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Some Properties of *p*-Type Gallium Antimonide between 15°K and 925°K

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Gallium antimonide has been produced by direct combination of gallium and antimony under hydrogen. The product was zone refined and pulled in single crystal form using the Czochralski technique. The product was *p* type, with resistivities in the range 0.08–0.1 ohm cm. Hall coefficient and resistivity were measured in the temperature range 15–925°K. The slope of the Hall curve at low temperatures yielded the value 0.024 ev for the ionization energy of the carriers. It has been shown necessary to assume an additional acceptor level at 0.037 ev. The room temperature mobility of several samples was about 800 cm^2/volt sec. The Hall mobility varied as $T^{-0.87}$ in the temperature range below room temperature, but the slope changed at about room temperature, and shifted nearly to a $T^{-\frac{3}{2}}$ law in the higher temperature range. The Hall coefficient changed sign at 357°C, as the sample became intrinsic. The mobility ratio was determined from the ratio of the extrapolated extrinsic resistivity and the actual resistivity at the Hall inversion temperature. The value was about 5. The effective mass and intrinsic band gap were estimated from the resistivity data and infrared measurements. The best values were estimated to be $0.20m$ for the effective mass of electrons, $0.39m$ for holes, and 0.80 ev for the intrinsic band gap at 0°K. The best value for room-temperature band gap was taken to be 0.71 ev; the coefficient of band gap with temperature 3×10^{-4}/°C.

INTRODUCTION

The properties of semiconducting intermetallic compounds have become of increasing interest during the last several years. Work on Mg_2Sn,[1] for example, indicated that intermetallic compounds could be semiconductors. The work of Welker[2] has focused attention on the intermetallic compounds of the third and fifth column elements. Recently, there have been a number of publications[3–7] dealing, in particular, with the properties of aluminum, gallium, and indium antimonide.

It is the object of the present work to present results on the temperature variation of some of the conduction properties of single crystals of gallium antimonide, in the temperature range 15°K to close to the melting point (about 700°C). The results are preliminary in the sense that they deal only with *p*-type material of rather high carrier density.

PREPARATION OF GALLIUM ANTIMONIDE SINGLE CRYSTALS

Purest available commercial antimony and gallium were used as starting materials and zone refining[8] was employed for additional purification of the antimony metal. The compound was prepared by direct combination of the two elements. Gallium metal was brought to a temperature of approximately 750°C in a crucible at the bottom of a quartz tube in an atmosphere of dry hydrogen. Antimony metal, at room temperature, was contained in a side arm connected to the main body of the tube through a ground joint. Antimony could thus be introduced into the molten gallium in small amounts making it possible to keep the temperature up to 750°C. This method insures intimate mixing and minimizes the evaporation of antimony.

The compound was subsequently zone refined and used for the production of single crystals ($\frac{1}{2}$ in. diam. $\times$3 in.) by the Czochralski technique, using seed crystals obtained from the zone-refined compound. Quartz crucibles and a hydrogen atmosphere were used.

EXPERIMENTAL MEASUREMENTS

Gallium antimonide is remarkably similar to germanium in appearance and many of its physical properties. Etching of the samples was accomplished with diluted $HF-HNO_3$, a standard etchant for germanium. As for *p*-type germanium, indium was found to make quite satisfactory nonrectifying contacts.

The low-temperature measurements were made on rectangular plates (1 cm$\times$0.5 cm$\times$0.2 cm) on which six contacts were indium-soldered for the Hall effect and resistivity measurements. The samples were mounted inside a low-temperature cryostat and a calibrated copper-constantan thermocouple was used for the temperature measurements. The reversal of the field could be made by rotation of the permanent magnet through 180°. All the voltage measurements were made with a Rubicon Type-B low-impedance potentiometer.

For the high-temperature measurements, the samples were cut in a form[9] such that the probes were all narrow projections from the sample itself. The samples were mounted inside a special high-temperature vacuum

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[1] W. D. Robertson and H. H. Uhlig, Trans. Am Inst. Mining Met. Engrs. **180**, 345 (1949). See also B. I. Boltaks, J. Tech. Phys. (U.S.S.R.) **20**, 180 (1950).

[2] H. Welker, Z. Naturforsch. **7a**, 744 (1952); **8a**, 248 (1953).

[3] Breckenridge, Hosler, and Oshinsky, Phys. Rev. **91**, 243 (1953); see also Phys. Rev. **90**, 488 (1953).

[4] Willardson, Beer, and Middleton, Phys. Rev. **91**, 243 (1953); see also Phys. Rev. **93**, 912 (1954).

[5] M. Tanenbaum and G. L. Pearson, Phys. Rev. **91**, 244 (1953); Phys. Rev. **93**, 912 (1954).

[6] M. Tanenbaum and J. P. Maita, Phys. Rev. **91**, 1009 (1953).

[7] D. A. Jenny, AIEE–IRE Semiconductor Devices Conference, Pennsylvania State College, July, 1953 (unpublished).

[8] W. G. Pfann, J. Metals **4**, 747 (1952).

[9] Dunlap, McMillan, and Brooks, Phys. Rev. **93**, 911 (1954).

furnace and chromel-alumel thermocouples were used for temperature measurements. This furnace was found to give almost complete freedom from errors arising from temperature inhomogeneity in the furnace and from the thermoelectric voltages arising therefrom. The sample was held in a quartz holder with graphite contacts to prevent chemical action between sample and contacts. A vacuum of better than 10^{-4} mm Hg was maintained in the system during heating and measurement.

In both the low- and the high-temperature measurements, it is necessary to restrict values of sample current in order that ohmic heating may not change the sample temperature and thus change the observed properties. At all temperatures the samples were found to obey Ohm's law satisfactorily.

RESULTS

The results on a typical sample are shown in Fig. 1 as the logarithm of both the Hall effect and resistivity *versus* the reciprocal temperature. It is seen that the Hall coefficient increases continuously as the temperature is lowered from room temperature, whereas the resistivity goes through a minimum and then increases. The slope of the Hall curve, although not quite constant, is used to estimate an ionization energy of about 0.024 ev, based upon the equation

$$1/R \propto n = n_0 \exp(-\Delta E/kT).$$

Both the Hall coefficient and the resistivity curves tend to flatten out at the lowest temperatures. This tendency was confirmed by a resistance measurement in liquid helium which showed that the resistance at 4°K was about 20 times that at 20°K. Thus there is evidence of a conductivity, in parallel with that of 0.024 ev ionization-energy carriers, which limits the resistance attainable on cooling. The present information is insufficient to determine whether this low-temperature conductivity is a bulk or surface effect.

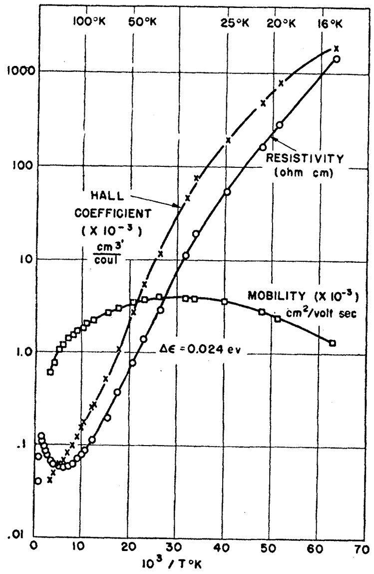

FIG. 1. Results of Hall effect and resistivity measurements on gallium antimonide single crystals at temperatures from 298°K down to 15°K.

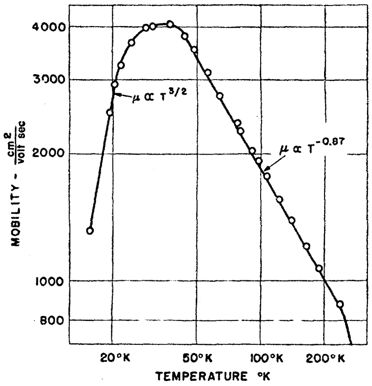

FIG. 2. Plot of log mobility *versus* log$T$ for a sample of gallium antimonide in the low temperature range. The maximum occurs at about 33°K.

The nature of the p-type centers in gallium antimonide has not been determined. They may be impurities, or they may be an excess of one of the constituents. In most cases studied to date, the carrier density at room temperature, as determined from the Hall data, was about $10^{17}/\text{cm}^3$.

The room temperature mobility varied somewhat from sample to sample, ranging from 700 to 850 cm^2/volt sec. Below room temperature, we see from Fig. 2 that the mobility increases with decreasing temperature, until 33°K is reached. Below this temperature, the mobility drops off.

Below the temperature of the maximum in Fig. 2, the mobility very nearly follows a $T^{\frac{3}{2}}$ law, as predicted for impurity scattering. However, employing the theory of Conwell and Weisskopf[10] and using the density of carriers at 33°K, one finds for the mobility due to impurity scattering $\mu_I \simeq 5 \times 10^5$ cm^2/volt sec. Since this value is large compared to the actual mobility, it appears that the drop in mobility below 33°K is determined by factors other than the charged impurity ions present. Possible factors could include effects of neutral impurities, imperfections and space-charge barriers in the material.

Above the temperature of the maximum in Fig. 2, the mobility obeys a $T^{-0.87}$ law. Since this temperature range is the region of deionization of carriers, it is necessary to consider scattering by charged and neutral impurities (with possibly comparable cross sections and differing temperature dependence). This makes interpretation difficult.

Figure 3 shows the mobility variation above room

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[10] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950).

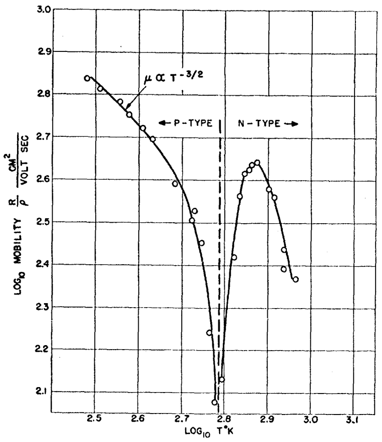

FIG. 3. Plot of log mobility *versus* log$T$ for the high-temperature region.

temperature on a logarithm mobility *versus* logarithm temperature scale. The beginnings of a change in mobility temperature dependence could be seen in Fig. 2 above 200°K. The straight line portion of the curve of Fig. 3 above room temperature and before the temperature at which intrinsic conduction begins indicates that the hole mobility follows very nearly a $T^{-\frac{3}{2}}$ law. We assume that this theoretical lattice scattering law ($T^{-\frac{3}{2}}$) is obeyed in the high-temperature range.

Figure 4 shows results of Hall and resistivity measurements on several samples of gallium antimonide, in the temperature range between 25°C and 650°C. The Hall coefficient changed sign at 357°C. It is seen that not all of the impurity centers become ionized until the temperature rises well above room temperature. This condition of the Hall coefficient continuously increasing as the temperature decreases will be considered in the next section.

Because of the low melting point (700°C) and the high impurity content, the sample never reached the condition that the number of intrinsic carriers greatly exceeded the number of impurity centers. For this reason, interpretation of the intrinsic resistivity line in terms of the theoretical band gap of the gallium antimonide lattice becomes more difficult than is usually the case. The detailed analysis is given in the next section.

DISCUSSION

Acceptor Level Model

The experimental shape of the Hall coefficient curve from about 30°K to the inversion temperature, cannot be justified on the assumption of a single acceptor level or one acceptor level plus donor levels. A model of two acceptor levels will, however, quite satisfactorily fit the experimental data. Calculations indicated that, in this model, donor levels play no part in the observed properties. The two acceptor levels needed to fit the data are at $E_{A1}=0.024$ ev and $E_{A2}=0.037$ ev and have a density of $N_{A1}=1.1\times10^{16}/\text{cm}^3$ and $N_{A2}=1.7\times10^{17}/\text{cm}^3$, respectively, for the particular samples studied here.

The Hall data provide the hole density and Fermi level at any temperature plus the experimental value of E_{A1}, as 0.024 ev. The charge neutrality condition is

$$p+p_{A1}+p_{A2}=N_{A1}+N_{A2}$$

where p is the hole density in the valence band, p_{A1} is the hole density in acceptor level A_1 whose density is N_{A1}, and p_{A2} is the hole density in acceptor level A_2 whose density is N_{A2}. At low temperatures (e.g., 50°K), A_2 may be neglected and N_{A1} determined. At higher temperatures (e.g., 100°K), these values are used to determine E_{A2} and N_{A2} which are interdependent. Since the ratio of acceptor-level densities is ten, it seems unlikely that they may both be attributed to a single imperfection.

Determination of the Mobility Ratio b

From an analysis of the Hall and resistivity data, one can determine the mobility ratio b for electrons and holes. The method essentially involves the determination of the actual resistivity and the extrapolated extrinsic resistivity, at the temperature of inversion of the Hall coefficient. For the sample studied most intensively, this temperature (T') was 357°C.

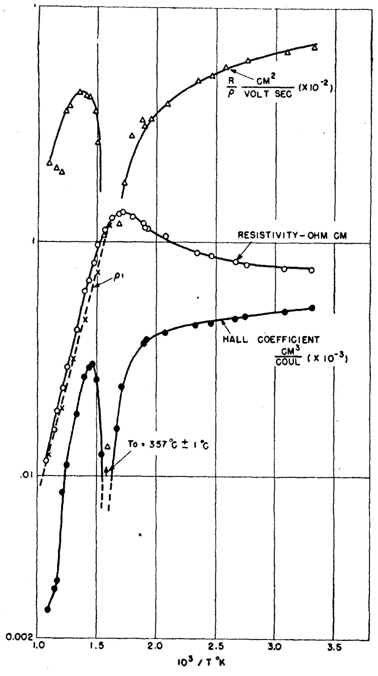

FIG. 4. Results of Hall effect and resistivity measurements on gallium antimonide single crystals at temperatures from 298°K up to 925°K.

At the inversion temperature, the Hall coefficient is zero, and the Hall formula,[12]

$$R=\frac{3\pi}{8e}\frac{nb^2-p}{(nb+p)^2}, \tag{1}$$

reduces to

$$n_{T'}b^2=p_{T'}. \tag{2}$$

Since $p=n+p_0$, where p_0 is the hole concentration arising from complete ionization of the impurity centers,

$$n_{T'}=p_0/(b^2-1). \tag{2a}$$

Likewise, the conductivity $\sigma=e(n\mu_n+p\mu_p)$ is given by

$$\sigma=e[n(\mu_n+\mu_p)+p_0\mu_p)], \tag{3}$$

and this yields

$$n=(\sigma-ep_0\mu_p)/e(\mu_n+\mu_p). \tag{3a}$$

Combining (2) and (3), we find

$$b=\left[\frac{1}{1-(ep_0\mu_p/\sigma)}\right]_{T'}. \tag{4}$$

It is thus possible to determine b by using the extrapolated value of μ_p at T', assuming a $T^{-\frac{3}{2}}$ law, and solving for p_0 using Eq. (1), which for the extrinsic range becomes

$$R=3\pi/8ep_0. \tag{5}$$

This method is quite sensitive to small errors in the determination of μ_p and p_0. It is, therefore, preferable to use the extrapolated extrinsic conductivity σ_{ext} where

$$(\sigma_{\text{ext}})_{T'}=(ep_0\mu_p)_{T'}. \tag{6}$$

This extrapolation of σ_{ext} is considered to be valid since the contribution of intrinsic carriers at temperatures below the intrinsic temperature is seen from Fig. 5 to be orders of magnitude below the value of p_0. Thus,

$$b=\left[\frac{1}{1-\sigma_{\text{ext}}/\sigma}\right]_{T'}. \tag{7}$$

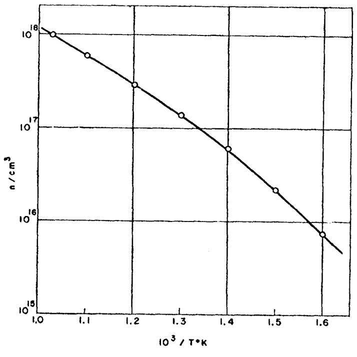

FIG. 5. Plot of ln$n$ *versus* $1/T$. n is the theoretically calculated density of electrons.

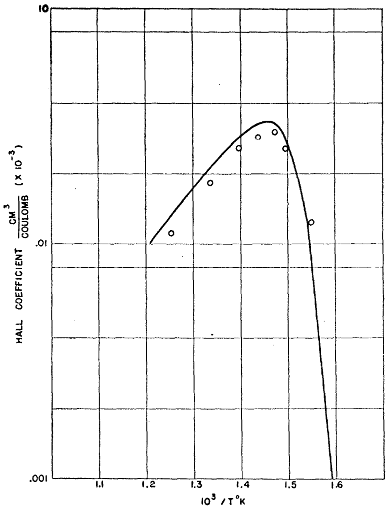

FIG. 6. Comparison of theoretically calculated Hall coefficient with experimental results, in intrinsic range of temperature above 357°C.

Using the data of Fig. 4, $\{(\sigma_{\text{ext}})_{T'}=6.9,\ \sigma_{T'}=8.7$ ohm^{-1} cm$^{-1}\}$, a value of 5.0 for the mobility ratio is then found from Eq. (7).

Determination of the Impurity Carrier Concentration

For the determination of p_0, the density of carriers when ionization is complete, the Hall coefficient for the extrinsic region was extrapolated to a temperature of 600°K.

Equation (5) yields $p_0=1.85\times10^{17}/\text{cm}^3$. From Eq. (6) $\mu_p)_{T'}=230$ cm^2/volt sec, and thus $\mu_n)_{T'}=1150$. From (2a) or (3a), $n)_{T'}=7.7\times10^{15}/\text{cm}^3$, and thus $p)_{T'}=1.9\times10^{17}/\text{cm}^3$.

Analysis of the Intrinsic Region

a. The calculation of the intrinsic Hall curve

Figure 5 shows a plot of ln$n$ *vs* $1/T$, determined from Eq. (3a) assuming a $T^{-\frac{3}{2}}$ law for the mobilities. It is helpful in calculations involving n and p at any temperature.

The theoretically determined Hall coefficient for the intrinsic region above T' [obtained from Eq. (1) using calculated values of n, p, μ_n, and μ_p] is shown in Fig. 6 as the solid curve. The circles indicate the experimental Hall coefficient values. This comparison, it is believed, demonstrates the degree of consistency between the conductivity data (used to determine b, n, and p) and the Hall data. The degree of agreement also indicates that for gallium antimonide there may be little or no difference between "Hall mobility" and "conductivity" or "drift" mobility.[13]

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[12] See W. Shockley, *Electrons and Holes in Semiconductors* (D. Von Nostrand Company, Inc., New York, 1950), Chap. 8.

[13] See reference 12, p. 206.

b. Determination of the intrinsic band gap E_g and the effective masses

Consider the theoretical expression for a simple model

$$(np)^{\frac{1}{2}}=2(2\pi mk/h^2)^{\frac{3}{2}}(m^*)^{\frac{3}{2}}T^{\frac{3}{2}}\exp[-(E_0-\alpha T)/2kT], \quad (8)$$

where $m^*=(m_n m_p)^{\frac{1}{2}}/m$; m_n and m_p are the effective masses of the electron and hole, respectively, m the free-electron mass.

Also, $E_g=E_0-\alpha T$ is the temperature-dependent band gap, E_0 the band gap at absolute 0.

Normally, in a pure semiconductor it is possible to determine E_0 from the slope of the log resistivity *vs* $1/T$ curve at high temperatures. This is so since at high temperatures the impurity carrier concentration is usually negligible in comparison to the intrinsic carrier concentration ($n \simeq n_i$) and ρ is an excellent approximation to ρ_i. In the present case, however, the impurity concentration is high enough—and the melting point of the compound low enough—that at 50° below the melting point the density of electrons n is only about three times the impurity density p_0. Thus, for p-type material, the measured slope of the intrinsic conductivity curve *vs* $1/T$ can be equal to, greater than, or less than that for intrinsic material, depending upon the temperature range chosen. Since the number of electrons is always less than that for intrinsic material and the actual and intrinsic resistivities are equal at the inversion temperature, (for $b>1$), it follows that the resistivity curve overshoots that for intrinsic on the high temperature side and at much higher temperatures the slope returns to the same value as that for intrinsic material.

For n-type material, on the other hand, the intrinsic resistivity always exceeds the actual resistivity, and there is no overshoot.

Therefore, to obtain E_0 it is necessary to calculate ρ_i or $(np)^{\frac{1}{2}}/T^{\frac{3}{2}}$ as a function of temperature. Logarithm ρ_i and $(np)^{\frac{1}{2}}/T^{\frac{3}{2}}$ *versus* reciprocal temperature are shown in Figs. 4 and 7, respectively. These plots are, of course, not independent of each other.

The slope of either curve yields the value

$$E_0=0.80 \text{ ev.}$$

Unpublished infrared transmission data on gallium antimonide, by Newman of this laboratory, at 298°K and 77°K indicate a temperature dependence of the band gap. It can be seen from Eq. (8) that this dependence may be accounted for by adjustment of two parameters, namely m^* and α. With no other evidence available, we have chosen α so as to yield a band gap agreeing with the room-temperature infrared transmission results. From this value of α, using Eq. (8), a value for m^* may be determined.

Because of the lack of sharpness at the absorption edge, the band gap determined from infrared data will depend upon an arbitrary choice of absorption coefficient. The value of room-temperature band gap selected (0.71 ev) corresponds to an absorption coefficient of 100 cm^{-1}.

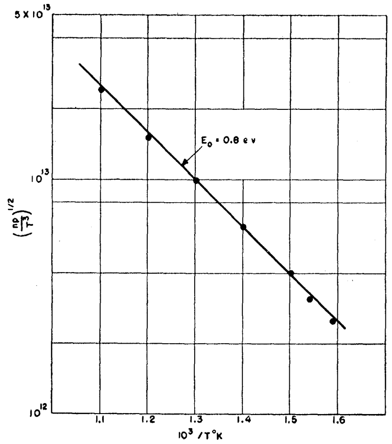

FIG. 7. Plot of $(np)^{\frac{1}{2}}/T^{\frac{3}{2}}$ *versus* $1/T$ for gallium antimonide. This method is used instead of the actual resistivity *versus* $1/T$ because of the effects of high impurity content.

A band gap of 0.71 ev dictates a temperature coefficient α of 3×10^{-4} ev/°K. These values plus the data of Fig. 7 yield a value of $m^*=0.28$.

From this value of m^* and the ratio of electron to hole mobility, it is possible to calculate a reasonably significant value of the separate effective masses of holes and electrons. According to Shockley, the mean free path of either carrier depends reciprocally upon the square of the effective mass:[14]

$$l=\pi h^4 C_{ll}/(E_{1n}{}^2 kTm_n{}^2), \quad (9)$$

where C_{ll} and E_{1n} are parameters of the lattice, independent of the effective mass. Also, the mobility depends upon mean free path according to the law:

$$\mu=4el/3(2\pi m_n kT)^{\frac{1}{2}}. \quad (10)$$

Thus, the ratio of electron to hole mobility depends upon $(m_n/m_p)^{-5/2}$. Solving the two equations:

$$(m_n m_p)^{\frac{1}{2}}=0.28m,$$

and

$$(m_n/m_p)^{-5/2}=5,$$

one finds

$$m_n=0.20m,$$

$$m_p=0.39m.$$

An independent evaluation of the effective mass of holes is available from the value of the ionization energy of the holes, determined from the low-temperature data, namely 0.024 ev. Now, it should be noted that the source of carriers in gallium antimonide is as yet unidentified. However, tentatively assuming a hydrogen-like system, and using the value 14.0 for the dielectric constant of K gallium antimonide,[15] one finds

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[14] See reference 12, p. 278.

[15] Briggs, Cummings, Hrostowski, and Tanenbaum, Phys. Rev. **93**, 912 (1954).

from the following equation:[16]

$$\Delta E=\frac{13.56}{K^2}\frac{m_p}{m}\text{ev} \qquad (11)$$

that the effective mass for holes is about $0.35m$. These values thus are in fairly good agreement. Since we have not made n-type gallium antimonide, no independent evaluation of the effective mass of electrons is available in our work.

SUMMARY AND CONCLUSIONS

Single crystals of gallium antimonide have been prepared, and their properties have been determined over a wide range of temperature. These properties have been found to fit well with the present theory of semiconductors. Of special interest among the results are the large ratio of electron to hole mobility (about five), the rather large intrinsic band gap (0.8 ev). Also, it is necessary to assume two acceptor levels in the energy scheme to fit the Hall data. A value of the hole effective mass has been estimated from the infrared absorption data, and from the electrical properties.

ACKNOWLEDGMENTS

We should like to thank Dr. R. Newman for the use of his infrared absorption data, and for fruitful discussions. We should also like to thank Dr. W. W. Tyler for growing the single crystals.

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[16] See reference 12, p 224.

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Theory of Secondary Electron Cascade in Metals

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A study is made of the cascade process which describes the diffusion, energy loss, and multiplication of secondary electrons within a metal. The secondaries interact mainly with conduction electrons through a screened Coulomb potential. For low secondary energy (<50 ev) the resultant scattering is nearly spherically symmetric and the transport equation which governs the cascade process can be approximately solved. The velocity distribution turns out to be spherically symmetric for low secondary energy. Energy distributions are in agreement with experiment for metals to which the theory is applicable. Calculations are also made of the rate of change of yield with work function and the results are in accord with observed values. Finally, rough estimates are made of the total yield and the theory is shown to be consistent with the observed values.

I

THE phenomenon of secondary electron emission[1] can be thought of as occurring in two distinct steps. First of these is the production of internal secondaries by collisions between fast primaries and electrons bound in the metal. The second is the subsequent cascade process in which these secondaries diffuse through the solid, multiplying and losing energy en route, until they either sink back into the sea of conduction electrons or reach the surface with sufficient energy to emerge as true secondary electrons. These two steps pose two separate problems, each of considerable complexity, which must be solved before one can understand the various phases of SE. To date, most of the theoretical work[2] in the field has concentrated on the first of these and treated the second in a radically simplified way. Usually the whole second step is lumped into an effective absorption coefficient α for the internal secondaries. Calculations using this approach have given fair agreement with the shapes of observed total yield *versus* primary energy curves, but they cannot predict the absolute magnitude of the yield since, without solving the diffusion problem, there is no way of estimating α.

Other aspects of SE probably depend even more critically on the details of the internal electron cascade. For example, the energy distribution of secondaries is observed to be independent of primary voltage. This suggests that the cascade process is almost entirely responsible for the shape of the spectrum and that the method of production of the internal secondaries is relatively unimportant. The aim of the present work is to investigate this internal electron cascade and to verify to what extent this hypothesis is correct. The picture of SE which will arise from this study turns out to be a reasonable and consistent one which accounts for a number of the experimental results.

To solve the problem of the internal cascade one must, of course, know the elementary interactions by which electrons lose energy within the metal. This

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[1] Hereafter abbreviated as SE.

[2] For a review and bibliography of work performed prior to 1948 see K. G. McKay's article in *Advances in Electronics* (Academic Press, Inc., New York, 1948). Other, more recent, articles are E. M. Baroody, Phys. Rev. **78**, 780 (1950); A. J. Dekker and A. van der Ziel, Phys. Rev. **86**, 755 (1952); J. F. Marshall, Phys. Rev. **88**, 416 (1952).