Scattering of Carriers from Doubly Charged Impurity Sites in Germanium

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(Received January 31, 1956)

The effect of doubly charged impurity sites on the mobility of carriers in Ge has been observed in both equilibrium and photoconductivity measurements. For equilibrium studies Zn-doped samples were used. Zn is a double-acceptor impurity in Ge, introducing levels at about 0.03 ev and 0.09 ev from the valence band. Studies of the magnitude of mobility indicate that the scattering cross section for holes from doubly charged Zn sites is approximately four times that for holes from singly charged Ga sites.

For *n*-type Ge crystals containing Fe, Ni, Mn, or Zn impurity sites, charged doubly negative by compensation, high light-level photoconductivity experiments indicate that an increase in the steady-state free electron concentration is associated with a corresponding increase in mobility. This mobility increase is attributed to a decrease in charge from two to one units at the sites of trapped holes. Its magnitude is consistent with a Z^2 dependence for charged impurity scattering. In heavily doped crystals, the mobility change represents an appreciable fraction of the conductivity change. On saturation of hole trapping (approximated in Fe- and Mn-doped samples), the concentration of trapped holes is observed to be approximately equal to the known double-acceptor impurity concentration. Thus hole trapping may be unambiguously identified with specific double-acceptor impurities.

I. INTRODUCTION

CERTAIN low-solubility impurities introduce two deep acceptor levels in the forbidden band of germanium.[1,2] The double-acceptor nature of these impurities has been inferred from the fact that the two impurity levels are present in about the same concentrations and from photoconductivity experiments, whose interpretation is simplified by the assumption of doubly charged impurity sites.[3] In general, the solubilities of these impurities are so low that it is difficult to show directly from mobility studies that the impurity sites are doubly charged. Quantitative demonstration of this would dispose of any possibility that the two acceptor levels associated with a given impurity are due to atoms at different types of sites in about the same concentrations.

In the first part of this paper, evidence is presented which indicates that Zn acts as a double-acceptor impurity in Ge with a maximum solubility, considerably higher than that of the other double-acceptor impurities investigated heretofore. Hall coefficient studies indicate that the two impurity levels associated with Zn exist in about the same concentration. Evidence that the Zn atoms may occur either in neutral, singly, or doubly charged states depending on temperature and degree of compensation, is obtained from the temperature dependence of mobility for a variety of samples. The magnitude of scattering from doubly charged Zn sites is shown to be about four times that from singly charged Ga sites, by careful comparison of mobilities for a series of Zn-doped crystals with mobilities for a series Ga-doped crystals.

The remainder of this paper is concerned with photoconductivity in Ge crystals containing double-acceptor impurities. Previous studies had led to the conclusion that hole trapping is the important photoconductive process in such crystals. The strongest evidence for this conclusion was obtained from studies of the Hall coefficient of optically excited carriers[3] in high resistivity *n*-type samples. It was observed that as a result of intrinsic optical excitation, producing electron-hole pairs, only the electrons were mobile, the holes being trapped. In these experiments it was assumed that the holes were trapped at the double-acceptor sites.

In the present work the emphasis is placed on high light-level experiments on low-resistivity *n*-type crystals doped with Fe, Ni, Mn, or Zn, with sufficient counter-doping to insure that the concentration of Sb or As is greater than twice the concentration of the specific double-acceptor impurity. Thus, in equilibrium, at low temperature, the double-acceptor impurity sites are all doubly charged negatively and the concentration of available hole traps is known. For Fe- and Mn-doped samples, with the light source used, hole trapping may be almost saturated in the sense that most of the impurity sites have been converted from doubly to singly charged. This identification of the known concentration of specific impurity sites with the concentration of trapped holes precludes the possibility that uncontrolled impurities or imperfections in the crystals are responsible for the photosensitivity. The magnitudes of mobility changes which are associated with the trapping of holes at the double-acceptor sites give further confirmation of the model.

II. EQUILIBRIUM MEASUREMENTS

A. Instrumentation and Temperature Scale

Most of the data to be presented were obtained using a single Dewar cryostat with instrumentation and techniques which have been described.[2] Temperature measurements were made with a copper-constantan thermo-

[1] For the properties of Au-doped Ge see W. C. Dunlap, Jr., Phys. Rev. **97**, 614 (1955).
[2] For properties of Fe-, Ni-, Co-, and Mn-doped Ge see: W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954); Tyler, Newman, and Woodbury, Phys. Rev. **97**, 669 (1955) and **98**, 461 (1955); H. H. Woodbury and W. W. Tyler, Phys. Rev. **100**, 659 (1955).
[3] W. W. Tyler and R. Newman, Phys. Rev. **98**, 961 (1955).

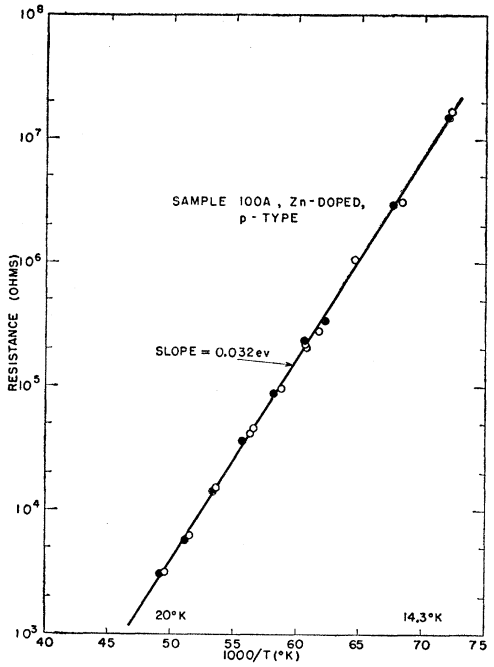

FIG. 1. Temperature dependence of resistance for the Zn-doped Ge thermometer, sample 100*A*. The sample was calibrated against the vapor pressure of hydrogen. Open circles represent the first calibration; closed circles represent a recalibration after four cycles between 300°K and 14°K.

couple whose calibration[4] was checked against vapor pressure in the nitrogen and hydrogen regions. The lowest temperature obtained using the single Dewar cryostat was 25°K.

Near the completion of the work on Zn-doped crystals, a double Dewar cryostat was built. With this cryostat, using liquid hydrogen in the inner Dewar, measurements have been made down to about 14°K, the triple point of hydrogen. The instrumentation and method of preparing and mounting samples for Hall coefficient and resistivity measurements were similar to that described before.[2] In the region from 14°K to 20°K temperature measurements were made using a calibrated Zn-doped Ge crystal[5] whose resistivity-temperature dependence is characteristic of the 0.03-ev level. (See text below.) Figure 1 shows this resistivity-temperature dependence as determined by calibration against the vapor pressure of hydrogen. Fused In was used for electrical contact to the thermometer. Both the thermometer and sample under study were fastened to the sapphire sample holder using "calorimeter adhesive"[2] and thus have similar thermal contact to the sample holder.

B. Hall Coefficient Measurements on Zn-Doped Crystals

Dunlap[6] has reported that Zn introduces an acceptor level in Ge at about 0.03 ev from the valence band. In view of the $4s^2$ electron configuration in Zn, it seemed reasonable, in analogy with subsequent observations[2] for Fe, Co, Ni, and Mn, that Zn should introduce two acceptor levels in Ge. This has been confirmed; the other level appears at about 0.09 ev from the valence band.

Crystals were grown by the conventional method using New Jersey Zinc Company "spectroscopically pure" Zn for doping the melt. In order to show up the deep Zn level, an Sb-Ge alloy was used as counter-doping material to compensate the lower levels. To obtain *n*-type samples containing doubly charged Zn

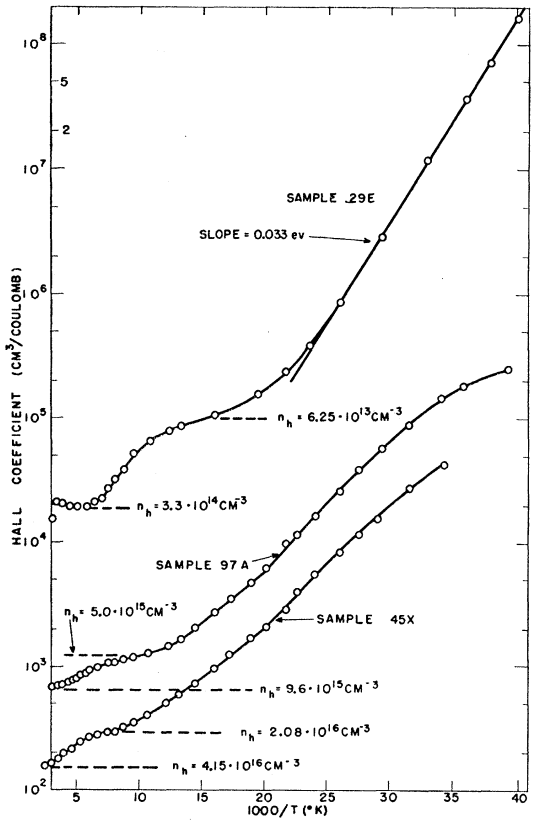

FIG. 2. Hall coefficient *vs* temperature for three *p*-type, Zn-doped Ge crystals containing different Zn concentrations. Estimated carrier concentrations characteristic of plateau values in the Hall curves are indicated in the figure. Samples 45*X* and 97*A* are uncompensated; sample 29*E* is partially compensated.

[4] We are indebted to W. DeSorbo for providing the constantan wire and calibration.

[5] Ge crystals doped with the appropriate impurities have several advantages as thermometers. As indicated in Fig. 1, very high sensitivity is attainable over restricted temperature ranges and the calibration is quite stable. The particular Zn-doped thermometer in use has been cycled many times between room temperature and 14°K with no observable change in calibration. The variety of impurity levels now identified in Ge permits fabrication of thermometers having high sensitivity over restricted temperature ranges for any temperature region from room temperature to about 4°K. Below 4°K, banding effects [See H. Fritzsche, Phys. Rev. **99**, 406 (1955); F. J. Darnell and S. A. Friedberg, Technical Report No. 1, Carnegie Institute of Technology, June 30, 1955 (unpublished)] in even the purest Ge crystals will evidently cause a saturation of resistivity and loss of sensitivity.

[6] W. C. Dunlap, Jr., Phys. Rev. **96**, 40 (1954).

atoms, sufficient Sb was used to compensate both of the Zn levels. Because of the relatively high rate of evaporation of Zn from the Ge melt, it is difficult to obtain accurate values of the distribution coefficient. The values of k_0 to be quoted were obtained by first melting the Ge, dropping the Zn pellet into the melt and immediately pulling the crystal. Hall coefficient measurements were made on a sample cut immediately adjacent to the seed. For several crystals, calibrated alloys of Zn and Ge were used to permit controlled doping with small quantities of Zn. The values of k_0 calculated for samples from 7 crystals ranged from 3×10^{-4} to 5×10^{-4}, with a value of 4×10^{-4} considered representative.[7,8]

Figure 2 shows Hall coefficient data for three samples which differ by a factor of 100 in Zn content. Unless noted, all Hall data to be presented were taken at 6100 gauss. Samples 97*A* and 45*X* were grown from Zn-doped melts with no deliberate compensation. The temperature regions of "freeze-out" due to the two acceptor levels are each associated with about the same change in carrier concentration, 5.0×10^{15} cm^{-3} for 97*A* and 2.1×10^{16} cm^{-3} for 45*X*. These numbers are assumed to be the Zn concentrations. In the low-temperature region, the slope of the Hall curves for uncompensated samples does not approach the 0.03-ev value which is observed to be characteristic of this level in samples which have been partially compensated. The tendency toward saturation of the Hall coefficient at the lowest temperatures in uncompensated samples seems to indicate the presence of about 2×10^{13} cm^{-3} uncontrolled low-ionization energy (0.01-ev) acceptor levels. Compensation of these uncontrolled impurities and a fraction of the 0.03-ev Zn levels yields samples whose Hall coefficient curves follow a 0.03-ev slope with no tendency toward saturation. Sample 29*E* contains about 3×10^{14} cm^{-3} Zn atoms. Because of Sb counterdoping, about 2.9×19^{14} cm^{-3} of the Zn atoms have the lower acceptor level compensated. The observed slope of 0.033 ev is somewhat higher than the value reported by Dunlap.[6]

Figure 3 shows Hall coefficient data for a series of Zn-doped crystals from the same ingot, containing

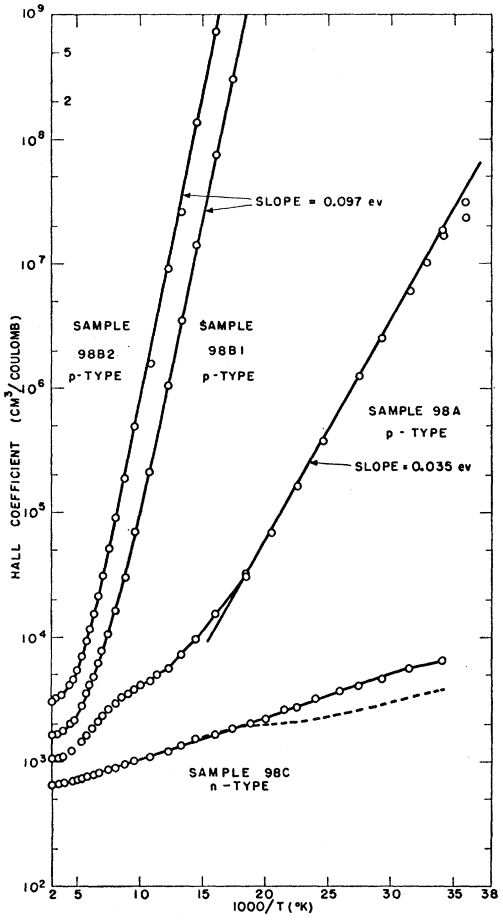

FIG. 3. Hall coefficient *vs* temperature for a series of Zn-doped crystals compensated with Sb. Sample 98*A* has part of the 0.03-ev levels compensated. Samples 98*B*1 and 98*B*2 have the lower levels completely filled. Sample 98*C* is *n*-type, having all the Zn levels compensated. (The dashed line indicates the temperature dependence of Hall coefficient for sample 98*C* on exposure to light, see text.)

increasing Sb compensation ratios proceeding from *A* to *C*. Sample *A* has most but not all of the 0.03-ev levels compensated. Samples 98*B*1 and 98*B*2 contain sufficient concentrations of Sb to compensate all of the 0.03-ev levels and some of the upper levels. The measured slope for each of these curves is 0.097 ev, characteristic of the upper Zn level.[9] Values of this slope observed on other samples all lie between 0.09 and 0.10 ev.[10] For sample 98*C*, all of the Zn levels are

[7] J. A. Burton *et al.*, J. Chem. Phys. **21**, 1987 (1953), quoted the distribution coefficient of Zn in Ge as 0.01. This work is presented in greater detail by J. A. Burton *et al.* in Bell Telephone Laboratories Report No. 38139 (unpublished). A better statement of these early experimental results would have been $2\times10^{-4}<k_0<2\times10^{-2}$, with k_0 being of the order of 0.01 if the major fraction of Zn loss occurred before the Zn pellet dissolved in the melt and k_0 nearer the lower limit if the major Zn loss occurred gradually during the solidification of the crystal. Our experience indicates that no appreciably fraction of the Zn loss occurs immediately after doping the melt. We are indebted to J. A. Burton for providing us with a copy of BTL Report No. 38139.

[8] *Note added in proof.*—Recently, Zn-doped crystals have been grown in a horizontal boat enclosed in a quartz tube which precludes loss of Zn from the melt. Using this technique the value of k_0 obtained is $4.5\cdot10^{-4}$. Although the maximum Zn concentration observed in crystals pulled from the melt was 2×10^{16} cm^{-3}, single crystals containing 5×10^{17} Zn atoms cm^{-3} have been grown in the horizontal boat!

[9] R. Newman has studied photoconductivity in one Zn-doped sample in which the 0.03-ev levels had been compensated. The observed threshold for extrinsic photoconduction is consistent with the 0.1-ev value obtained from Hall coefficient measurements.

[10] The value of these energy levels at absolute zero temperature can be obtained by taking the slope of the R_H *vs* $1000/T$ curve and correcting for the $T^{\frac{3}{2}}$ dependence of the density of states. This correction gives values for the energy levels approximately 10% lower than the slopes of the R_H curve. When one applies this correction, the best values of these Zn levels are 0.030 ± 0.003 ev and 0.090 ± 0.005 ev. Any simple temperature dependence of the energy of these levels with temperature cannot be observed by this type of measurement.

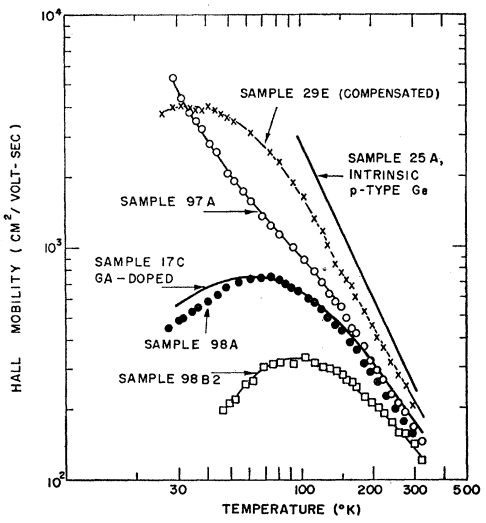

FIG. 4. Hall mobility data for a series of Zn-doped crystals. Solid curves, shown for comparison, indicate the temperature dependence of mobility for a high-purity p-type sample ($25A$) and a Ga-doped sample ($17C$) containing about 1.6×10^{16} Ga atoms per cm^3.

compensated with an excess Sb concentration of about 10^{16} cm^{-3}. The rise in Hall coefficient on cooling is consistent with the ionization energy characteristic of Sb (0.01 ev), assuming 3.4×10^{16} cm^{-3} Sb atoms of which about 2.4×10^{16} cm^{-3} provide electrons to compensate Zn levels. The Zn concentration is approximately 1.2×10^{16} cm^{-3}. Hall coefficient measurements on a series of Zn-doped samples with varying concentrations of counterdoping impurity have yielded no evidence for levels other than the two acceptor levels described.

C. Hall Mobility in Zn-Doped Crystals

Figure 4 indicates the temperature dependence of Hall mobility (R_H/ρ at 6100 gauss) for a series of p-type Zn-doped samples. The line designated intrinsic represents the temperature dependence of mobility (measured at 6100 gauss) characteristic of a p-type sample in which impurity scattering is negligible ($N_A+N_D<5\times10^{13}$ cm^{-3}). Also shown for comparison with the Zn-doped samples is the solid curve representing the temperature dependence of mobility for an uncompensated Ga-doped sample, $17C$, containing 1.6×10^{16} Ga atoms per cm^{+3}. (R_H data for $17C$ is shown in Fig. 5.) The mobility dependence shown in Fig. 4 for $97A$ is characteristic of Zn-doped samples with no compensation. As this sample is cooled, its mobility becomes appreciably higher than the mobility of Ga-doped sample $17C$ even though their mobilities at room temperature are comparable. This difference in mobility is associated with the decrease in charge of the Zn sites as the sample is cooled. In particular, the variations in the mobility of sample $97A$ can be associated with the freeze-out of carriers into the 0.09-ev level in the region of 150°K and the freeze-out into the 0.03-ev level in the region 50°K. At low temperatures, the mobility of the lightly doped sample $29E$ crosses that for $97A$ because of compensation which insures that about 2×10^{14} cm^{-3} charged scattering centers remain as sample $29E$ cools. At the temperature for which the mobilities of $97A$ and $29E$ are comparable, Fig. 2 indicates that the concentration of singly charged Zn atoms in sample $97A$ is also about 2×10^{14} cm^{-3}. In contrast to uncompensated Zn-doped crystals, samples such as $98A$ and $98B2$ show low mobility at low temperature because of the compensated Zn levels and ionized Sb sites. Samples $97A$ and $98A$, for comparison, have approximately the same Zn concentration (5×10^{15} cm^{-3}). However, sample $98A$ contains in addition about 4×10^{15} cm^{-3} Sb atoms.

Detailed comparison of 300°K mobility values for uncompensated Zn-doped crystals and Ga-doped crystals gives evidence that the Zn sites are doubly charged. Figure 6 shows values of 300°K mobility plotted as a function of Ga concentration. On the same figure are shown values of 300°K mobility for a series of uncompensated Zn-doped samples assuming the Z^2 scattering law, i.e., for each Zn-doped sample the value of the abscissa used in plotting the mobility is four times (Z^2) the Zn concentration as determined from Hall data in the manner described. A correction was applied to the Zn data to account for the fact that at 300°K an appreciable fraction of the Zn sites are not doubly charged in the most heavily doped samples (see Fig. 2). As an example, this correction amounted to 12%

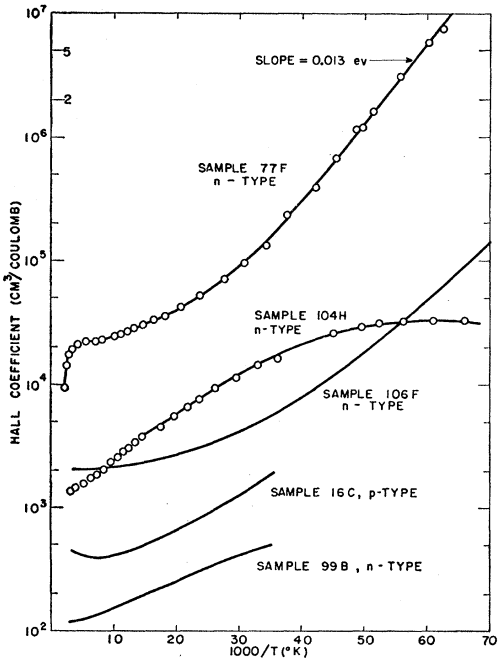

FIG. 5. Hall coefficient data for a group of Ge crystals which are discussed at various places in the text. (*Note:* "Sample 16C" should read "Sample 17C.")

for sample 97*B*. Because of these corrections and other uncertainties such as the magnetic field effects described below, an exact Z^2 dependence has not been established. However, it has been determined that Zn sites have a scattering cross section at least three times that of Ga sites and thus must be doubly charged.

The data shown in Fig. 6 were all taken using the same equipment with a magnetic field of 6100 gauss. The samples and the fused In contacts were of approximately the same size for both Ga-doped and Zn-doped samples. Thus although the absolute accuracy of mobility values may possibly be in error by as much as 10% due to sample geometry, size of contacts[11] or instrumental errors, the relative values should not be in error by more than 5%.

For the near-intrinsic Ga-doped samples, values of Hall coefficient are dependent on the magnetic field.[12] On extrapolation of Hall coefficient data to high magnetic field values, using results of Willardson *et al.*,[12] the mobility-concentration plot shows a plateau value at about 2000 cm²/volt-sec in the region of low impurity concentration, in reasonable agreement with drift mobility measurements.[13] (Conversely, this plateau value may be moved up to about 3500 cm²/volt-sec using 600-gauss data.) For samples of impurity concentration in the region for which comparison is made in Fig. 6, from about 10^{16} cm^{-3} to 10^{17} cm^{-3} and above, magnetic field effects (up to 6100 gauss) are negligible. This is probably because mobility values for both fast and slow holes have decreased to such an extent that the weak-field approximation is applicable even at 6000 gauss.[12] In the absence of knowledge concerning the dependence of the ratio of mobility of fast holes to slow holes on impurity scattering, it is not possible to deduce exact carrier concentrations from Hall coefficient data. Thus there may be some uncertainty in impurity concentrations quoted in this paper, all

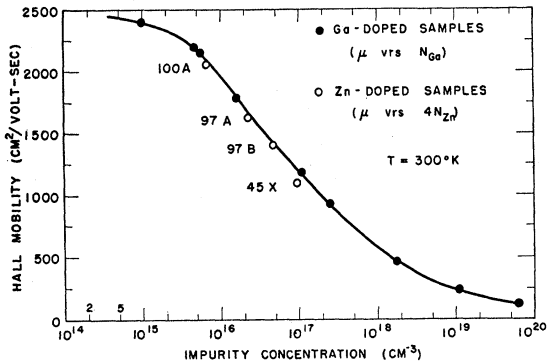

FIG. 6. Solid circles represent the Hall mobility measured at 300°K and 6100 gauss plotted against impurity concentration (N_{Ga}) for a series of uncompensated Ga-doped Ge crystals. The squares show mobility also at 300°K and 6100 gauss, for a series of uncompensated Zn-doped crystals plotted against $4N_{Zn}$, where N_{Zn} is the estimated Zn concentration.

[11] W. C. Dunlap, Jr., Phys. Rev. **79**, 286 (1950).
[12] Willardson, Harman, and Beer, Phys. Rev. **96**, 1512 (1955).
[13] M. B. Prince, Phys. Rev. **92**, 681 (1953).

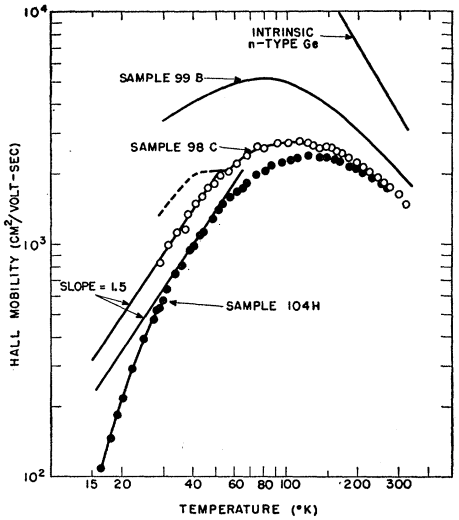

FIG. 7. Hall mobility *vs* temperature for two *n*-type Zn-doped samples. Hall coefficient data for 98*C* are shown in Fig. 3 and for 104*H* in Fig. 5. Mobility data for intrinsic *n*-type Ge and for an uncompensated Sb-doped sample containing about 5×10^{16} Sb atoms per cm³ are shown for comparison. For 98*C*, the dashed curve indicates the affect of exposure to light on mobility (see text).

of which have been calculated from the simple relation $n=1/R_He$.

Figure 7 shows mobility data for *n*-type Zn-doped samples 98*C* and 104*H* compared with that for 99*B*, containing only Sb. For the *n*-type samples there is no method of obtaining the Zn concentration directly from R_H values. Because of the Zn evaporation problem, the most reliable method of obtaining Zn concentrations in *n*-type samples is by comparison with similarly positioned samples in crystals grown at the same rate with same initial Zn concentration in the melt but with no compensation.[14] The Zn concentration is estimated to be about 1.2×10^{16} cm^{-3} for 98*C* and somewhat higher for 104*H*. The excess Sb concentration ($N_{Sb}-2N_{Zn}$) for 98*C* and 104*H* and the Sb concentration for 99*B* may be obtained from the Hall coefficient curves of Figs. 3 and 5. Within the uncertainty of our knowledge of impurity concentrations for these Zn-doped samples, comparison of mobility values with 99*B* again indicates that the Zn sites must be doubly charged.

Because of the strong impurity scattering in samples such as 98*C* and 104*H* and because the scattering is predominantly due to centers whose charge is not changing with temperature, it is of interest to look for the $T^{\frac{3}{2}}$ dependence predicted for charged impurity scattering.[15] The direct observation of a possible $T^{\frac{3}{2}}$

[14] The assumption is made that the distribution coefficient for Zn is not affected by the presence of Sb in the melt. R. N. Hall has shown experimentally that no significant interactions of this nature exist in the case of Ge crystals grown from melts containing both In and Sb (or Ga and Sb) at concentrations compared to those used in this work.
[15] E. Conwell and V. F. Weisskopf, Phys. Rev. **77**, 388 (1950); also see H. Brooks, Phys. Rev. **83**, 879 (1951); N. Sclar, Bull. Am. Phys. Soc. Ser. II, **1**, 48 (1956); and F. J. Blatt, Bull. Am. Phys. Soc. Ser. II, **1**, 48 (1956); for refinements of this theory.

dependence for samples doped only with the conventional hydrogen-like impurities is not possible in this temperature range because the number of charged centers is not constant.[16] For both 98*C* and 104*H*, a $T^{\frac{3}{2}}$ dependence is observed only over a limited temperature range. For sample 104*H*, on which measurements were carried to lower temperatures, the mobility falls faster than the $T^{\frac{3}{2}}$ dependence below 30°K. However, in the low-temperature range, R_H values for this sample do not increase with decreasing temperature in a manner characteristic of higher purity *n*-type samples but rise to a saturation value (which may be a broad maximum) characteristic of impurity banding.[5] Figure 5 shows R_H data for 104*H* in comparison with 106*F*, which have about the same carrier concentration at 300°K (3×10^{15} cm^{-3}). However, the Sb concentration in 104*H* is about 3×10^{16} cm^{-3} because of the Zn compensation. Because of this evidence of banding, the mobility behavior is not expected to follow a $T^{\frac{3}{2}}$ dependence. For both Ge[5] and Si,[17] the onset of impurity banding seems to be associated with a rapid decrease of mobility with decreasing temperature.

III. PHOTOCONDUCTIVITY EXPERIMENTS

The experimental arrangement used for these measurements has been described.[3] Except where noted, the sample was exposed to light from a tungsten lamp operating at about 3000°C, after filtering by a band-pass interference filter transmitting energies from about 1.5 microns to 1.9 microns and by a 1-mm thick Ge crystal held at the temperature of the sample. Under these conditions, the excitation in the sample is predominantly intrinsic and reasonably homogeneous. The interference filter was used primarily to prevent heating

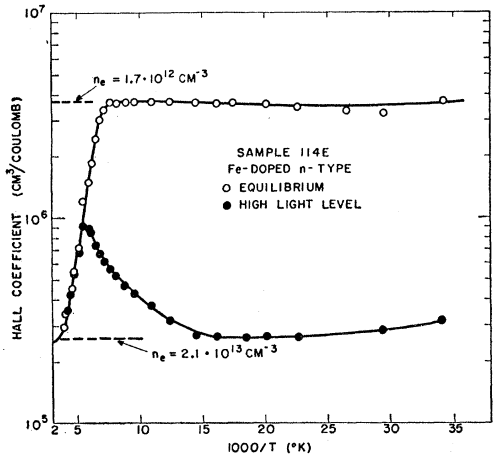

FIG. 8. Hall coefficient *vs* temperature for a compensated Fe-doped crystal containing about 2×10^{13} Fe atoms per cm^3. At high light levels, the steady-state increase in free-electron concentration is about equal to the Fe concentration.

[16] See P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954); for a discussion of mobility measurements in a series of As-doped crystals.

[17] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954); R. O. Carlson, Phys. Rev. **100**, 1075 (1955).

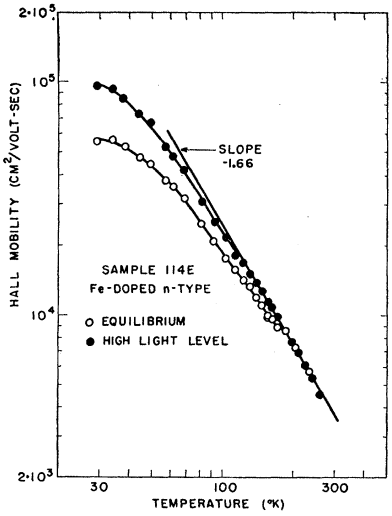

FIG. 9. Hall mobility values corresponding to the Hall coefficient data of Fig. 8. The increase in free-carrier concentration under illumination is accompanied by an increase in the Hall mobility.

of the sample. Hall coefficient and resistivity measurements as a function of temperature were made both in the dark and with the maximum constant light level obtainable under the conditions described. A series of low-resistivity *n*-type samples containing compensated double-acceptor impurities was studied.

Figures 8 and 9 show Hall coefficient and mobility data for an Fe-doped crystal containing about 2×10^{13} cm^{-3} Fe atoms as determined from Hall coefficient measurements.[2] The compensating *n*-type impurity, which was present in the Fe as an impurity, (thought to be phosphorus) supplied about 1.7×10^{12} cm^{-3} atoms in excess of those necessary to compensate the two acceptor levels per Fe atom. The rise in dark values of Hall coefficient between 250°K and 170°K represents the freeze-out of carriers into the upper Fe levels. Sensitivity to light appears at about 200°K. In the temperature region below 80°K, the increase in steady-state free-electron concentration under illumination is approximately equal to the known Fe concentration, indicating that with the light level used, the lifetime of trapped holes is sufficiently long that hole trapping at Fe sites may be effectively saturated. This agreement between values of excess carrier concentration under illumination and the known Fe concentration, identifies Fe as the impurity giving rise to the photosensitivity. Associated with hole trapping at the doubly negative Fe sites is the increase in mobility indicated in Fig. 9. The effect is not large except at the lowest temperatures, because of the small number of impurities involved. The high light-level mobility data follow the usual 1.6 slope to appreciably lower temperature than do the dark data.

Similar results were obtained for a compensated *n*-type sample containing about 6×10^{13} Ni atoms per cm^3. Below about 170°K both the Hall coefficient and mobility values were changed appreciably under illumination. However, for the case of the Ni-doped sample with the light level available, only about $\frac{1}{3}$ of

the Ni atoms were converted from doubly to singly charged by hole trapping. For n-type Zn-doped samples 98C and 104H, similar measurements showed appreciable changes in Hall coefficient and mobility values, only when the samples had been cooled to below 55°K. For sample 98C the effect of light on mobility is shown by the dashed line in Fig. 7 and the corresponding Hall coefficient change is shown by the dashed line in Fig. 3. With the light level used, the change in free-carrier concentration induced by light is only about 10^{15} cm^{-3} or about 10% of the estimated Zn concentration. However, because of the low temperature associated with photoconductivity in the Zn-doped samples, free electrons may be captured in Sb sites and the steady-state free-electron concentration does not necessarily indicate the concentration of trapped holes at Zn sites.

These relatively large photoconductive effects observed in compensated n-type samples seem to be a general characteristic of crystals containing double-acceptor impurities and are related to the long lifetime of holes captured at the doubly charged negative sites. No such sensitivity is observed for p-type samples of comparable resistivity which contain the same concentrations of double-acceptor sites, in addition to conventional hydrogenlike acceptor impurities. At comparable light levels and temperatures, conductivity changes are at most 1%. In low-resistivity p-type samples the principal effect of double-acceptor impurities is to reduce the recombination lifetime.

In concluding the description of high light-level photoconductivity experiments on low-resistivity samples,

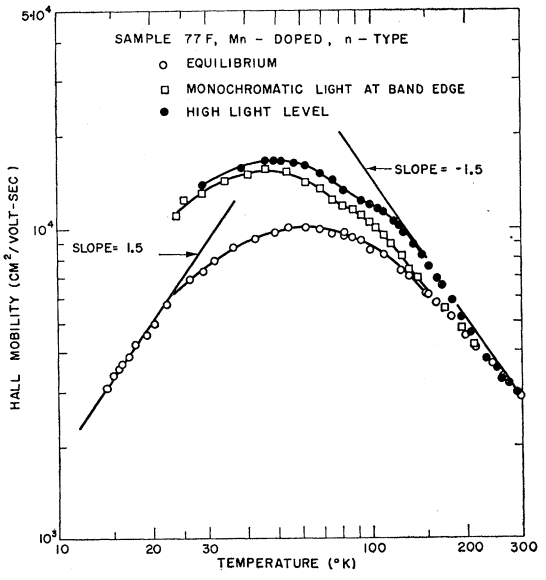

FIG. 10. Hall mobility data corresponding to the Hall coefficient data of Fig. 11. Equilibrium values, which were measured down to 14°K, show a $T^{\frac{3}{2}}$ dependence over a limited temperature range. Mobility values corresponding to "intermediate light level" data of Fig. 10, lie between the values designated by squares and closed circles.

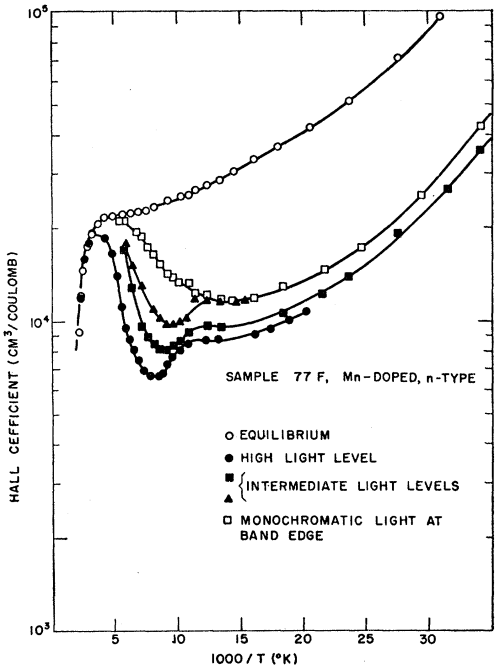

FIG. 11. Hall coefficient data for n-type Mn-doped crystal 77F in equilibrium and under various conditions of illumination. The three lowest curves represent response to filtered light from a W lamp operated at different temperatures. The data designated by open squares indicate response to monochromatic light at 1.6μ.

some slightly more detailed results for Mn-doped samples will be presented. n-type samples were prepared containing between 5×10^{14} cm^{-3} and 10^{15} cm^{-3} Mn atoms with sufficient arsenic to compensate the Mn states and to provide about 3×10^{14} cm^{-3} excess free electrons in equilibrium. Equilibrium Hall coefficient data for one such Mn-doped sample, 77F, are given in Fig. 5. The low-temperature rise in R_H values indicates a slope of 0.013 ev, the ionization energy for As.[18] No evidence for impurity banding in this temperature range is observed for this sample, in which the As concentration is about 2×10^{15} cm^{-3}. Equilibrium mobility data for this sample are shown in Fig. 10. Over a limited temperature range, an approximate $T^{\frac{3}{2}}$ slope is observed.[15] In the temperature range showing the $T^{\frac{3}{2}}$ dependence, although some change in the free-carrier concentration is observed (Fig. 5), the major temperature-independent contribution to the scattering is due to the doubly charged Mn sites and the ionized As sites which have provided compensating electrons.

Figure 10 also shows values of mobility for sample 77F under various conditions of illumination, in addition to the equilibrium data. Corresponding Hall coefficient data are shown in Fig. 11. Data for a similar sample but from a different crustal are shown in Figures 12 and 13. Because the upper Mn level is very near the center of the band, it is difficult to distinguish between

[18] T. H. Geballe and F. J. Morin, Phys. Rev. **95**, 1085 (1954).

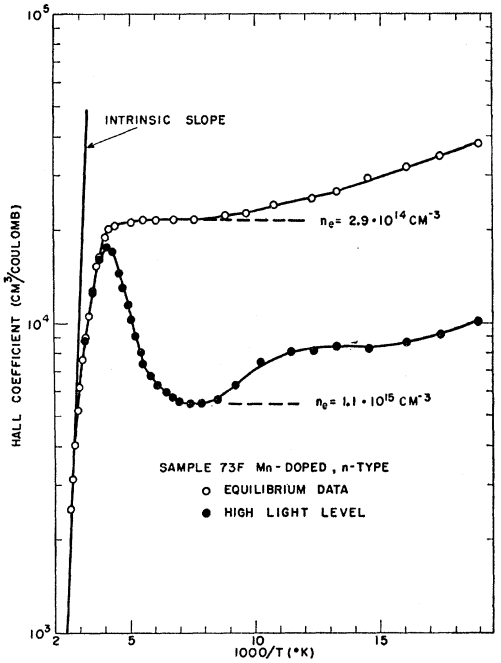

FIG. 12. Hall coefficient data for n-type Mn-doped sample 73F in equilibrium and under high light-level excitation. The increase in free carrier concentration under excitation is approximately equal to the Mn concentration.

intrinsic and extrinsic regions on Hall coefficient curves. Figure 12, which is plotted on a somewhat expanded scale, illustrates this difficulty. Data points seem to deviate from the intrinsic slope at Hall coefficient values of about 7×10^3 (cm^3/coulomb) but the separation is not clear. Thus it is not possible to make a very accurate estimate of Mn content in these samples. By comparison with p-type Mn-doped samples prepared under similar conditions, it is estimated that the Mn concentration in 77F and 73F is between 5×10^{14} cm^{-3} and 8×10^{14} cm^{-3} and is somewhat higher for 73F than for 77F.

Figures 11 and 12 indicate that photosensitivity in the Mn-doped samples becomes apparent at the temperature associated with complete freeze-out of electrons into the upper Mn levels. Below this temperature, in equilibrium, the Mn sites are doubly charged. Hall coefficient data designated as high light level in Figs. 11 and 12 were obtained using maximum light available from the W lamp at 3000°K with the filtering described above Under these conditions the maximum increase in carrier concentration observed at about 130°K, is approximately equal to the estimated Mn concentration for each sample. As for the case of the Fe-doped sample, we interpret these results by assuming saturation of hole trapping at the Mn sites.

The increase in R_H values at low temperatures for both equilibrium and high light-level values is attributed to freeze-out of electrons into As levels. However, several features of the high light-level Hall coefficient curves have not been explained in detail. For both samples, some structure is observed at about 100°K in the curves representing high light-level data, even though the incident light flux remains constant. For sample 77F, R_H values were measured at lower light levels as indicated in Fig. 11. Data designated as intermediate light levels were obtained by merely decreasing the temperature of the W filament. Data designated by open squares were obtained by passing light from the W lamp through a Gaertner Monochromator with wavelength setting of 1.6μ and slit widths set at $\frac{1}{2}$ mm. For these data the structure is not apparent although for the data designated by triangles, giving the same response at 70°K and lower, structure is apparent in the 100°K region. Thus the exact shape of the R_H curve depends on the spectrum of the excitation. For data taken without use of the monochromator, some component of the quench spectrum characteristic of Mn-doped samples[19] is present in the excitation spectrum. The temperature dependence of the ratio of quench to excitation may affect the shape of the R_H curves in the manner observed.

Preliminary studies of the intensity dependence of carrier concentration have been made for sample 77F. Measurements were made using the filtered W lamp radiation, decreasing the light intensity with a series of neutral filters. At 70°K, it was observed that decreasing the light levels by a factor of 100 from the maximum value decreased the excess electron concentration only by a factor of 2. This very pronounced lack of proportionality is expected as the condition of saturation of available hole traps is approached. The nature of this variation depends on temperature, and

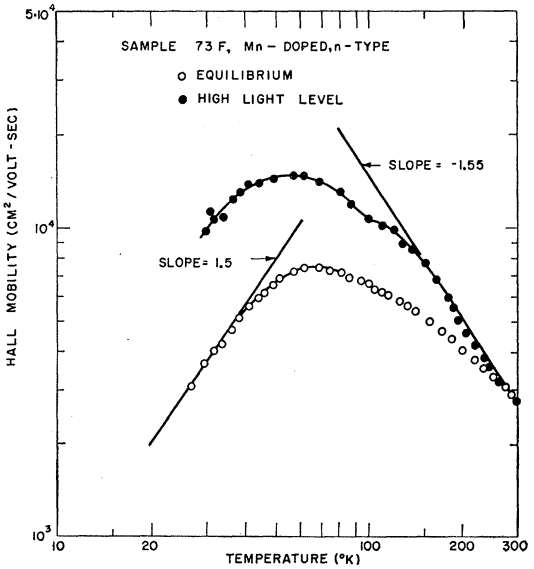

FIG. 13. Hall mobility data for sample 73F under conditions of equilibrium and high light-level excitation.

[19] Newman, Woodbury, and Tyler, this issue [Phys. Rev. **102**, 613 (1956)].

the temperature dependence of Hall coefficient values under constant illumination will be affected by this fact. Although the details of the dependence of excess carrier concentration on the light spectrum and intensity are not available, the important observation, emphasized here, is that at high light levels, the excess electron concentration in steady state is approximately equal to the Mn concentration.

Associated with the changes in Hall coefficient induced by light are the mobility changes indicated in Figures 10 and 13. These large increases in mobility associated with the increases in carrier concentration are attributed to a decrease in charged imputity scattering as a result of hole trapping at the doubly charged Mn sites. In spite of some uncertainty in establishing the exact Mn concentration, the magnitude of observed changes in mobility associated with the increases in free-electron concentration may be explained only by assuming that the scattering at the doubly charged Mn sites is reduced by a factor of about 4 as a result of hole trapping. Mobility changes are much too large to permit the assumption that hole trapping is equivalent to the reduction of a singly charged center to a neutral center.

IV. SUMMARY AND DISCUSSION

Evidence has been presented indicating that Zn is a double-acceptor impurity in Ge with acceptor levels at 0.03 ev and 0.09 ev from the valence band. Mobility studies indicate that the scattering from doubly charged Zn sites is about four times that from singly charged Ga sites. Photoconductivity experiments in n-type Ge samples containing Fe or Mn impurities indicate that at high light levels, the steady-state increase in free-electron concentration is approximately equal to the known concentrations of double-acceptor impurities. Mobility increases associated with this increase in electron concentration provide additional confirmation of the assumption that holes trapped at doubly charged impurity sites are responsible for the photosensitivity.

The mechanism for high-yield photosensitivity in Ge, first proposed[2] to explain photoconductivity in Fe-doped Ge, is based on the assumption that double-acceptor impurities introduce sites which may be made doubly charged negatively in equilibrium. Because of Coulomb forces, the capture cross section for holes at these sites is very large but the cross section for the subsequent capture of electrons at the singly charged negative sites is low, giving rise to long free-electron lifetimes and high photosensitivity. This hypothesis of hole trapping has proven satisfactory in interpreting high photoconductive yields, infrared quenching of photoconductivity, Hall coefficient studies of optically excited carriers, and the related mobility changes discussed in this paper.

A complete description of photoconductivity in Ge doped with double-acceptor impurities requires quantitative determination of capture cross sections for electrons and holes at impurity sites under different conditions of charge. Some progress has been made in determining the relevant cross sections. The cross section for electron capture at neutral double-acceptor sites has been determined to be comparable with atomic dimensions ($10^{-15}-10^{-16}$ cm^2) for several of these impurities (Fe, Co, Ni, Mn). These values are obtained from the low-temperature plateau in the temperature dependence of lifetime in low-resistivity p-type samples containing known concentrations of double-acceptor impurities. In such samples these impurities act simply as recombination centers, the capture cross section for the minority carrier being smaller than the subsequent capture cross section for the majority carrier.

In low-resistivity n-type samples in which the double-acceptor sites are doubly charged in equilibrium, the important cross sections are those for hole capture at doubly charged negative sites and the subsequent electron capture at singly charged sites. In such samples the usual recombination theories,[20] assuming no charge storage do not apply, the capture cross section for the minority carriers being much greater than that for majority carriers. The capture cross section for a hole at the doubly charged site has not been measured directly but is assumed to be very large because of the strong attractive Coulomb forces. The subsequent capture cross section for electrons at the singly charged sites is very small and may in principal be deduced from studies of the decay of photoconductivity in n-type samples. Measurements on Mn-doped samples such as 77F and 73F indicate that the capture cross section for an electron at a singly charged Mn site is probably less than 10^{-22} cm^2. In fact, it seems probable that for the case of Mn (except possibly at very low temperatures), recombination never does take place at the Mn site but rather that the trapped hole is eventually evaporated into the valence band with recombination, perhaps after multiple trapping events, taking place at surfaces or other uncontrolled impurity sites.

ACKNOWLEDGMENTS

We are indebted to T. J. Soltys for assistance in all phases of the experimental work and to R. Newman, E. O. Kane, and R. N. Hall for valuable comments and criticisms.

[20] R. N. Hall, Phys. Rev. **83**, 228 (1951); **87**, 387 (1952); W. Shockley and W. T. Read, Jr., Phys. Rev. **87**, 835 (1952).