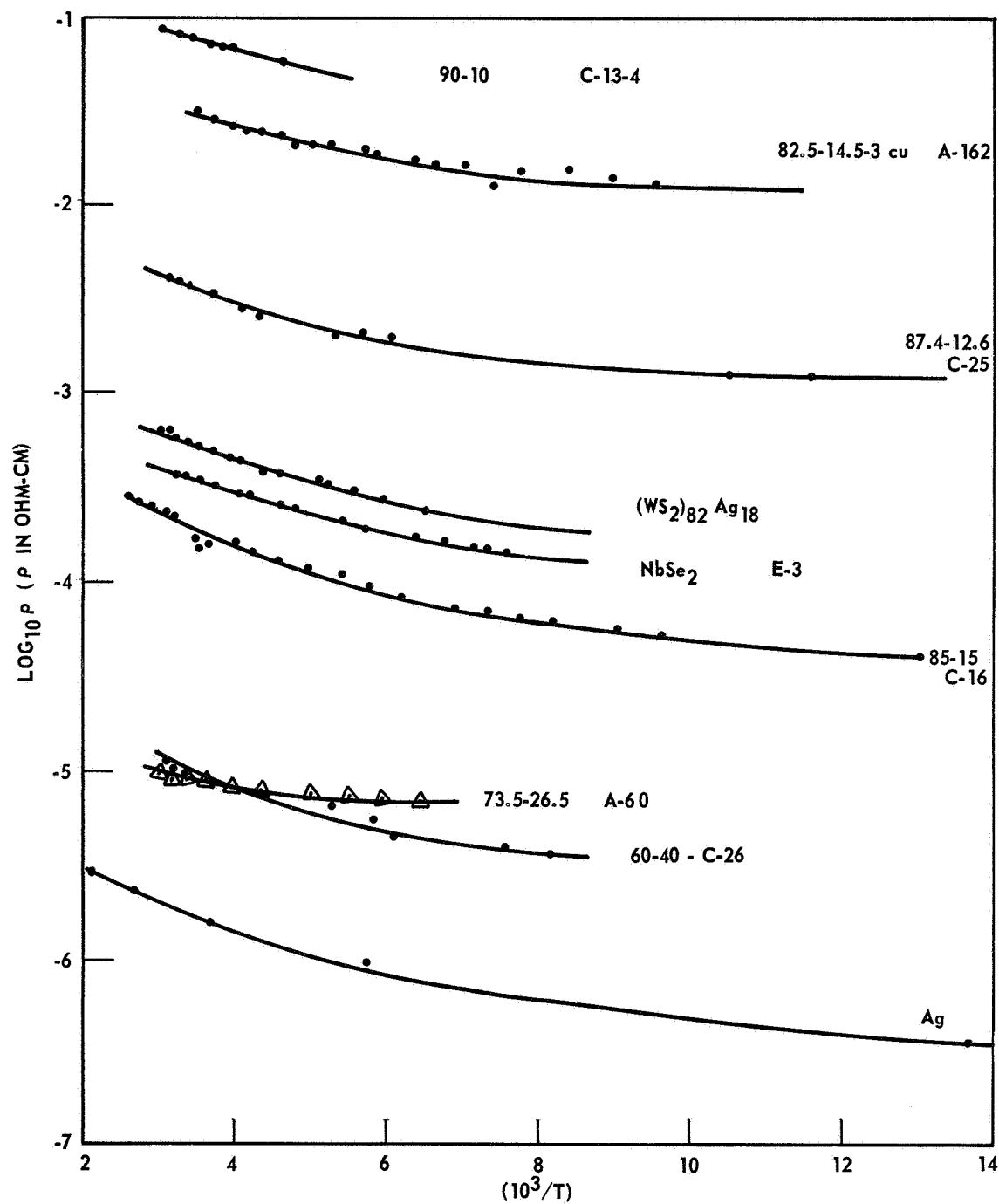
FIGURE 14. - RESISTIVITY VS. RECIPROCAL TEMPERATURE OF 8 ELECTRICAL BRUSH SPECIMENS COMPARED TO PURE SILVER

REFERENCES

1. Kittel, C.: Introduction to Solid State Physics. Second ed., John Wiley and Sons, Inc., New York, 1956.

2. Putly, E. H.: The Hall Effect and Related Phenomena. Butterworth, Inc., Washington, D. C., 1960.

3. Dekker, A. J.: Solid State Physics. Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1962.

4. Shockley, W.: Electrons and Holes in Semiconductors. D. Van Nostrand Company, Inc., Princeton, New Jersey, 1950.

5. Warschauer, D. M.: Semiconductors and Transistors. McGraw-Hill Book Company, Inc., 1959.

6. Blakemore, J. S.: Semiconductor Statistics. Pergamon Press, New York, 1962.

7. Brooker, A. A.: Clay, and Young: J. Sci. Instr., Vol. 34, 1957, p. 512.

8. Jerrard, H. G., and McNeill, D. B.: Theoretical and Experimental Physics. Chapman and Hall, London, 1960.

9. Anon: Development of Improved Thermoelectric Materials for Spacecraft Applications. Seventh Monthly Report, (NAS8-11075), March 1964.

10. Gray, D. E., et. al.: American Institute of Physics Handbook. Second Ed., McGraw-Hill Book Company, Inc., 1963.

DETERMINATION OF RESISTIVITY AND HALL COEFFICIENT
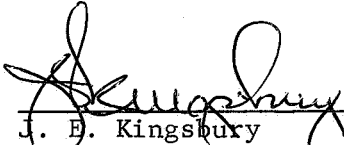OF SEMICONDUCTING MATERIALS BETWEEN 80°K AND 375°K

By R. C. Ruff

The information in this report has been reviewed for security classification. Review of any information concerning Department of Defense or Atomic Energy Commission programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.
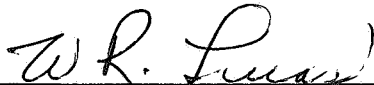
This document has also been reviewed and approved for technical accuracy.

E. C. McKannan
Chief, Engineering Physics Branch

J. E. Kingsbury
Chief, Materials Division

W. R. Lucas
Director, Propulsion and Vehicle Engineering Laboratory

DIR	Dr. von Braun
DEP-T	
I-RM-M	
R-P&VE-DIR	Dr. Lucas
R-P&VE-S	Mr. Kroll
R-P&VE-P	Mr. Paul
R-P&VE-A	Mr. Goerner
R-P&VE-M	Mr. Kingsbury (6)
R-P&VE-M	Mr. Gray
R-P&VE-M	Mr. Holmes
R-P&VE-M	Mr. Riehl
R-P&VE-MM	Mr. Cataldo
R-P&VE-MN	Mr. Curry
R-P&VE-ME	Mr. McKannan
R-P&VE-RM	Miss Scott
R-P&VE-MEV	Mr. Horton
R-P&VE-MEV	Mr. Ruff (25)
R-QUAL-DIR	Mr. Grau
R-QUAL-A	Mr. Henritze
R-ASTR-DIR	Dr. Haeussermann (2)
R-RP-DIR	Dr. Stuhlinger
MS-IP	Mr. Remer
MS-IL	Miss Robertson (8)
MS-T	Mr. Wiggins (6)
MS-H	Mr. Akens
PAT	Mr. Wofford

Scientific and Technical Information Facility (25)
P. O. Box 33
College Park, Maryland 20740
        Attn: NASA Representative (S-AK/RKT)

38