

## Properties of Germanium Doped with Iron. I. Electrical Conductivity

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Measurements of the temperature dependence of electrical resistivity in *p*- and *n*-type iron-doped germanium crystals indicate that Fe introduces impurity levels in Ge at  $0.34 \pm 0.02$  eV from the valence band and  $0.27 \pm 0.02$  eV from the conduction band. Such samples show very high resistivity at 77°K. At this temperature, *n*-type samples also show high photosensitivity and slow photoresponse, presumably because of hole traps.

### I. INTRODUCTION

CHEMICAL impurities in the Ge lattice may introduce localized energy levels in the energy gap between the valence and conduction bands. Impurity elements which have been studied most extensively are those of columns III and V of the periodic table.<sup>1</sup> For these elements, the hole or electron is considered to be loosely bound in a large hydrogen-like orbit. Ionization energies, calculated on the basis of this model, agree fairly well with the measured values of approximately 0.01 eV. Group III and V elements are assumed to be substitutional in the Ge lattice. Their solubilities are relatively high.

More recent work has yielded information concerning localized energy levels introduced into the Ge band structure by Zn,<sup>2</sup> Cu,<sup>3,4</sup> Ni,<sup>4</sup> Li,<sup>5</sup> Au,<sup>6</sup> and Pt.<sup>7</sup> Except for Li, the levels introduced by these impurities are characterized by ionization energies which are appreciably larger than for the elements of columns III and V. The hydrogen-like model is not applicable, presumably because of the greater localization of wave functions. Also, the maximum impurity concentration attainable in single crystals of Ge is considerably less for these elements than for those of columns III and V.

In order to extend present information concerning the properties of Ge crystals containing impurity elements, we have studied the properties of Fe-doped Ge crystals.<sup>8</sup> The present paper contains information concerning the method of preparation and some electrical properties of these crystals. The following paper reports studies of their optical properties.

### II. PREPARATION OF SAMPLES

The Ge crystals used were pulled from a melt in the usual manner using pulling rates of about 2 in. per hour and rotating rates of about 100 rpm. The direction of growth was (100). Zone-melted polycrystalline Ge

of resistivity  $>40$  ohm-cm at 300°K was used as raw material. During growth, Fe was introduced into the melt at a concentration between 0.04 and 0.1 atomic percent. Due to the rejection of Fe by the growing Ge crystal, the total amount of Fe in the melt remained substantially constant until its concentration reached about 0.3 atomic percent. At this concentration, under the conditions of growth described, pronounced lineage markings appeared abruptly on the surface of the growing crystal, although the crystals remained grossly single down to the sprout, i.e., the crystal faces persisted after lineage appeared. It was demonstrated, using radioactive Fe, that the onset of lineage in the crystals is accompanied by the incorporation of relatively large amounts of Fe in pockets in the growing crystal. The specific activity of the radioactive Fe used and the amount of Fe incorporated in the crystal before the onset of lineage were so low that no estimate of the Fe concentration in crystal regions containing no observable lineage could be made by this technique. All of the experimental data to be reported pertain to samples cut from those parts of the crystal above the observable lineage.

The two sources of Fe used for doping were "Puron" electrolytic Fe obtained from Westinghouse Manufacturing Company and Fe of carbonyl origin obtained from the National Research Corporation and labeled "NRC-64." Although both of these sources were considered relatively pure, Ge crystals doped with Fe from these sources consistently showed different results. Resistivity data to be described below indicates that the concentration of Fe in the crystals used for experimental work is always less than about  $2 \times 10^{18}$  atoms/cc. This represents an effective distribution coefficient of less than  $10^{-6}$  at the doping levels used. Impurities in the Fe which have high distribution coefficients, such as boron ( $k_0 \approx 10$ )<sup>9</sup> and phosphorus ( $k_0 = 0.12$ )<sup>10</sup> are important at concentrations as low as one part in ten million for B,<sup>11</sup> and 10 parts per million for P. Chemical analyses of the two types of Fe indicated that the P

<sup>1</sup> E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952); P. P. Debye and E. M. Conwell, Phys. Rev. **93**, 693 (1954).

<sup>2</sup> W. C. Dunlap, Jr., Phys. Rev. **85**, 945 (1952).

<sup>3</sup> F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

<sup>4</sup> Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

<sup>5</sup> C. S. Fuller and J. A. Ditzenberger, Phys. Rev. **91**, 193 (1953).

<sup>6</sup> W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).

<sup>7</sup> W. C. Dunlap, Jr., Phys. Rev. **94**, 1419 (1954).

<sup>8</sup> Tyler, Woodbury, and Newman, Phys. Rev. **94**, 1419 (1954).

<sup>9</sup> R. N. Hall, J. Phys. Chem. **57**, 836 (1953).

<sup>10</sup> Burton, Kolb, Slichter, and Struthers, J. Chem. Phys. **21**, 1991 (1953). This paper contains a fairly complete listing of known distribution coefficients for Ge.

<sup>11</sup> Under certain conditions it should be possible to make very sensitive analyses of the relative B content of a series of Fe samples by studying the properties of Ge crystals doped with these samples.

content of each might be as high as 20 ppm (parts per million). To measure the B content, the two sources of Fe were compared spectrographically with a calibrated sample (National Bureau of Standards steel No. 151) containing 27 ppm of B. These tests indicated that the NRC Fe contains about  $15 \pm 5$  ppm of B, whereas the Puron Fe contains less than 5 ppm of B.<sup>12</sup> Spectroscopic analyses of the two types of Fe indicated no significant differences between the two in content of In, Sb, As, or Bi. Ga was detected in the NRC Fe, but was probably at a level of several ppm or less. It was not detected in the Puron. It is believed that the differences in behavior of the NRC and Puron-doped Ge crystals to be described below are due to an effective excess of B over P in the NRC Fe and P over B in the Puron Fe.

The samples studied were about 2 mm×3 mm×10 mm and were cut from the ingots with the long dimension perpendicular to the direction of growth in order to minimize effects of inhomogeneity. After heavy etching (80 percent nitric acid, 20 percent hydrofluoric acid), contacts were fused on in a hydrogen atmosphere after which the samples were again etched. For *n*-type samples contacts were of fused Sn; for *p*-type samples contacts were of fused In. Contacts were considered satisfactory if the current between any two was reversible within 20 percent with maximum applied voltage of one volt and if the saturation photovoltage between any pair was <0.01 volt. Except where mentioned, four contacts were used for resistivity measurements with two additional contacts for Hall measurements. Heavy etching after fusing on contacts was found to be particularly important in *p*-type samples.

### III. EXPERIMENTAL DETAILS

A conventional cryostat is used for measurements of resistivity and Hall coefficient as a function of temperature. Figure 1 shows a diagram of the sample holder. A single crystal sapphire plate 0.025 in. thick is used to provide good thermal contact<sup>13</sup> and electrical insulation between the Ge sample and the Cu block to which the thermocouple is attached. In order to seal the sapphire to the Cu, it is first coated on one side with a slurry of titanium hydride and lead which is then fused at high temperature.<sup>14</sup> This surface is then soldered directly to the Cu using a layer of In solder which gives good thermal contact and allows relative motion of sapphire and Cu to accommodate differences in thermal expansion. The sample is then fastened to the sapphire with "calorimeter adhesive."<sup>15</sup> Although the metal cryostat is light tight, the radiation shield, which assumes the same temperature as the sample, is necessary to prevent 300°K radiation from the outer

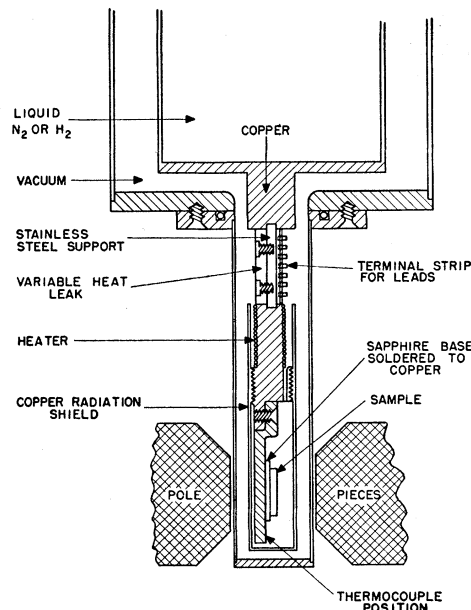


Fig. 1. Cryostat sample holder used for resistivity, Hall coefficient, and photoconductivity decay experiments. For the latter, a small neon light was included next to the sample.

wall of the cryostat from falling on the sample. This shield can be removed in order to observe the effect of room temperature radiation on the properties studied.

All potential measurements for resistivity or Hall coefficient data were taken by using an Applied Physics Corporation vibrating reed electrometer. The high input resistance of this instrument insured that the current drawn through the potential contacts was negligible compared with the current flowing through the sample. The sample current was provided by a calibrated current source which had a series resistance at least 100 times the sample resistance throughout the temperature range investigated. Potential differences across the samples were always less than one volt, minimizing injection and other high field effects.

In order to study steady state and transient photoconductivity effects, the sample holder shown in Fig. 1 was slightly modified. A smaller sapphire plate was used allowing room for a small neon light (G. E. bulb N. E.-2) to be mounted next to the sample, inside the radiation shield. For the measurement of the transient photoconductivity effects, both two and four probe methods were used. No significant differences were noted between these methods as long as the contacts were "ohmic" and gave no evidence of photovoltage. The recovery was studied at short times (<10 seconds) using a Tektronix dc oscilloscope and a DuMont Land-type camera and at long times (up to 20 minutes) using the electrometer and a stop watch. Although the decay characteristic of the neon lamp is not known in detail, experiments indicated it to be less than one millisecond. No attempt was made to measure times

<sup>12</sup> We are indebted to L. B. Bronk of the Analytical Chemistry Unit for all spectroscopic studies of these samples.

<sup>13</sup> R. Berman, Proc. Roy. Soc. (London) **208**, 90 (1951).

<sup>14</sup> R. J. Bondley, Ceram. Age **58**, 15 (1951).

<sup>15</sup> General Electric compound No. 7031 diluted with alcohol and toluene.

shorter than several milliseconds when using the neon bulb. For recombination rate measurements at room temperature a spark light source was used.

#### IV. EXPERIMENTAL RESULTS

##### A. Steady State Resistivity and Hall Mobility Measurements

Both *n*- and *p*-type crystals have been prepared which show very high resistivities at 77°K as a result of doping with Fe. Measurements of resistivity *versus* temperature for *n*-type samples dominated by the Fe impurity indicate ionization energies of  $0.27 \pm 0.02$  ev. For *p*-type samples dominated by Fe, the ionization energies measure  $0.34 \pm 0.02$  ev. These values have been calculated directly from the slopes of  $\log \rho$  plotted against reciprocal temperature for nine *n*-type samples from six different ingots and four *p*-type samples from three different ingots. Throughout the remainder of the paper, samples whose  $\log \rho$  vs  $1/T$  curves show these characteristic slopes over at least five decades in  $\rho$  will be designated simply as high-resistivity *n*-type or high-resistivity *p*-type samples. Samples not dominated by the Fe content but showing a maximum in the equilibrium value of resistivity between 300°K and 100°K will be designated as low resistivity samples. Actually the resistivity for all of the samples to be discussed, except two, is intrinsic at 300°K.

For all ingots in which high resistivity *n*- or *p*-type samples were obtained as a result of Fe doping, the resistivity of samples taken from the ingot before the

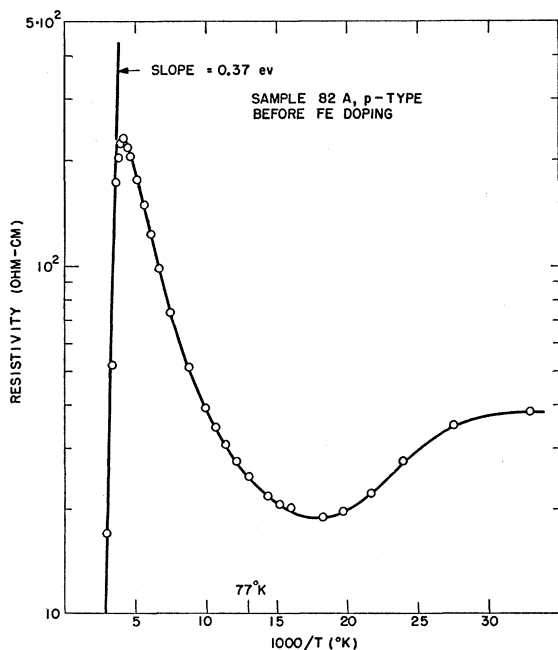


FIG. 2. Resistivity vs reciprocal temperature for sample A from crystal 82, before Fe doping. This curve is typical of undoped regions of several crystals studied.

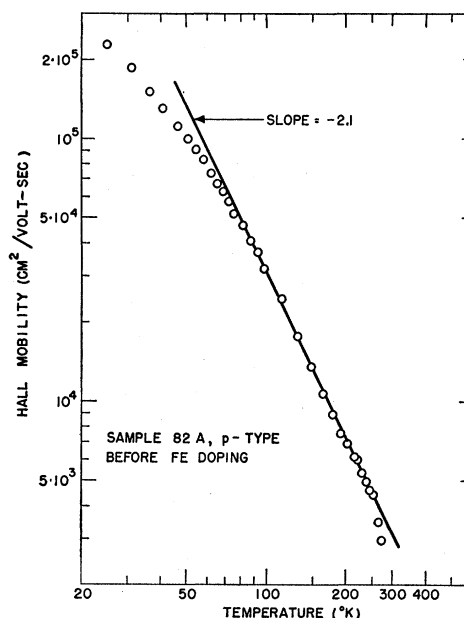


FIG. 3. Hall mobility vs temperature for sample 82A.

Fe was added to the melt show a maximum between 200 and 400 ohm-cm when cooled below room temperature. These samples were always *p*-type, indicating that the purity of the melt is limited by an acceptor impurity or that an acceptor impurity, such as Cu, diffuses into the ingot during growth. In any event the concentration of carriers from uncontrolled, uncompensated impurities was about  $5 \times 10^{12}$  per cc or less.

Figure 2 indicates the dependence of  $\rho$  on  $T$  for a typical sample before Fe doping. The rise in resistivity at 50°K may be due to Cu which is reported to introduce a state with ionization energy of 0.04 ev.<sup>3</sup> Figure 3 shows the dependence of mobility on temperature for the same sample. In agreement with the early work of Dunlap<sup>16</sup> on *p*-type samples, the variation of mobility with temperature is more rapid than the  $T^{-3/2}$  law which has been predicted by theory.<sup>17</sup> Mobility values were calculated in the conventional manner<sup>1,3</sup> by taking the ratio of Hall coefficient divided by resistivity. For all of the data on mobility presented in this paper, the value of the magnetic field used was about 4000 gauss. For sample 82A careful studies of the dependence of mobility on magnetic field strength have been carried out and agree well with data reported recently by Harman *et al.*<sup>18</sup> It is evident that the observed temperature dependence of the mobility will depend to some extent on the magnetic field strength. However, for the magnetic field strength used, the field dependence appears to have saturated. The departure of mobility data at low temperature from

<sup>16</sup> W. C. Dunlap, Jr., Phys. Rev. **79**, 286 (1950).

<sup>17</sup> F. Seitz, Phys. Rev. **73**, 549 (1948); J. Bardeen and W. Shockley, Phys. Rev. **80**, 72 (1950).

<sup>18</sup> Harman, Willardson, and Beer, Phys. Rev. **94**, 1065 (1954).

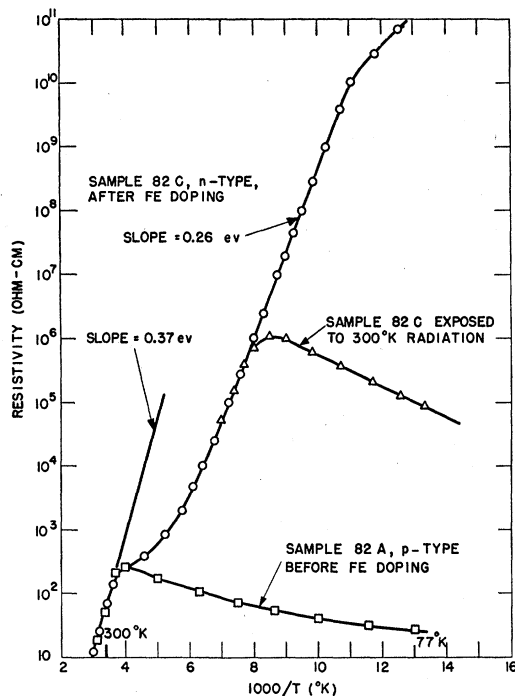


FIG. 4. Resistivity vs reciprocal temperature for a high-resistivity *n*-type Fe-doped sample from crystal 82, compared with data for sample 82A (Fig. 2) before Fe doping. Also shown is the effect of 300°K radiation from the outer wall of the cryostat on the resistivity of the Fe-doped sample.

the approximate power relationship is probably the result of scattering from imperfections or impurities.<sup>1</sup> The general form of the temperature dependence of the mobility observed for this sample and for high-resistivity samples after Fe doping is cited as evidence that the samples are homogeneous and typical of high-purity Ge, justifying the calculation of ionization energies from resistivity data.

Figure 4 shows the dependence of resistivity on temperature for a high-resistivity Fe-doped *n*-type sample which was cut from crystal 82 after Fe doping. For convenience it is compared with the data of Fig. 2. Two contacts were used in taking these data for sample 82C. Later measurements using four contacts were in agreement with the two contact data. With proper shielding of the sample from light and from thermal radiation, the relationship between  $\log \rho$  and  $1/T$  is linear over seven decades. Removal of the radiation shield (shown in Fig. 1) exposes the sample to 300°K radiation and causes the resistivity to reach a maximum at about 115°K and then decrease to a value at 77°K which is about 7 decades below the extrapolated equilibrium value. With the best radiation shielding attained the data deviate somewhat from the linear relationship at about  $10^{10}$  ohm-cm, presumably because of leakage currents. During initial experiments on this sample, it was observed that a bright etched surface was essential. Grinding or lightly sand blasting the

sample creates a low resistance surface layer which shorts the sample with an effective resistance of the order of one megohm as the sample is cooled. This effect is presumably due to the introduction of low ionization energy levels as a result of surface fracture.

Crystal 82 provided the first high-resistivity samples obtained as a result of Fe doping and demonstrated the high photosensitivity later found to be characteristic of high resistivity *n*-type samples. Puron Fe was used in doping this crystal. It was subsequently observed that doping with Puron Fe, if the melt was sufficiently free of other impurities, consistently gives *n*-type material which shows high-resistivity behavior at the point of doping but gives low-resistivity *n*-type material further down the ingot. Doping with the NRC Fe always gives low-resistivity *p*-type material at the point of doping. The resistivity then rises progressively down the ingot, which eventually may yield high-resistivity *p*-type material before lineage develops. Figure 5 shows resistivity plotted against reciprocal temperature for the first high-resistivity *p*-type sample obtained, using NRC Fe for doping. No appreciable change in the curve was observed when the sample was exposed to 300°K radiation.

The properties of a series of crystals doped with either Puron or NRC Fe are consistent with the assumptions that the concentration of Fe included in the growing crystal is relatively independent of the concentration in the melt at the concentrations used ( $\sim 0.08$  percent) and that the Puron Fe contains an excess of P as impurity and the NRC Fe an excess of

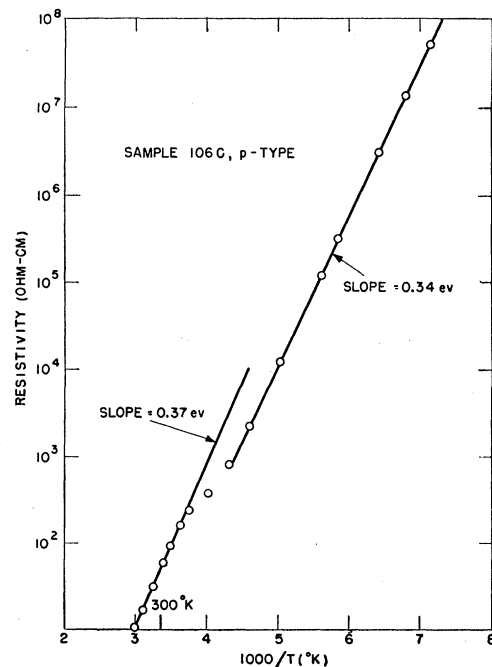


FIG. 5. Resistivity vs reciprocal temperature for a high-resistivity *p*-type Fe-doped sample.

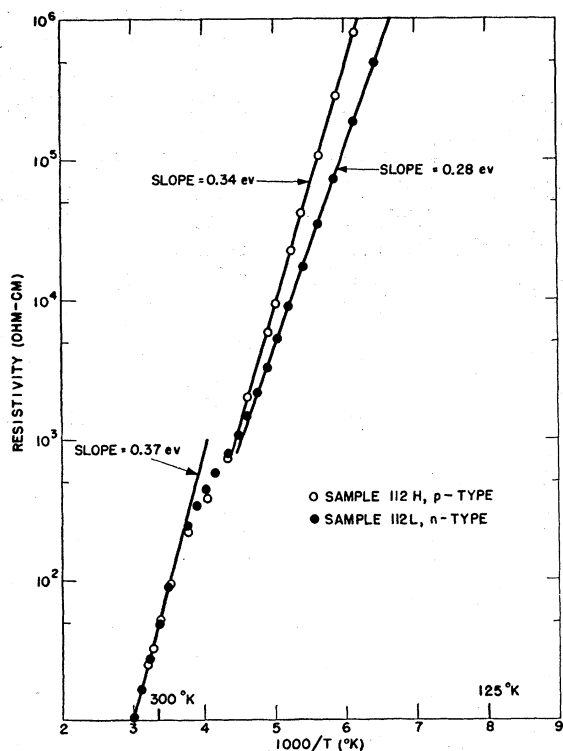


FIG. 6. Resistivity curves for high-resistivity *n*- and *p*-type Fe-doped samples cut from crystal 112 just before and after conversion from *p*- to *n*-type.

B. Mixing the two sources of Fe in the proper proportions, and thus compensating the impurities in the two sources, permits growth of crystals containing both high-resistivity *p*- and *n*-type regions, converting from *p*- to *n*-type down the ingot. Overdoping the melt with Fe (>0.1 percent) from either source insures that no

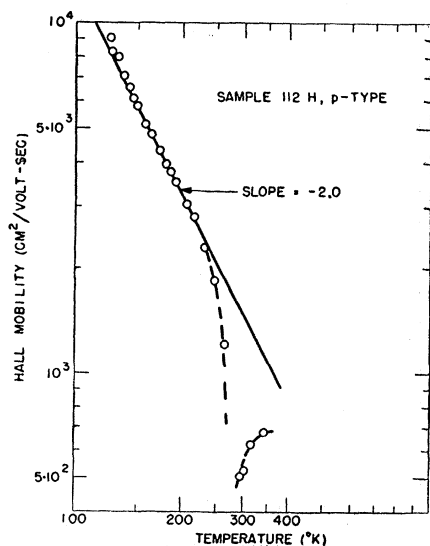


FIG. 7. Hall mobility vs temperature for high-resistivity *p*-type Fe-doped sample 112H. The change in sign of the Hall coefficient occurs at about 275°K.

high-resistivity samples are obtained due to the complete domination of the crystals by the impurities in the Fe and the early onset of lineage.

Figure 6 shows curves of  $\rho$  vs  $1/T$  for *p*- and *n*-type high-resistivity samples obtained from the same crystal just before and just after the change in type. This crystal was grown from a melt containing a mixture of 2 parts NRC to 1 part Puron Fe. Mobility data for the *p*- and *n*-type samples are shown in Fig. 7 and Fig. 8, respectively. These mobility data were measured to a resistivity level of  $10^9$  ohm-cm for sample 112H and  $10^8$  ohm-cm for sample 112L. For sample 112H (*p*-type) the mobility versus temperature slope agrees within experimental error with that of the undoped *p*-type sample 824. The temperature dependence of the mobility for sample 112L (*n*-type) agrees within experimental error with values obtained on low-resistance *n*-type samples.<sup>1</sup> None of the *n*-type

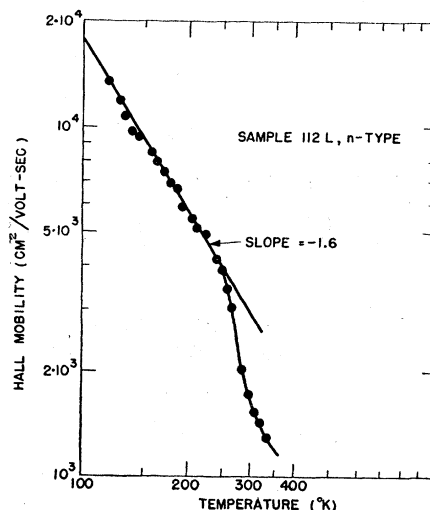


FIG. 8. Hall mobility vs temperature for high-resistivity *n*-type Fe-doped sample 112L.

samples studied show any appreciable magnetic field dependence up to 4000 gauss.

The sensitivity of *n*-type high-resistivity samples to 300°K radiation permitted the measurement of mobility in such samples down to liquid hydrogen temperatures by simply removing the light shield. Figure 9 compares the dependence of resistivity on temperature for *n*-type sample 95G (Puron-doped) with and without the radiation shield. With the shield, the resistivity continued to rise on the linear curve to a resistivity of at least  $10^9$  ohm-cm. Without the shield, the resistivity reaches a maximum at 120°K and then decreased as shown to a value of about  $8 \times 10^8$  ohm-cm at 30°K. Figure 10 shows the corresponding mobility data. Between 250°K and 90°K a slope of  $-1.6$  represents the data fairly well. There is no difference greater than experimental error for mobility data with and without the radiation shield in the region of overlap. The effec-

tive mobility in the presence of radiation continues to be characteristic of electron mobility in slope and magnitude down to low temperatures, even though the number of steady-state carriers induced by the radiation becomes many orders of magnitude greater than the equilibrium number. Similar measurements were made for the *n*-type sample 112L with similar results.\*

As mentioned above, crystals grown from melts doped with Puron Fe will always give low-resistivity *n*-type samples before lineage develops, due presumably to the accumulation of some donor impurity such as P in the melt. If the failure to show high-resistivity behavior is due to an excess number of electrons, it should be possible to heat treat such samples to compensate for the excess electrons, and thus obtain high

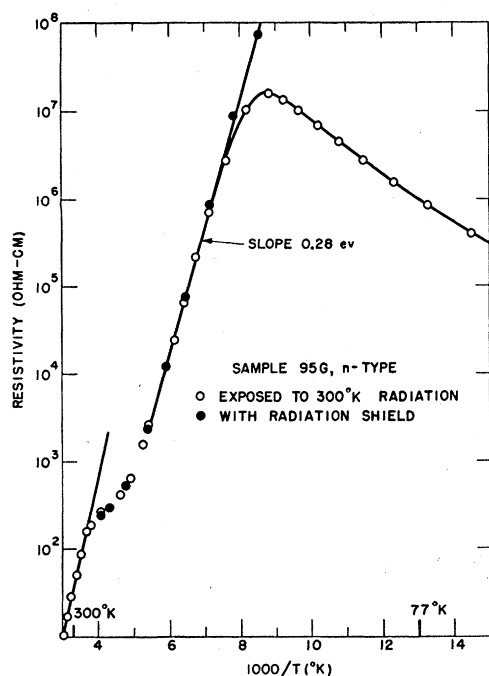


FIG. 9. Resistivity vs reciprocal temperature for high-resistivity *n*-type Fe-doped sample 95G showing the effect of 300°K radiation.

resistivity material dominated by the Fe states. Figure 11 shows the results of such an experiment. Before heat treatment, the resistivity shows a plateau of approximately 45 ohm-cm, a slight increase at about 200°K due to the presence of the Fe, and then a decrease due to mobility changes. The sample was

\* Note added in proof.—The sensitivity of *n*-type Fe-doped samples to 300°K radiation is primarily due to absorption of photons in the energy region from 0.3 eV to 0.7 eV, rather than to intrinsic absorption (see following paper). This was determined by comparing the dependence of resistivity on temperature for sample 82C with direct exposure to 300°K radiation and with filtered 300°K radiation. The filter used was a Ge crystal which was thick compared with the test sample and held at the temperature of the test sample. The difference in conductivity with and without the filter could be explained by reflection losses at the surfaces of the filter. Essentially none of the radiation giving rise to carriers was absorbed in the filter.

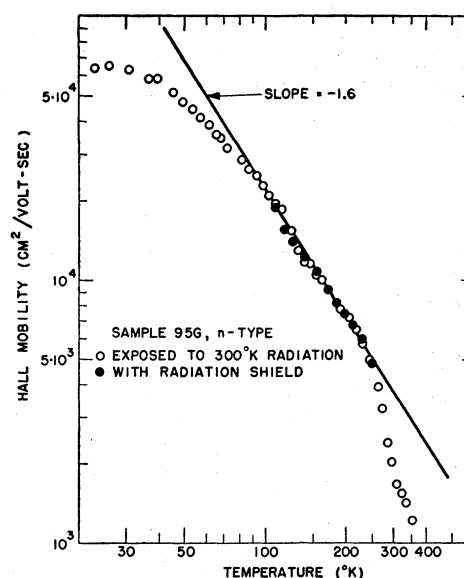


FIG. 10. Hall mobility vs temperature for sample 95G. Exposure to 300°K radiation permits measurement of mobility down to 25°K. At 107°K, mobility values with and without radiation agree within experimental error although resistivity values differ by a factor of  $10^2$ .

heat treated by rinsing under tap water, drying, and then heating to 650°C for several minutes. This treatment effectively compensates about  $5 \times 10^{13}$  excess

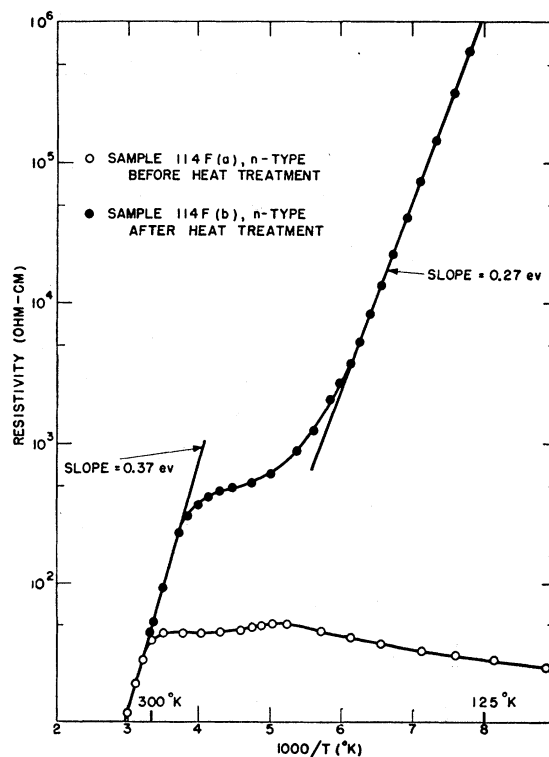


FIG. 11. Resistivity vs reciprocal temperature for an initially low-resistivity *n*-type Fe-doped sample before and after heat treatment.

electrons. The sample is still *n*-type but is now dominated by the Fe states and shows the ionization energy characteristic of *n*-type Fe-doped material.

### B. Transient Photoconductivity Experiments

Room temperature recombination rate studies were made using a spark light source and an oscilloscope to measure the decay of photoconductivity. These indicate that both *n*- and *p*-type crystals grown from melts containing approximately 0.08 atomic percent Fe have a recombination lifetime of  $<5$  microseconds. The lifetime for typical samples (such as 82A) taken from crystals before the addition of Fe to the melt measures between 300 and 500 microseconds. The lifetime for crystals grown from melts containing approximately 0.04 atomic percent Fe measures from 15 to 20 microseconds, indicating that we cannot make the simple approximation that the Fe content of the crystal is independent of the concentration in the melt at this level.

On cooling, it is found that *n*-type samples show high photosensitivity and also a slow decay of photoconductivity after exposure to light whereas the *p*-type samples remain relatively fast. Figure 12 shows the relative resistance values for sample 82C measured as a function of time after exposure to unfiltered light from the neon lamp. For *p*-type high-resistivity samples at the same temperature with the same light

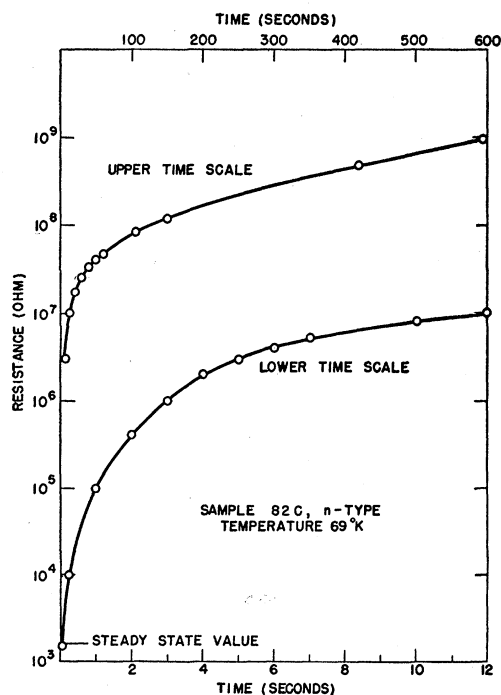


FIG. 12. Recovery of resistance after exposure to light for the high-resistivity *n*-type Fe-doped sample 82C. The equilibrium value of resistance at the temperature of measurement ( $69^\circ\text{K}$ ) is  $\sim 10^{11}$  ohms. These data are characteristic of the most photosensitive samples. The recovery is never exponential.

source and relative geometry, the steady-state value of the resistivity with light is at least a factor of 100 greater than for 82C. After turning off the neon lamp, the resistivity of all *p*-type samples increases 100 fold in less than several milliseconds.

The data shown in Fig. 12 combine oscilloscope and electrometer data. They are characteristic of high-resistivity *n*-type samples showing the highest photosensitivity. Exponential recovery is never observed, and it does not seem possible to explain the results on the basis of a simple model involving only the evaporation of trapped holes from discrete levels. Nor have we as yet been able to deduce from our experiments an approximate number for the density of traps. However, we are able to exert some control over the relative sensitivity of *n*-type high-resistivity samples by controlling the amount and type of Fe used for doping. Samples such as 112L cut from a crystal shortly after conversion from *p*-type are consistently less photosensitive than are samples taken from an all *n*-type crystal grown from a melt doped with only Puron Fe. In order to test the hypothesis that the photosensitivity of an *n*-type sample was related to the trapping ratio (the ratio of the number of electrons occupying the upper Fe levels, to the number of upper levels), crystal number 110 was grown using the proper ratio of Puron to NRC Fe so that it converted from *p*- to *n*-type

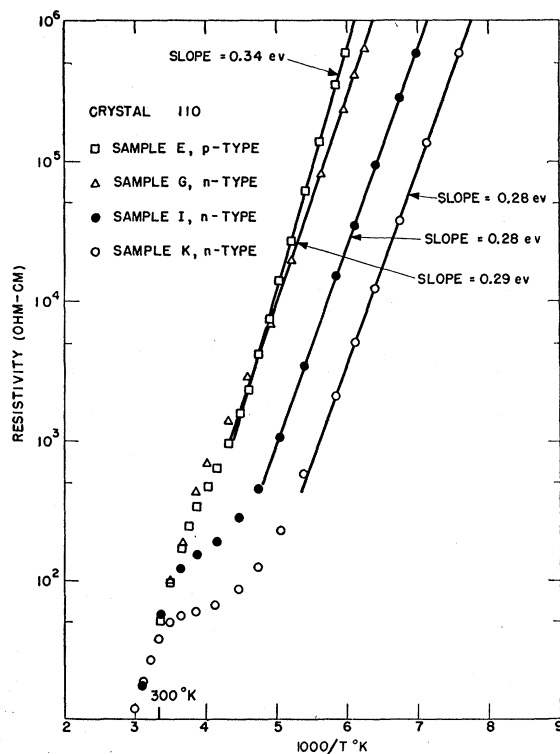


FIG. 13. Resistivity curves for a series of high-resistivity samples from the same Fe-doped crystal. The series of *n*-type samples G, I, and K show increasing photosensitivities and increasing recovery times.

shortly below the point of doping. This crystal gave a series of high-resistivity  $n$ -type samples characterized by increasing amounts of Fe, but, what is considered more important, larger trapping ratios due to the increasing concentration of donor impurities in the melt. Figure 13 shows resistivity data for the four samples. As expected, the three  $n$ -type samples show increasing photosensitivity and increasing recovery times progressing from  $G$  to  $K$ . Comparison of the photosensitivity of these samples and arbitrarily defined recovery times is given in detail in the next paper.

### V. SUMMARY

Two energy levels in germanium crystals have been identified with the presence of Fe in the melt from which the crystals are grown. On the basis of resistivity measurements, these levels have been located at  $0.27 \pm 0.02$  eV from the conduction band and  $0.34 \pm 0.02$  eV from the valence band. Hall coefficient studies indicate that both  $n$ - and  $p$ -type Fe-doped crystals, which go to very high resistivities as the samples are cooled below room temperature, show increasing mobilities with decreasing temperature in general agreement with previous measurements of mobility in high-purity germanium. The maximum concentration of Fe which we have been able to introduce in single crystals of Ge free of obvious structural defects is about  $2 \times 10^{13}$  per cc. Because we have not obtained Fe sufficiently pure to insure that the total number of donor or acceptor atoms introduced into the melt with the Fe is appreciably less than  $2 \times 10^{13}$  per cc, we have not been able to show whether the states introduced by Fe are donor or acceptor states.

At 300°K the only obvious indication of the presence of  $2 \times 10^{13}$  Fe atoms/cm<sup>3</sup> in Ge crystals is the pronounced reduction in the recombination lifetime. Rough calculations indicate that the capture cross section of the Fe centers for either electrons or holes is of the order of  $10^{-15}$  cm<sup>2</sup> at 300°K.

Transient and steady-state photoconductivity measurements below room temperature and in samples dominated by the Fe content indicate that  $p$ -type samples are relatively insensitive and fast in response, whereas  $n$ -type are more photosensitive and slower in response to changes in light levels. The high photosensitivity in  $n$ -type samples is reproducible and controllable in the sense that the photosensitivity of the samples can be varied over a factor of at least 100 by the choice of the amount and type of Fe used for doping. The slow response of the  $n$ -type samples suggests the presence of hole traps. This is confirmed by optical measurements to be reported in the following paper. However, studies of photoconductivity decay in  $n$ -type samples cannot be interpreted quantitatively in terms of simple trapping model nor is the effective number of hole traps known.

### VI. DISCUSSION

It would be of interest to know whether the Fe atoms are substitutional, interstitial, or lodged at imperfections in the Ge lattice. It is possible for instance to accommodate  $3 \times 10^{13}$  atoms per cc along dislocation edges if dislocations are present at a density of about  $10^6$  per cm<sup>2</sup> in the crystals. There is no evidence to indicate how the Fe atoms are dissolved in the Ge lattice. In fact there is no direct evidence that any Fe is taken into the solid above the region of lineage. Conceivably, the observable results could be due to imperfections in the crystals which develop because of the high concentration of Fe in the melt. However, this is considered very improbable because of the consistency and uniqueness of the results.

Although we have not established whether the Fe levels are donor or acceptor, we tentatively assume both of them to be acceptor levels in analogy with Dunlap's results on gold doping.<sup>6</sup> This assumption leads to a possible explanation for the observation of hole traps in  $n$ -type material. Assume  $N$  Fe atoms per cc, each contributing two acceptor states. If the crystal contains an excess of holes due to uncontrolled impurities of low ionization energy in the Ge and in the Fe, we shall not observe high-resistivity material as a result of Fe doping. We shall therefore assume that the crystal contains  $n$  excess electrons per cubic centimeter due to uncompensated low ionization energy impurities. If  $0 < n < N$ , we shall observe high-resistivity  $p$ -type material. At low temperatures in thermal equilibrium, each Fe atom will either be neutral or possess a single negative charge. If  $N < n < 2N$ , we shall observe high-resistivity  $n$ -type material, and at low temperatures in thermal equilibrium each Fe atom will possess either one or two negative charges. For  $n > 2N$ , low-resistivity  $n$ -type material will be observed with  $n - 2N$  electrons characterized by low ionization energies. All of the Fe centers will possess two negative charges.

These assumptions give a tentative hypothesis for the observation of hole traps in  $n$ -type material under nonequilibrium conditions. An Fe site which in thermal equilibrium possesses two negative charges may trap a hole after which it is still negatively charged and has a low cross section for the capture of an electron because of an activation energy produced by Coulomb repulsion. Thus the return to equilibrium via this mechanism is slow. For high-resistivity  $p$ -type material the Fe sites in equilibrium have at most one negative charge. After the capture of a hole, the site is neutral and has a finite cross section for capture of an electron, acting as a recombination center rather than a trap. This hypothesis explains why  $n$ -type samples taken from crystals immediately after conversion from  $p$ -type show low photosensitivity but become progressively more photosensitive down the ingot. If  $n$  varies more rapidly than  $N$ , the trapping ratio increases and the effective concentration of hole traps increases, ap-



proaching the value  $N$  just before  $n$  becomes greater than  $2N$ .

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## Properties of Germanium Doped with Iron. II. Photoconductivity

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Photoconductivity in  $n$ - and  $p$ -type Fe-doped Ge was measured at 77°K. The impurity photoconduction in both types has approximately the same spectral dependence, indicating ionization energies of about 0.3 ev. The intrinsic photoconductive response measured at 0.83 ev was found to be a function of sample composition, the photosensitivity increasing as the samples became more  $n$ -type. Intrinsic photosensitivity and the time of response seem linearly related. For  $n$ -type samples of highest sensitivity the minimum detectable radiation level at 0.83 ev was estimated to be  $2 \times 10^{-13}$  watt. In such samples quenching effects were found in the spectral region from 0.3 ev to 0.7 ev. Experimental results are discussed in terms of a model in which the impurity center is capable of accepting two excess electrons.

#### INTRODUCTION

IN the preceding paper<sup>1</sup> it was shown that iron introduces energy levels near the middle of the forbidden region of germanium. The temperature-resistivity measurements located levels 0.27 ev from the conduction band and 0.34 ev from the valence band. It was also shown that the presence of iron in  $n$ -type germanium produces effects which can be described in terms of a trapping of photoinjected carriers.

This paper will describe the results of some measurements on the spectral dependence of impurity photoconduction in iron-doped germanium which yield values of the impurity ionization energies. It will also describe some measurements of the intrinsic photoconduction and of quenching phenomena which it is believed bear on the aforementioned trapping effects.<sup>2</sup>

#### EXPERIMENTAL

Samples were obtained in the form of small bars whose dimensions averaged about  $3 \times 5 \times 10$  mm. These were cut from the original ingots in such a way as to maximize sample homogeneity. Fused Sn contacts were used for  $n$ -type samples. Fused Sn or In contacts were used for  $p$ -type samples. The data quoted here were obtained from samples for which temperature-resistivity data were also available. Seven  $n$ -type samples (from four ingots) and five  $p$ -type samples (from four ingots) were studied. Samples were mounted in a cryostat

which was located at the exit port of a Perkin-Elmer spectrometer equipped with a  $\text{CaF}_2$  prism. Unless otherwise stated all data were obtained at 77°K.

For the samples which possessed a high intrinsic sensitivity, the problem of distinguishing the true from the stray light response was severe. For example, at photon energies less than  $\sim 0.35$  ev, even when a Ge filter was used and when the stray light was supposedly monitored by use of a thick glass block, false signals often obtained. Where this occurred the residual response occurring at a monochromator setting of  $\sim 0.15$  ev was subtracted from the response observed at the higher energies. The correction was only important in the lowest decade of response.

Unless otherwise specified, the data quoted refer to measurements using unmodulated light. A sample was maintained at constant voltage (in most cases 6 volts) in a series circuit consisting of the sample, a battery, and a load. For photocurrents in the range  $10^{-12}$ – $10^{-6}$  amp, the load was a resistor. The current was detected using a "vibrating-reed electrometer" as a voltmeter across the load resistance. For larger photocurrents, the load was simply a sensitive ammeter. At low voltages ( $< 20$  volts), the photocurrent was usually linear in voltage. Nonlinearity appeared to be a function of the contacts and with care it could be minimized.

#### IMPURITY PHOTOCONDUCTION

Figures 1 and 2 show the spectral response of the photoconductivity of  $n$ - and  $p$ -type Fe-doped germanium at 77°K. The curves shown are typical of those found for all samples studied. The resolution of these curves into two spectral regions is obvious. Above

<sup>1</sup> W. W. Tyler and H. H. Woodbury, Phys. Rev. 96, 874 (1954).

<sup>2</sup> R. Newman and W. W. Tyler, Phys. Rev. 94, 1419 (1954). Describes a preliminary report of this work.