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Hall Effect Studies of Doped Zinc Oxide Single Crystals

A. R. Hutson
Bell Telephone Laboratories, Murray Hill, New Jersey

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Measurements of the Hall coefficient and the electrical conductivity of single-crystal specimens of *n*-type ZnO at temperatures between 55°K and 300°K are reported. An analysis of carrier concentration *vs* temperature indicates that "as-grown" crystals contain more than one active donor. Crystals with low initial donor concentrations were doped with H or interstitial Zn or Li, allowing a single-donor-level analysis. Doping was accomplished by interstitial diffusion followed by a rapid quench. Each of the added donors gives rise to a hydrogen-atom-model donor center whose ionization energy is $E_D=0.051$ ev for $N_D<5\times10^{16}$ cm^{-3}. Lithium was also found to introduce a small concentration of acceptors, presumably due to an exchange between interstitial and substitutional positions. The quantity $(m^{(N)}/m)^{\frac{3}{2}}D^{-1}$, where $m^{(N)}=$"density-of-states" effective mass and $D=$donor degeneracy, was found to be about 0.19 for all three donors, indicating that if $D=2$ then $m^{(N)}=0.5$. The low-frequency dielectric constant of ZnO was redetermined as $\kappa=8.5$. The effective mass associated with the electron found in a hydrogen-like orbit is then $m^{(H)}=0.27m$, and the observed decrease of E_D with increasing N_D corresponds to the overlap of these large orbits.

The Hall mobility is 180 cm^2 volt^{-1} sec^{-1} at 300°K and increases with decreasing temperature. It has been analyzed for lattice and impurity scattering. The optical-mode scattering mobility has been calculated from both the perturbation and intermediate-coupling theories making use of the effective mass, $m^{(H)}$, so that no adjustable parameters were included. The two theories agree for ZnO since it turns out to have a polar-mode electron coupling constant of $\alpha=1$. The mobility so obtained is in good agreement with experiment and indicates that optical-mode scattering is important above 200°K. Some acoustical-mode scattering also appears to be present. At low temperatures the mobility appears to be limited by impurity scattering.

I. INTRODUCTION

ZINC oxide has been recognized as an extrinsic, *n*-type semiconductor for many years. However, the bulk of the past studies has been concerned with the measurement of electrical properties (chiefly electrical conductivity) on sintered powder samples as a function of oxidation and reduction treatments at high temperatures.[1–6] The difficulties of analysis associated with the high-resistance boundaries connecting the crystalline grains in samples such as these have been summarized by Miller.[7]

More recently Harrison[8] has measured the Hall effect and conductivity on two single-crystal specimens as well as a number of sintered powder samples. He found that his data for the concentration of conduction electrons as a function of temperature were not consistent with a one-donor-level semiconductor model and a density-of-states in the conduction band characteristic of the free mass of the electron. However, since no evidence existed to show that only a single donor level was active in providing conduction electrons, or just what donor or donors were actually present, it was not possible to arrive at any conclusions about donor density, donor ionization energies, or density-of-states in the conduction band. The work along these lines in the German literature has been characterized by an empirical relation known as "Meyer's rule" which states that at a given temperature, the temperature coefficient of the conductivity is lower, the higher the conductivity of the sample. All of this bespeaks a complicated situation with a number of unknown donor levels playing an active role. In the present study, the Hall effect and the electrical conductivity have been measured as a function of temperature on single crystals of ZnO. Those crystals were selected which had exceptionally low carrier concentrations at room temperature. They were then doped with donors of a single type (either hydrogen, zinc, or lithium) to a carrier concentration at least an order of magnitude greater than they possessed originally. In this way the complicating presence of a number of different donor species was avoided.

II. SAMPLE PREPARATION

The crystals of ZnO were grown in these laboratories by D. G. Thomas and S. Vitkovits by a vapor-phase reaction between zinc and oxygen at about 1200°C, as originally discussed for ZnO by Scharowsky.[9] The resulting crystals are transparent needles of hexagonal cross section about 0.2 mm in diameter and 5 to 10 mm in length. (ZnO is a hexagonal crystal with the wurtzite structure). Their specific electrical conductivity at room temperature varied from about 0.01 ohm^{-1} cm^{-1} to 3.0 ohm^{-1} cm^{-1} from batch to batch, with large variations between those from a single batch. In an attempt to achieve high purity, spectroscopically pure zinc was used, and the furnace reaction zone was lined with "Degussit" purified alumina. Spectrochemical analysis of the crystals indicated the presence of Ca, Cu, Fe, Mg, and Si all in quantities less than one part in 10^5.

For the electrical measurements, the crystals were mounted on a sample holder in the vacuum space of a

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[1] W. Jander and W. Stamm, Z. anorg. Chem. **199**, 165 (1931).

[2] H. H. V. Baumbach and C. Wagner, Z. physik Chem. (B) **22**, 199 (1933).

[3] O. Fritsch, Ann. Physik **22**, 375 (1935).

[4] P. H. Miller, Jr., Phys. Rev. **60**, 890 (1941).

[5] Bevan, Shelton, and Anderson, J. Chem. Soc. 1729 (1948).

[6] E. E. Hahn, J. Appl. Phys. **22**, 855 (1951).

[7] P. H. Miller, Jr., *Semiconducting Materials* (Butterworth's Scientific Publications, Ltd., London, 1951), pp. 172–9.

[8] Sol. E. Harrison, Phys. Rev. **93**, 52 (1954).

[9] E. Scharowsky, Z. Physik **135**, 318 (1953).

simple Dewar. A block of copper wound with a heater served as a thermal mass so that temperature drift of the sample was negligible during the time of a measurement. The temperature range for this apparatus was from 55°K to about 400°K. A few measurements at higher temperatures were made in a small vacuum oven which would fit between the poles of the electromagnet.

The problem of making satisfactory contacts to these small crystals was somewhat alleviated by the discovery that gallium and indium wet ZnO, and tend to make ohmic and relatively low-resistance contacts. The crystals were mounted as shown in Fig. 1. This simple mounting scheme virtually eliminated crystal breakage and allowed the removal of a crystal for cleaning and re-doping. While in most high conductivity crystals the electrical contact resulting only from probe pressure was satisfactory, it was occasionally necessary to "form" a contact by discharging a small capacitor through it. No changes in the measured parameters were detected due to "forming."

The temperature of the crystal was measured with copper-advance thermocouples at either end. Thermocouple calibration was supplied by T. H. Geballe and checked at the boiling point of nitrogen. The current in the crystal was always kept below values at which Joule heating could be detected. Voltage measurements were made with a Leeds and Northrup Type-K Potentiometer with a provision for the use of a vacuum-tube electrometer in cases of high sample resistance. The magnetic field of 4650 gauss was applied in each direction for all Hall points, and the direction of current through the crystal was frequently reversed. Because of the growth habit of our zinc oxide crystals, all measurements were made with the current along the c axis.

The temperature variation of carrier concentration, obtained from the Hall coefficient, R, is shown in Fig. 2 for a number of crystals "as grown" and two doped crystals. We shall use the relation $n=[\mu_H/\mu][1/Re]$ for the electron concentration with $[\mu_H/\mu]=3\pi/8$. The relationship between activation energy and carrier concentration evident for the "as grown" crystals is suggestive of Meyer's rule, and is probably due to the presence of a number of donors in differing amounts. The doped crystals, H-6 and 33, are seen to violate Meyer's rule. Sample 46 is typical of our purest crystals, and the doping experiments were carried out on crystals of this type.

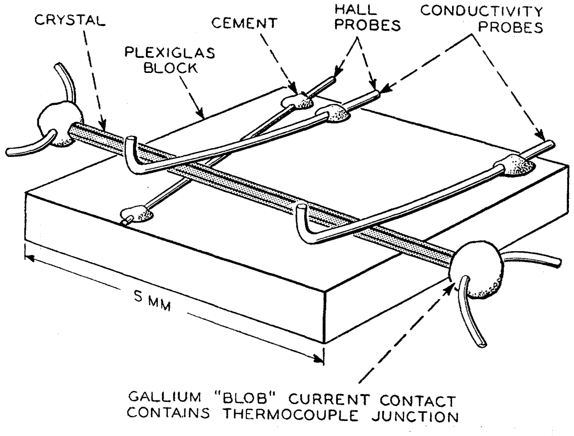

FIG. 1. Method of mounting small needles of ZnO for Hall effect and conductivity measurements. Probes are indium-coated phosphor bronze wires.

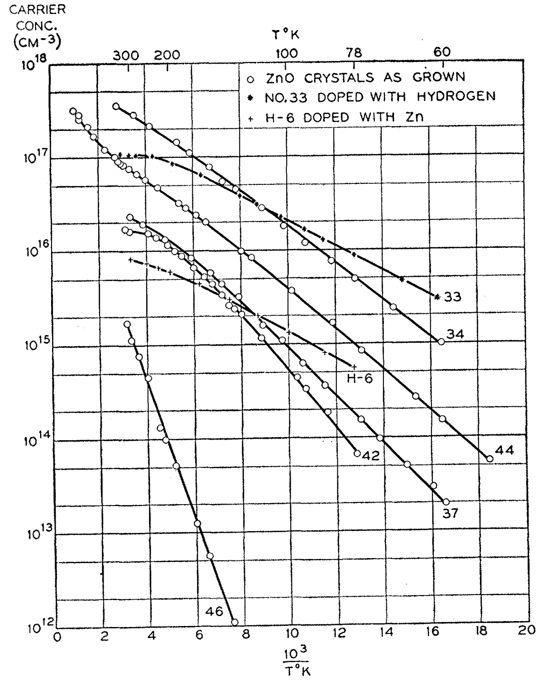

FIG. 2. Electron concentration as a function of $1/T$ from Hall measurements on as-grown crystals and two doped crystals.

The doping of zinc oxide crystals with the donor impurities hydrogen, interstitial zinc, and interstitial lithium has been accomplished by D. G. Thomas and J. J. Lander of these laboratories.

The solubility and diffusion of hydrogen is satisfactory for the doping of these crystals at temperatures of the order of 500°C and pressures of 1 atmos and greater.[10] It is believed that the actual donor centers are hydroxyl ions formed at oxygen ion sites. The possibility that the donor species introduced by hydrogen could be interstitial zinc produced at the surface is ruled out by direct measurements of the diffusion and solubility of interstitial zinc from a zinc atmosphere or bath.[11] These results agree quantitatively with the observations on the rate of growth of ZnO films on zinc metal. The magnitude and temperature variation of the diffusion show that the diffusing species is interstitial zinc. At higher temperatures there is evidence for the motion of a stoichiometric excess of zinc of

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[10] D. G. Thomas and J. J. Lander, J. Chem. Phys. **25**, 1136 (1956).

[11] D. G. Thomas, Bull. Am. Phys. Soc. Ser. II, **1**, 348 (1956).

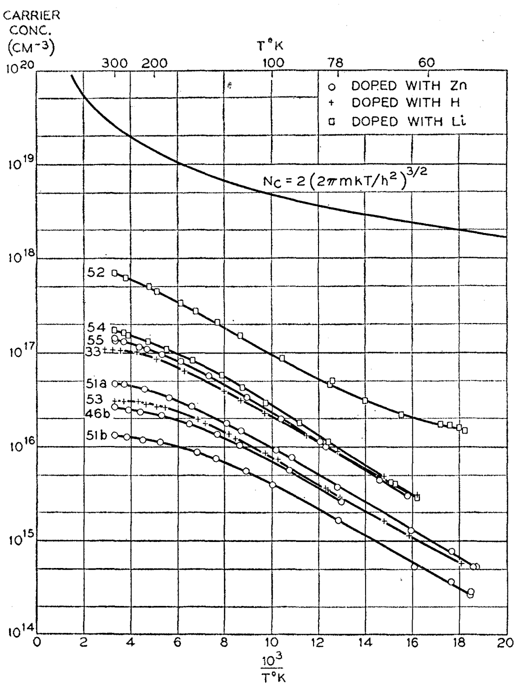

FIG. 3. Electron concentration as a function of $1/T$ from Hall measurements on zinc oxide crystals doped with hydrogen, zinc, and lithium. The temperature dependence of the density-of-states in the conduction band is plotted for comparison.

some other form, which is also a donor,[12] and it is perhaps this species which provides some of the conduction electrons in the crystals as grown. Lithium as an interstitial donor in ZnO has not been studied in detail; however it appears to diffuse about as rapidly as interstitial zinc, and to have a greater solubility. It also appears gradually to take up substitutional sites where it acts as an acceptor, and hence when doping with lithium one should not maintain the crystal at the high temperature too long. The doping technique involved holding the crystal at a high temperature in contact with the proper atmosphere long enough for the concentration of the diffusant to become uniform and then quenching the crystal very rapidly to room temperature.

III. HALL EFFECT STUDY OF DOPED CRYSTALS

The carrier-concentration data for the doped crystals are shown in Fig. 3. The range of concentrations is limited on the low side by the necessity for doping to a level an order of magnitude above the "as grown" concentration, and on the high side by the solubilities of the donors at temperatures low enough so that unwanted, extraneous effects would not occur (such as, perhaps, the diffusion of oxygen vacancies in from the surface). One may note that the curves in Fig. 3 all look very much the same, with no suggestion of Meyer's rule. The low-temperature behavior of sample 52 may indicate an appreciable overlap of wave functions on neighboring donors. The temperature variation of the density-of-states in the conduction band, N_C, assuming that a conduction election has its free mass, is plotted for reference in Fig. 3. It can be seen that the variation in N_C is comparable with the variation in carrier concentration, and that the latter is approaching saturation over a large part of the temperature range. Thus, no accurate information may be obtained directly from the slopes of the curves of Fig. 3.

The analysis to be used for these carrier-concentration data assumes that the Fermi level is always a few kT below the conduction band, and that in each sample, one has only to consider a single donor level. In this case, an expression for the carrier concentration, n, may be written as

$$\frac{n^2}{(N_D-n)N_C}=\left[\frac{m^{(N)}}{m}\right]^{\frac{3}{2}} D^{-1}\exp\left(\frac{-E_D}{kT}\right), \qquad (1)$$

for samples with negligible compensation where N_D is the concentration of donors, D is the donor degeneracy, E_D is the energy difference between the donor and the bottom of the conduction band, and $m^{(N)}$ is the density-of-states electron mass. The donor degeneracy is the number of ways that the electron may occupy the donor state, and usually has the value 2 arising from

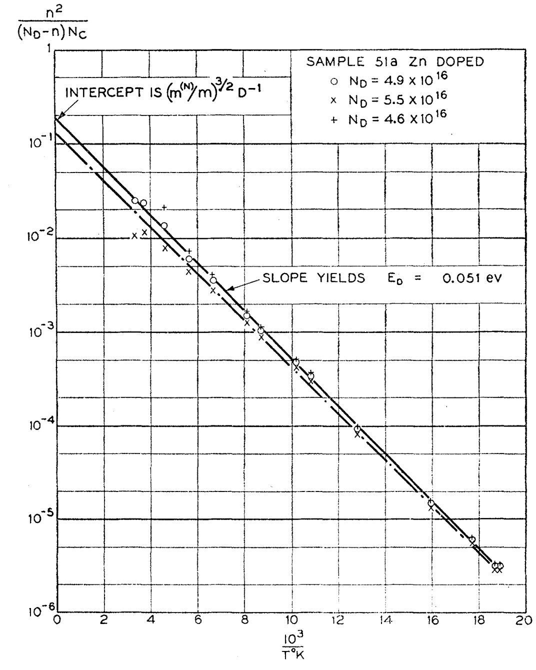

FIG. 4. Single-donor analysis of the carrier concentration of a doped crystal. The circles are for the best estimate of N_D. The sensitivity of the analysis to relatively large errors in the estimate of N_D is illustrated by the +'s and ×'s.

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[12] Radioactive-tracer diffusion results of R. Lindner, Acta Chem. Scand. **6**, 457 (1952), and of W. J. Moore and J. K. Lee, Trans. Faraday Soc. **47**, 501 (1951); chemical determinations of excess zinc, E. Mollwo and F. Stöckmann, Ann. Physik **3**, 223 (1948), and J. J. Lander (private communication).

the two possible spin orientations. If the logarithm of the left-hand side of (1) is plotted against the reciprocal of the absolute temperature, one should obtain a straight line whose slope gives E_D, and whose intercept is $[m^{(N)}/m]^{\frac{3}{2}}D^{-1}$. In making such a plot, a value for the parameter, N_D, must be chosen. A first estimate of N_D may be made by inspection of the carrier-concentration curves of Fig. 3, then the estimate of N_D may be improved by inspection of the high-temperature end of the plot of Eq. (1). Plots of Eq. (1) for a zinc-doped sample are shown in Fig. 4 for three choices of N_D. The circles represent the best choice of N_D, and the plus signs and crosses represent the same data with N_D chosen too low and too high. One can see that it is a relatively easy matter to choose N_D with sufficient precision to obtain accurate values for the slope and intercept of this plot.

The plots of Eq. (1) for five doped samples are shown in Fig. 5. The intercept is about 0.18 and is the same for all of these samples. For the four samples which were doped to concentrations less than 5×10^{16} cm^{-3}, the ionization energy is 0.051 ev for both hydrogen and zinc donors. The relatively low value of E_D and the fact that it is the same for these two different donors suggests that we are dealing with a hydrogen-like center. The decrease in E_D at concentrations of the order of 10^{17} cm^{-3} is similar to the lowering of the ionization energy of hydrogen-like states in germanium and silicon.

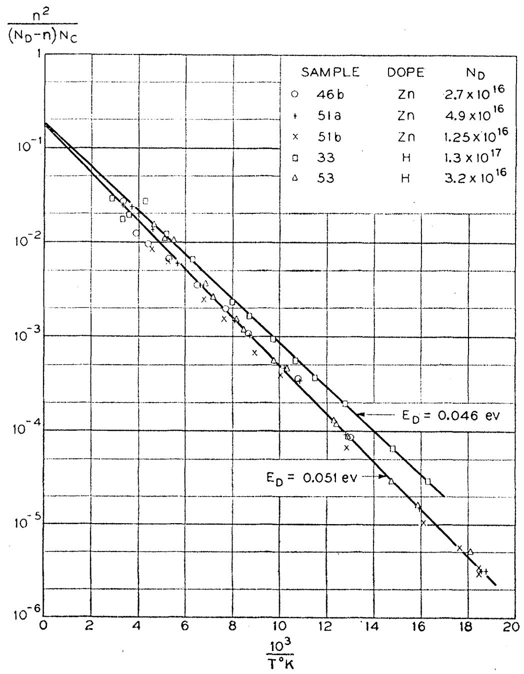

FIG. 5. Single-donor analysis of the carrier concentrations of crystals doped with hydrogen and zinc. Note the common intercept.

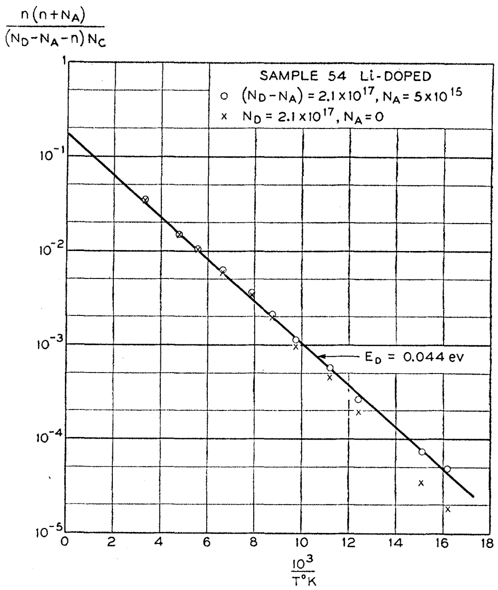

FIG. 6. Carrier-concentration analysis of a lithium-doped crystal including the effect of a small amount of compensation. Note that the intercept is the same as for hydrogen and zinc donors.

In order to obtain a density-of-states electron mass from the intercept, it is necessary to assume a value for the donor degeneracy. The fact that the intercept is the same for both zinc and hydrogen suggests that $D=2$, corresponding simply to the spin degeneracy. The conclusion that an interstitial zinc donor has a degeneracy of 2 was not immediately obvious, since in the singly ionized state the zinc atom has an unpaired electron. Therefore, a sample was analyzed which had been doped with interstitial lithium which in its ionized state has no unpaired electrons and hence should definitely have a degeneracy of 2. In analyzing the lithium-doped sample it was necessary to take account of the compensating acceptor states introduced by the appearance of lithium at interstitial positions. If one assumes that any compensating acceptors always lie sufficiently below the Fermi level so that they are always filled, Eq. (1) becomes

$$\frac{n(n+N_A)}{(N_D-N_A-n)N_C}=\left[\frac{m^{(N)}}{m}\right]^{\frac{3}{2}}D^{-1}\exp\left(\frac{-E_D}{kT}\right), \tag{2}$$

where N_A is the concentration of acceptors. Again, one plots the log of the left side of the equation against T^{-1}. In this case, however, one must pick the parameter N_A as well as N_D. For small concentrations of acceptors, this turns out to be relatively easy, as may be seen in Fig. 6, where the data for a lithium-doped sample are plotted. The crosses show what happens in this sort of plot when compensation is not taken into account. A distinct "tailing-off" at low temperatures is evident; however, the assumption of only about 2% compensation brings the points (circles) back up to the straight line at low temperatures. Since the final choices of N_D and N_A are made on the basis of the behavior of the

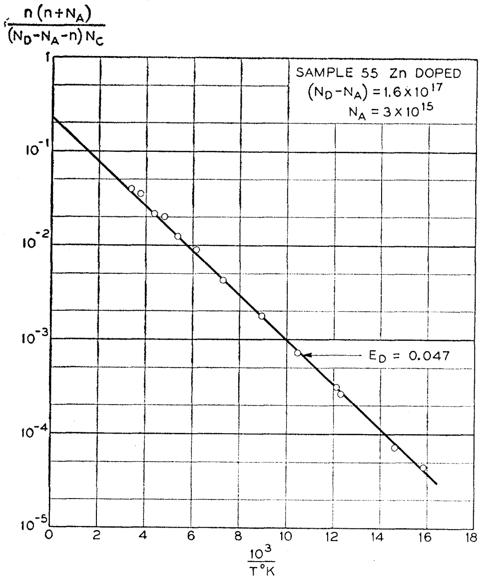

FIG. 7. Carrier-concentration analysis of a crystal doped to a high concentration of zinc and requiring the assumption of a small amount of compensation.

plot at opposite ends of the temperature scale, the choice of one has virtually no effect upon the choice of the other. As may be seen in Fig. 6, the intercept for a lithium-doped sample is the same as for hydrogen or zinc doping, indicating that $D=2$ for all three donors. The ionization energy for this lithium-doped sample is just about what one would expect for a sample doped to the same concentration with hydrogen or zinc. Figure 7 shows an additional zinc-doped sample which required the assumption of a small number of compensating acceptor levels of undetermined origin. Again, the intercept is in agreement with the other samples and $E_D=0.047$ ev is about what one would expect at a concentration of 1.6×10^{17} cm^{-3}.

IV. EFFECTIVE MASS, DIELECTRIC CONSTANT, AND DONOR IONIZATION ENERGY

The effective mass of an electron in the conduction band is a parameter which is used to describe the manner in which the energy-momentum relationships near the minimum-energy band-edge point(s) of the Brillouin zone enter into the interpretation of experimental results. For most semiconductors, certain average properties of a very complicated situation are lumped into this parameter. In germanium and silicon, due in large part to the combination of cyclotron resonance experiments and accurate calculations of energy bands, the relationships connecting experimental measurements of such quantities as Hall constant and mobility, magnetoresistance, and thermoelectric power have been investigated in quantitative detail. These relationships have been discussed for a semiconductor which may be represented by a "many-valley" model by Herring.[13]

Since virtually no information as to the energy band structure in zinc oxide exists, we shall have to start from the beginning in interpreting the results of the present experiments and be content with a rough internal consistency and agreement with theory. There are three ways in which the present experimental results may be related to the band structure of zinc oxide, and they may be characterized by three effective masses: the "density-of-states" mass, $m^{(N)}$; the effective mass associated with the ionization energy of hydrogen-atom-model donor states, $m^{(H)}$; and the effective mass to be used in comparing experiment with theories of electron mobility. (If the surfaces of constant energy were spheres centered about the origin in **k** space, all of these masses would be the same.)

The density-of-states mass modifies N_C in order to take account of the band structure. In terms of the simple many-valley model,

$$m^{(N)}=N_V^{\frac{2}{3}}(m_1m_2m_3)^{\frac{1}{3}}, \tag{3}$$

where N_V is the number of valleys and m_1, m_2, m_3 are the mass parameters relating energy and momentum along the three principal axes of the ellipsoidal energy minima. For the hydrogenic donor states, the ionization energy may be written as

$$E_D=\frac{13.6(m^{(H)}/m)}{\kappa^2}\text{ ev}, \tag{4}$$

where κ is the static dielectric constant.[14] The relationship between $m^{(H)}$ and the principal masses of a single valley can be obtained by equating the energy of Eq. 4 with the binding energy obtained from a variational solution of the effective-mass Schrödinger equation for an electron in a medium of dielectric constant κ attracted by a single positive charge. (We shall neglect the fact that $m^{(H)}$ observed is probably a little greater than $m^{(H)}$ computed because of the penetration of the wave function into the central cell.) Lampert,[15] among others, has carried through a solution of this type for valleys which are ellipsoids of revolution (effective masses $m_{\parallel}$, $m_{\perp}$, $m_{\perp}$). One can get an idea of the effect of mass anisotropy upon $m^{(H)}$ from his plot of binding energy *vs* $m_{\parallel}/m_{\perp}$, which may be represented for $m_{\parallel}/m_{\perp}<10$ by

$$m^{(H)}/m_{\perp}=1+0.84\log_{10}(m_{\parallel}/m_{\perp}). \tag{5}$$

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[13] C. Herring, Bell System Tech. J. **34**, 237 (1955).

[14] Equation (4) is applicable to shallow bound states in polar crystals when E_D is small compared with the energy of an optical phonon, $\hbar\omega_l$. For $E_D\gg\hbar\omega_l$ the lattice polarization will not be able to follow the electron's motion and a treatment similar to that of S. Pekar and M. F. Deygen, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 481 (1948); or that of J. H. Simpson, Proc. Roy. Soc. (London) **A197**, 269 (1949), and **A231**, 308 (1955) would be more appropriate. As discussed in Sec. V, E_D is slightly less than $\hbar\omega_l$ in ZnO.

[15] M. A. Lampert, Phys. Rev. **97**, 352 (1955).

There are really two effective masses to be considered in analyzing lattice-scattering mobility. With the usual assumption that the relaxation time, τ, is a function only of energy, the mobility may be written as

$$\mu=\frac{e}{m^{(I)}}\frac{\langle\epsilon\tau\rangle}{\langle\epsilon\rangle},\qquad(6)$$

where $m^{(I)}$ is an inertial mass for the direction of current flow. Unlike the cubic semiconductors in which $m^{(I)}$ has one isotropic value, we may expect $m^{(I)}$ to have different values for current flow parallel and perpendicular to the hexagonal axis in zinc oxide. If the hexagonal axis should turn out to be principal for the valleys, $m^{(I)}$ would correspond to the principal mass in that direction. The energy average of τ in Eq. (6) contains a power of the density-of-states mass for a single valley, $(m_1m_2m_3)^{\frac{1}{3}}$. For scattering by the acoustical modes, this mass appears to the $-\frac{3}{2}$ power in μ and for scattering by optical modes it appears to the $-\frac{1}{2}$ power.

The density-of-states mass may be obtained from the common intercept of the plots in Figs. 4–7 making use of the evidence that $D=2$, $m^{(N)}\cong 0.5m$, provided also that our assumption that $[\mu_H/\mu]=3\pi/8$ is not too far from the truth. There are two separable effects which might affect $[\mu_H/\mu]$: first, the dependence of relaxation time upon energy which will probably not have any large effect, even with a considerable amount of optical-mode or impurity scattering; and second, the possible effect of the anisotropy of the effective mass if the hexagonal axis is not principal, which we are not yet in a position to evaluate.

In order to obtain $m^{(H)}$ from Eq. (4) with the value $E_D=0.051$ ev found for dilute donor concentration, we must have a value for κ. There have been four determinations of this quantity reported in the literature for zinc oxide using three different methods.[16] Glemser used a substitution method in which ZnO powder was introduced in a liquid cell containing mixtures of benzene and nitrobenzene and obtained a value of $\kappa=36.5$. Soos measures the standing-wave pattern at $\lambda=5$ cm in front of a metal-backed, pressed-slab of ZnO (with microwave technique typical of 1940) and obtained $\kappa=7.9$. Kamiyoshi applied a new deduction formula to data on powdered ZnO (no specification of experimental technique) and states that $\kappa=8.5$. Hahn packed ZnO powder into a cylindrical capacitor and measured the capacity and losses with a Boonton Q-meter as a function of packed density, arriving at $\kappa=12$ and $\sigma=5\times10^{-7}$ ohm^{-1} cm^{-1}. Although Hahn's value has been frequently quoted in the recent literature, the very low conductivity which he observed is probably almost entirely due to poor contacts between the ZnO grains, and therefore his measurement of κ was probably in error due to the Maxwell-Wagner effect. In view of the inadequacy of the published data, T. S. Benedict and the author have measured the dielectric constant of low-conductivity single crystals of ZnO by a microwave cavity perturbation technique at $\lambda=1$ cm. It was only possible to make accurate measurements with the electric field directed along the length of the crystal needles (along the c axis), so that in using our result in calculations one assumes that the static dielectric constant is not very anisotropic. We obtained $\kappa=8.5$ for ZnO. The method was checked by inserting a similar needle of silicon with about the same losses. We obtained $\kappa=11.5$ for silicon, in satisfactory agreement with optical and other microwave measurements.

Inserting our values of $\kappa=8.5$ and $E_D=0.051$ ev into Eq. (4), we arrive at the value $m^{(H)}=0.27\ m$, for the effective electron mass associated with the hydrogen-like binding of an electron to a donor. As might be expected, $m^{(H)}$ is less than $m^{(N)}$.

We may also estimate the donor concentration at which the donor ionization energy may be expected to go to zero. Brooks[17] has developed the criterion $D=3.23r_1$, where D is the critical spacing between donors at which E_D goes to zero, and r_1 is the radial extension of the wave function of an electron bound to a donor. If spherical symmetry is assumed, $r_1=\kappa(m/m^{(H)})a_0$, so that with the present data for ZnO, $D=54$ A; i.e., the critical donor concentration is $N_D=6\times10^{18}$ cm^{-3}. The critical donor concentrations for germanium and silicon are, respectively, $N_D=2\times10^{17}$ and 2×10^{18} cm^{-3}, and the decrease of E_D with increasing donor concentration in ZnO appears to scale properly with N_D when compared with germanium and silicon.

V. ELECTRON MOBILITY ANALYSIS

The scattering processes which determine the electron mobility and its temperature dependence arise from the thermal vibrations of the lattice and from impurity centers. The lattice vibrations should play the dominant role at higher temperatures and the impurities may be expected to become more important at low temperatures. Since zinc oxide is a crystal with considerable ionic character, one expects lattice scattering by the optical modes of vibration as well as by the acoustical modes. Impurity scattering is presumed to be due to the screened Coulomb fields of ionized centers and to the interaction of conduction electrons with the electrons bound in the large orbits of the hydrogen-atom-like neutral donors.

Typical mobility data for a crystal with a small concentration of donors is shown in Fig. 8 (filled circles). The variation of mobility with temperature suggests that lattice scattering is dominant, but that impurity scattering is also contributing at the low-temperature end. We shall attempt to fit the experimental data with

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[16] O. Glemser, Z. Elektrochem. **45**, 865 (1939); A. N. Soos, Doklady Akad. Nauk S.S.S.R. **33**, 210 (1941); K. Kamiyoshi, Sci. Repts. Research Insts., Tôhoku Univ. **A2**, 180 (1950); E. E. Hahn, J. Appl. Phys. **22**, 855 (1951).

[17] H. Brooks, in *Advances in Electronics* (Academic Press, Inc., New York, 1955), Vol. 7, pp. 106, 107.

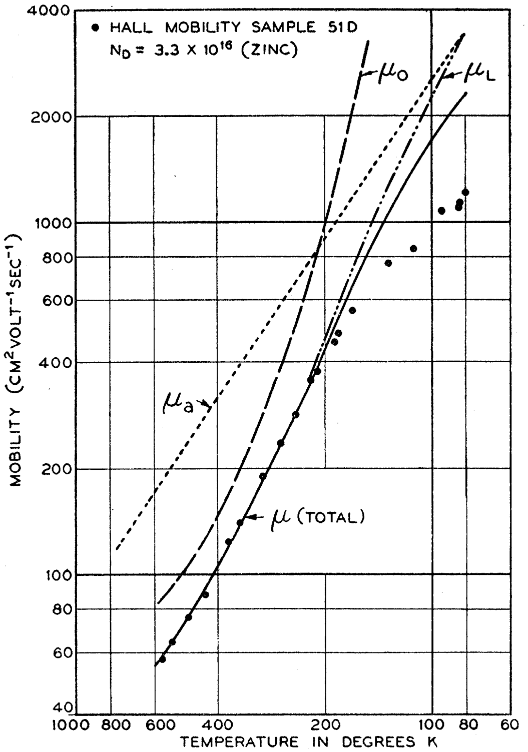

FIG. 8. Analysis of the Hall mobility of a typical crystal of zinc oxide. The circles are experimental data. The mobility to be expected due to optical-mode scattering alone is given by μ_0. The lattice scattering mobility which fits the data above 200°K is given by μ_l, and the amount of acoustical-mode scattering which has been assumed for this fit is illustrated by μ_a. The solid curve includes a small contribution from impurity scattering at low temperatures.

existing scattering theories using simply a scalar effective mass and thereby neglecting the difference between $m^{(I)}$ and $(m_1m_2m_3)^{\frac{1}{3}}$. There are essentially two theoretical approaches to the scattering by the optical modes of lattice vibration. The first is a perturbation treatment developed chiefly by Fröhlich and Mott[18] and by Howarth and Sondheimer.[19] The second is an "intermediate-coupling" theory due to Lee, Low, and Pines.[20] The two theories are briefly discussed, and some minor corrections noted in an article on the mobility of electrons in PbS by Petritz and Scanlon.[21] The perturbation theory is based upon an expansion in powers of the coupling constant, α, which is a measure of the strength of the interaction between the electrons and the polar vibration modes. The expansion is expected to converge satisfactorily for $\alpha \ll 1$, and is not restricted to temperatures small compared with the Debye temperature, $\Theta_l = h\nu_l/k$, characteristic of the longitudinally polarized optical vibrations. The "intermediate-coupling" theory on the other hand is best suited to the situation $\alpha \geq 1$, but its validity is in doubt for temperatures approaching Θ_l. The coupling constant may be written as

$$\alpha = \frac{e^2}{\hbar}\left(\frac{m}{2k\Theta_l}\right)^{\frac{1}{2}}\left(\frac{\kappa-\kappa_0}{\kappa\kappa_0}\right)\left(\frac{m^*}{m}\right)^{\frac{1}{2}}, \tag{7}$$

where m is the mass of the free electron, m^* is the scalar inertial mass of the electron in the conduction band, and κ and κ_0 are respectively the static and optical dielectric constants. For zinc oxide, $\kappa = 8.5$ (as discussed above) and $\kappa_0 = n^2 = 4$ as determined by Mollwo[22] in the visible. The frequency of the transverse optical vibrations in zinc oxide has been estimated by Kröger and Meyer[23] from infrared absorption data to be $\nu_t = 310$ cm^{-1}. Making use of the relation $\nu_l/\nu_t = (\kappa/\kappa_0)^{\frac{1}{2}}$, we obtain $\Theta_l = 660°$K. The effective mass, m^*, is a quantity which we shall specify independently of the mobility data so that in comparing optical-mode scattering theory with experiment we have no adjustable parameters (a situation not previously attained for polar crystals). In the expression for α, and in both the perturbation and "intermediate-coupling" theories, m^* is the effective mass that the electron would have if the lattice were rigid, i.e., unpolarizable. The mass parameter which we would like to make use of is $m^{(H)}$ obtained from the binding energy of the hydrogen-like donor states. Now a slowly moving electron in the conduction band of a polar crystal polarizes the lattice in its vicinity. The unit consisting of the electron plus its associated lattice polarization is called a polaron, and intuitively, one can see that the polaron mass, $m^{(P)}$, must be greater than m^*. When the electron is weakly bound to an attractive center, we may expect it to behave as a polaron if the binding energy is small compared with $h\nu_l$. For zinc oxide, $h\nu_l = 0.057$ ev and $E_D = 0.051$ ev so that $m^{(H)}$ probably lies somewhere between m^* and $m^{(P)}$. Since it will turn out that $m^{(P)}$ is not very much greater than m^*, we shall assume that $m^{(P)} = m^{(H)}$. It should be emphasized here that $m^{(H)}$ as determined above may very well be too large due to the central cell correction to the binding energy. The intermediate-coupling theory yields a relation between $m^{(P)}$ and m^*:

$$m^{(P)} = m^*(1+\alpha/6) \quad \text{for} \quad \alpha < 6. \tag{8}$$

Solving (6) and (7) simultaneously for zinc oxide, with $m^{(P)} = m^{(H)} = 0.27m$, we find $m^* = 0.23m$ and $\alpha = 1$. By way of comparison, the alkali halides have coupling constants of the order of 3 to 6.

The expression for the electron mobility for optical-mode scattering alone resulting from the perturbation

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[18] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. (London) **A171**, 496 (1939).

[19] D. Howarth and E. Sondheimer, Proc. Roy. Soc. (London) **A219**, 53 (1953).

[20] Lee, Low, and Pines, Phys. Rev. **90**, 297 (1953); F. E. Low and D. Pines, Phys. Rev. **91**, 193 (1953).

[21] R. L. Petritz and W. W. Scanlon, Phys. Rev. **97**, 1620 (1955).

[22] E. Mollwo, Z. angew. Phys. **6**, 257 (1954).

[23] F. A. Kröger and H. J. G. Meyer, Physica **20**, 1149 (1954).

theory is

$$\mu_0=\frac{8a_0e}{3}\frac{1}{(2\pi mk\Theta_l)^{\frac{1}{2}}}\left(\frac{\kappa\kappa_0}{\kappa-\kappa_0}\right)\left(\frac{m}{m^*}\right)^{\frac{3}{2}}\frac{\chi(Z)(e^Z-1)}{Z^{\frac{1}{2}}},\quad(9)$$

where $a_0=\hbar^2/me^2$ and $Z=\Theta_l/T$. The function $\chi(Z)$ is given in references 19 and 21, and is slowly varying. Since there is very little difference between the numerical results for ZnO in the temperature range of interest between the perturbation and intermediate-coupling theories, we have chosen to use the former. [There is no real inconsistency in using the intermediate-coupling theory to obtain from $m^{(H)}$ the m^* used in Eq. (9).] The mobility, μ_0, from Eq. (9), which would result from optical-mode scattering alone in ZnO, is shown in Fig. 8. When compared with the experimental Hall mobility, the agreement between theory and experiment is very satisfying. The curve of μ_0 lies just above the experimental points so that the addition of some acoustical-mode scattering is possible. The presence of acoustical-mode scattering in this temperature range is required to explain the presence of a "phonon-drag"[24] contribution to the thermoelectric power in these crystals.[25] Since $\mu_0\sim(m/m^*)$,$^{\frac{3}{2}}$ it is clear that m^* cannot be appreciably larger than the value we have obtained from the ionization energy of the hydrogen-like donor states, though it may be somewhat lower. There are indications from the phonon-drag effect that the ratio of μ_a/μ_0 is smaller than that shown in Fig. 8. Anisotropy of the inertial mass as well as a "central cell" correction to $m^{(H)}$ might have this effect.

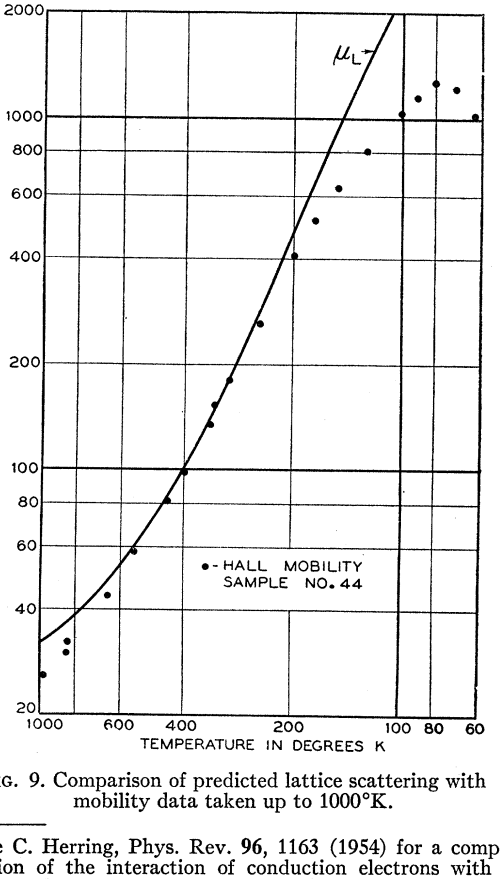

FIG. 9. Comparison of predicted lattice scattering with mobility data taken up to 1000°K.

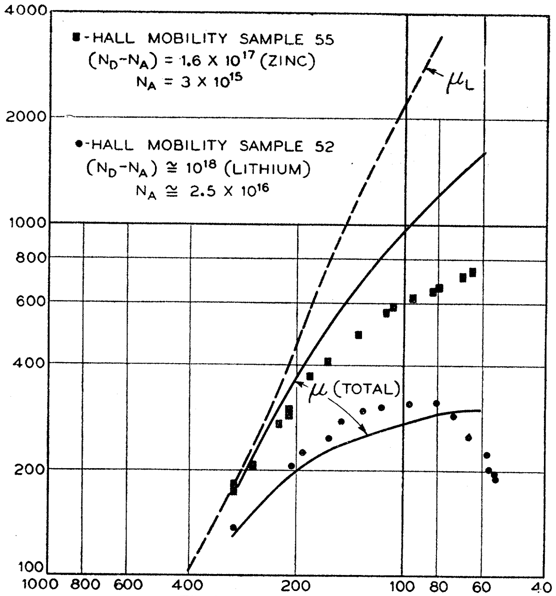

FIG. 10. Mobility data for two heavily doped samples compared with a combination of the lattice scattering and ionized and neutral impurity scattering.

Above 200°K the Hall mobility shown in Fig. 8 was obtained on all zinc oxide crystals with donor concentrations below 10^{17} cm^{-3} within the experimental error of about 10% resulting from geometrical uncertainties. Thus, we may assume that only lattice scattering need be considered above 200°K, and proceed to add an acoustical-mode contribution of the form $\mu_a\sim T^{-\frac{3}{2}}$. The lattice scattering mobility, $\mu_L=\mu_a\mu_0/(\mu_a+\mu_0)$ is shown in Fig. 8, as well as the μ_a required to bring μ_l into agreement with the experimental points. At present there is insufficient information available to calculate the magnitude of μ_a independently.

The temperature variation of our μ_l seems to agree with experiment in the range 200°K to 600°K. Measurements of Hall mobility up to 1000°K were carried out on sample 44 as shown in Fig. 9. The discrepancy between μ_l and the data above 600°K may have been due to the fact that donor concentrations were changing by diffusion during the measurement.

Impurity scattering mobilities have been computed by using the Conwell-Weisskopf, Brooks-Herring formula for the ionized centers and Erginsoy's formula for neutral donors.[26] The scalar effective mass $m^{(P)}=0.27m$ was used throughout and the concentrations

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[24] See C. Herring, Phys. Rev. **96**, 1163 (1954) for a complete discussion of the interaction of conduction electrons with the acoustical phonons resulting in the "phonon-drag" contribution to the thermoelectric power.

[25] A. R. Hutson, Bull. Am. Phys. Soc. Ser. II, **2**, 56 (1957).

[26] See reference 16, pp. 156–162.

of neutral and ionized centers were obtained from the Hall effect analysis. The total mobility was obtained simply from the sum of the reciprocals of the individual mobilities. The solid line of Fig. 8 shows the mobility (total) compared with the data. It appears that either the impurity concentrations obtained from the Hall analysis are not sufficient to account for the scattering at low temperatures, that our simplified application of impurity scattering theory to ZnO is too crude, or that μ_a/μ_0 is smaller than indicated in Fig. 8. Some justification for the latter alternative is illustrated in Fig. 10 where the same mobility analysis has been applied to two highly doped samples. The mobility is seen to drop at least qualitatively in agreement with the prediction of the impurity scattering theories. However, the concentration of donors in sample 52 is so high that the distance between ionized donors is less than the wavelength of a thermal electron, a situation which probably invalidates the present theory of impurity scattering. In the foregoing, no heed has been paid to the subtleties of the relation between the Hall and microscopic mobilities as the scattering mechanism changes with temperature, or to the errors inherent in summing the reciprocal mobilities obtained from different scattering mechanisms. It is felt that such refinements are as yet unwarranted in view of our present limited knowledge of the band structure of zinc oxide.

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Copper-Doped Germanium as a Model for High-Resistivity Photoconductors

P. J. VAN HEERDEN
General Electric Research Laboratory, Schenectady, New York

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In the electrical behavior of high-resistivity copper-doped germanium the nature of the electrodes plays an essential role. Three different types of space-charge contacts can be distinguished. For two types of contacts only primary photocurrents are observed, for the other both primary and secondary photocurrents. The secondary photocurrent is observed only in samples with the electrodes prepared in such a way that they show the space-charge-limited current. A simple theory on the magnitude of the secondary photocurrent is confirmed experimentally. Also, some observations are given on the space-charge-limited current and some experiments which throw light on the mechanism of electrical breakdown in this material.

1. INTRODUCTION

IN a previous article[1] the author derived a condition under which primary photocurrents can be observed in photoconduction. This condition (already derived earlier by Ryvkin[2]) is that the time T required for a carrier to traverse the photoconductor is small with respect to the dielectric relaxation time ($\rho\epsilon$), so: $\beta\equiv T/\rho\epsilon\ll 1$. It was proposed then to study copper-doped germanium, because it would be possible in that material to vary the resistance in one sample, by varying the temperature, from a high resistance in which the above condition is satisfied to a resistance where β becomes of the order of or larger than unity. This should give the rise of the secondary photocurrent from an unobservably small value at liquid nitrogen temperature to a magnitude comparable to that of the primary photocurrent at room temperature. An investigation of copper-doped germanium has now been carried out and is reported in this paper. However, the experimental results changed the author's views somewhat and the experiments presented here are different therefore from the one he had originally in mind. The reason is the following: the original condition for the observation of the primary photocurrent was derived for an *ohmic* contact, defined as one in which the Fermi level in the electrode material is exactly equal to the one in the photoconductor. Since this is only a point in an infinite spectrum of possibilities, in which the Fermi level in the electrode material lies either higher or lower, this condition can in practice "hardly ever" be realized. Now many authors have used the term "ohmic contact" for contacts in which the Fermi level in the electrode material lies higher than the one in the photoconductor, so that free entry of electrons into the latter is possible. This terminology is correct for all practical purposes in the case of low-resistivity photoconductors like germanium and silicon at room temperature, since this contact leads to an "ohmic" current, that means a current obeying Ohm's law and determined by the resistivity of the photoconductor. However, in high-resistivity photoconductors (and "high resistivity" will

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[1] P. J. van Heerden, Phys. Rev. **106**, 468 (1957).

[2] S. M. Ryvkin, Doklady Akad. Nauk S.S.S.R. **106**, No. 2, 250 (1956).