stated at this stage that existence of a hysteresis effect, as discovered by Bömmel,[2] has been confirmed and that in the normal metal, the absorption does depend strongly on magnetic field (so far applied only along the specimen). This effect was also originally found by Bömmel[15]; in the specimen described here, at the shorter length and at 3.9°K, about 200 oersted will double the amplitude of the transmitted pulse.

The author is very grateful for advice given by Dr. H. J. McSkimin of the Bell Telephone Laboratories in the making of the transducer-specimen bond and also to Dr. H. E. Bömmel for early information about his work. (This investigation was started independently without the knowledge that other work was being done, but the discovery of the effect is due to Dr. Bömmel.) He also acknowledges with thanks assistance given during the measurements by graduate students and others at Brown University.

He would also like especially to thank Dean R. B. Lindsay for his encouragement throughout this work and for making possible his visit to Brown University. He is also grateful to the Headmaster and Governing Body of Charterhouse School for an extended leave of absence.

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[15] H. E. Bömmel (verbal communication).

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Properties of Germanium Doped with Manganese

H. H. Woodbury and W. W. Tyler
General Electric Research Laboratory, Schenectady, New York

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The temperature dependence of the electrical resistivity and Hall coefficient in *p*- and *n*-type manganese-doped germanium crystals indicates that manganese introduces two acceptor levels in germanium at 0.16 ± 0.01 ev from the valence band and 0.37 ± 0.02 ev from the conduction band. The distribution coefficient for manganese in germanium is $(1.0\pm0.2)\times10^{-6}$. Comparison is made with other fourth-row metals (V, Fe, Co, and Ni) as impurities in germanium.

I. INTRODUCTION

SINGLE crystal germanium has been doped with manganese in a manner similar to the doping of germanium with Fe,[1] Co,[2] and Ni.[3] This paper will present the pertinent data related to the properties of manganese-doped germanium followed by a short comparison of the known properties of the fourth-row transition elements as impurities in germanium.

II. CRYSTAL PREPARATION

The details of the preparation of doped single-crystal germanium and the cryostat and assorted equipment used to take the measurements reported below are described in reference 1. In what follows the words crystal and sample will always refer to manganese-doped single crystal germanium unless noted.

Zone-melted manganese prepared by F. H. Horn of this laboratory, manganese obtained from Johnson-Matthey Company and manganese from Electro-Manganese Corporation, Knoxville, Tennessee, were all used with essentially the same results from each source.

In order to control the position of the Fermi level, the germanium melts were counterdoped by adding specific amounts of a single crystal Ge-As alloy. When used below, counterdoping will refer specifically to the addition of the Ge-As alloy either to compensate low-ionization energy acceptor impurities or to fill the levels introduced by the manganese.

III. EXPERIMENTAL RESULTS

A. Crystal Growing

It was found that when the pulling rate of the growing crystal was reduced from approximately 6 cm/hr to approximately 1.5 cm/hr, roughly 10 times as much Mn could be incorporated into the single crystal before the abrupt onset of lineage markings occurred.[1] These markings are apparently the result of small pockets of Mn or of a different Mn-Ge phase being incorporated in the growing crystal. With the growing rate equal to 1.5 cm/hr and a manganese concentration of 10^{19} to 10^{20} atoms/cc in the melt, the distribution coefficient (k_0) was $(1.0\pm0.2)\times10^{-6}$. The maximum solubility under the above conditions was approximately 10^{15} manganese atoms per cc. All crystals were grown in the (100) direction.

B. Electrical Properties

When manganese alone was used to dope the germanium melt, the crystals were always *p*-type. By counterdoping with a small amount of donor material, a low-lying level at 0.05 ev from the valence band and a second level at 0.16 ev from the valence band could be

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[1] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954); R. Newman and W. W. Tyler, Phys. Rev. **96**, 882 (1954).

[2] Tyler, Newman, and Woodbury, Phys. Rev. **97**, 669 (1955).

[3] Tyler, Newman, and Woodbury, Phys. Rev. **98**, 461 (1955).

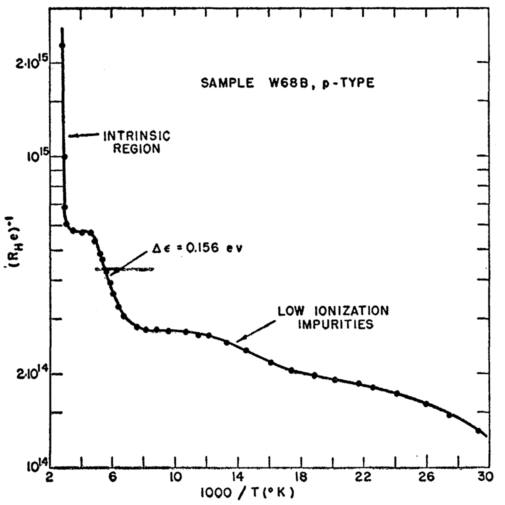

Fig. 1. *P*-type Mn-doped germanium crystal showing $(R_He)^{-1}$ *vs* reciprocal temperature. In the extrinsic region, the ordinate is equal to the number of carriers (holes). The Mn introduces a level at 0.16 ev as shown by the change in the ordinate between 4 and 8 on the abscissa. The change in the number of carriers between 10 and 20 on the abscissa corresponds to an energy of 0.054 ev.

observed as shown in Fig. 1. The source of the 0.05-ev level could not be ascertained. It does not seem to be directly related to the manganese although it is not usually found in undoped crystals and was observed when each of the different sources of manganese were used. The level does not seem to be due to copper because of the higher activation energy measured than that reported in the literature[4] but this possibility has not been eliminated. Spectrographic analysis of the manganese doping material did not show any impurities which could be correlated with the 0.05-ev level. The analysis did indicate though that there could be sufficient Al impurity in the Mn to account for the lowest energy acceptor states (0.01 ev) found. These lowest states cannot be due to boron, a possibility that could not be eliminated by the spectrographic analysis. Boron has a distribution coefficient appreciably greater than one and hence it would quickly be taken up by the growing crystal, causing the first part of the crystal to be "more *p*-type" than the latter part. No such evidence of this type of variation along the length of the crystals was observed, indicating that there was less than 0.01 ppm of boron impurity in the manganese.

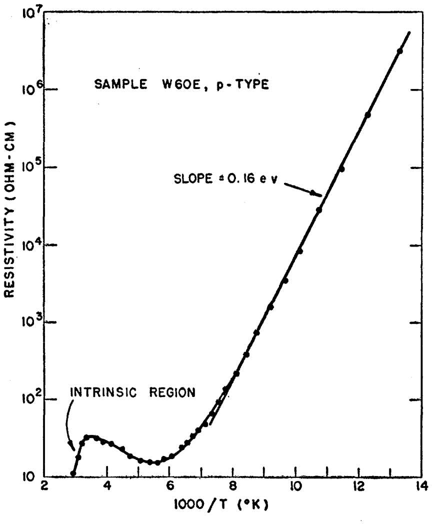

Fig. 2. Resistivity *vs* reciprocal temperature for a high-resistivity *p*-type Mn-doped germanium crystal.

After these low-lying *p*-type "impurities" have been compensated, the crystals go to high resistance as they are cooled as shown in Fig. 2. These crystals are still *p*-type and the results definitely indicate that Mn introduces an acceptor level in the forbidden band 0.16 ev from the valence band.

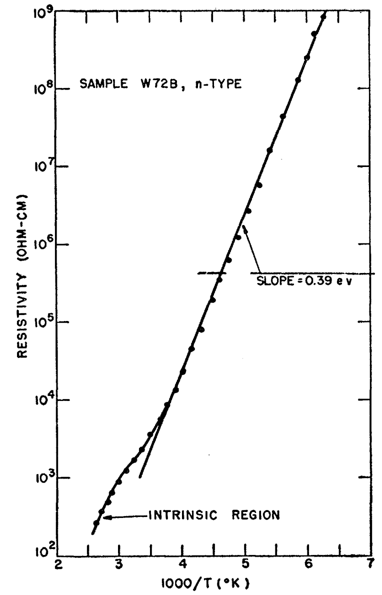

Fig. 3. Resistivity *vs* reciprocal temperature for a high-resistivity *n*-type Mn-doped germanium crystal.

Further counterdoping gives *n*-type material which goes to high resistance as shown in Fig. 3. The break in in the curve at $1000/T$ equal to approximately 3.5 marks the point between the extrinsic and the intrinsic regions. Still further counterdoping gives *n*-type material which does not go to high resistance when cooled as shown in Fig. 4. Because the characteristic energy of this *n*-type material is so near the middle of the forbidden band, it is impossible to unambiguously distinguish between the intrinsic and extrinsic regions in this case.

The levels at 0.16 ev and 0.37 ev have been directly related to manganese by varying the concentration of the manganese doping. Also, for a given concentration of manganese the amount of counterdoping necessary to fill the 0.16-ev level is the same, within the experi-

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[4] For example, see W. C. Dunlap, Jr., Phys. Rev. **96**, 40 (1954).

mental error of 20%, as that required to fill the 0.37-ev level. No such correlation with counterdoping is found for the 0.05-ev low-lying *p*-type level, and at the higher concentrations of manganese the number of 0.05-ev states is less than a third of the number of 0.16-ev states, as shown in Fig. 1. In investigating these levels, over 30 manganese-doped crystals have been grown, using varying amounts of counterdoping material.

The slope of log resistivity *versus* reciprocal temperature has been used as a measure of the ionization energy of the impurity states. In addition, for *p*-type samples that do not go to high resistance (such as shown in Fig. 1), direct computation of the ionization energy is possible since one knows from such curves the temperature at which the Fermi level is coincident with the impurity level. The average values obtained for these two levels are 0.16 ev±0.01 ev from the valence band for the one and 0.37 ev±0.02 ev from the conduction band for the other. The errors quoted are only a measure of the internal consistency of the data. Because of the manner of obtaining the energy from the temperature dependence of the resistivity, any linear dependence of the energy of the level with temperature would not be seen and the values quoted are taken to be the energy values of the levels at absolute zero.

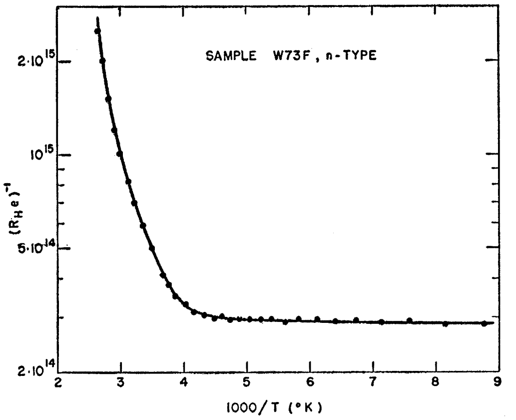

FIG. 4. *N*-type Mn-doped germanium crystal showing $(R_He)^{-1}$ *vs* reciprocal temperature. In the extrinsic region, the ordinate is equal to the number of carriers (electrons).

The temperature dependence of the mobilities of these samples and others has been measured. In general, agreement is found between Mn-doped crystals and Fe-,[1] Co-,[2] and Ni-doped[3] crystals previously reported. However, because of the higher impurity concentration attained with Mn-doping, evidence of appreciable impurity scattering due to the manganese has been obtained and further work on this problem is being carried out.

C. Photoexperiments

Infrared photoconductivity studies show a spectral dependence qualitatively similar to those reported previously for gold-,[5] iron-,[1] cobalt-,[2] and nickel-doped[3] germanium crystals. Threshold energies for impurity photoconduction in both *n*- and *p*-type samples are consistent with the energy values obtained from resistivity studies. The *n*-type manganese-doped crystals show very large quenching effects and high photosensitivity.[6]

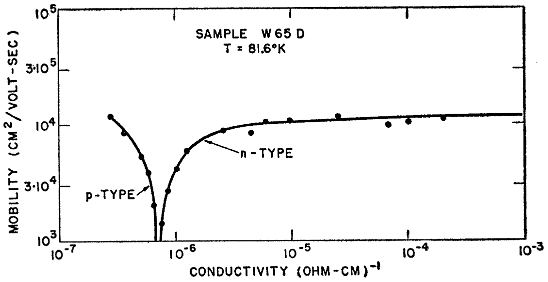

FIG. 5. Effective mobility *vs* conductivity of a *p*-type Mn-doped germanium crystal. The conductivity is changed by varying the amount of light falling on the sample.

Mobility measurements of optically excited carriers give results similar to the previously reported experiments on samples doped with Fe, Co, or Ni.[7] An example of such a measurement for a *p*-type Mn-doped sample is shown in Fig. 5. At a fixed temperature, the effective Hall mobility is plotted as a function of the conductivity which is changed by controlling the amount of light falling on the sample. The light is from a tungsten lamp at 3000°K and passes through a germanium filter held at the same temperature as the sample. The predominant effect of the light is to create electron-hole pairs but as shown in the figure, the holes are trapped since the sign of the Hall coefficient reverses when the conductivity is changed by less than a factor of three. In *n*-type samples no decrease in effective mobility is observed after an increase of conductivity by as much as a factor of 10^6. This again indicates that the holes created by the light are trapped, leaving only electrons to contribute to the conductivity.

The room temperature lifetime of *p*-type crystals has been measured using a spark light source and an oscilloscope to measure the decay of the photoconductivity. Within the experimental variations (a factor of 2) the room temperature lifetime is inversely proportional to the concentration of manganese impurity. For example, changing the number of manganese impurities from 0.3×10^{14} atoms/cc to 7×10^{14} atoms/cc causes a corresponding change in room temperature lifetime from 110 μsec to approximately 4 μsec. The product of the impurity concentration and the room temperature lifetime averages to 3×10^{8} sec atoms/cc. No limiting lifetime values, i.e., lifetimes of heavily doped *n*- or *p*-type samples have been determined.

For *n*-type crystals, the behavior near room tempera-

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[5] R. Newman, Phys. Rev. **94**, 278 (1954).
[6] R. Newman and H. H. Woodbury (to be published).
[7] W. W. Tyler and R. Newman, Phys. Rev. **98**, 961 (1955).

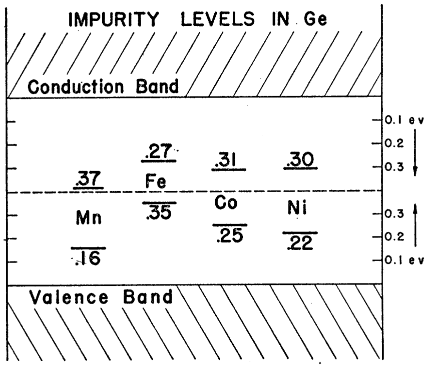

FIG. 6. Impurity levels introduced into germanium by various elements of the fourth row of the periodic chart. In addition to these elements, it is to be noted that vanadium is electrically inactive or is insoluble in germanium.

ture is quite different. At 60°C, the recovery times are roughly twice those for equivalent *p*-type material. As the samples are cooled to room temperature and below, the response time becomes longer and often nonexponential, showing evidence of hole trapping. Further work on the temperature dependence of photoconductivity decay is in progress.

IV. SUMMARY AND DISCUSSION

Figure 6 summarizes the observed energy values of the impurity levels introduced into germanium by transition elements of the fourth row of the periodic chart which have been investigated. The results of doping with iron, cobalt, and nickel are found in references 1, 2, and 3 respectively. Work on energy levels in germanium introduced by other impurity elements has been summarized by Burton.[8]

The evidence that the impurity elements noted in Fig. 6 introduce double acceptor levels in germanium is fairly conclusive. The evidence is direct from counterdoping experiments for all the elements except for iron. It is possible that for any one of the elements investigated, some acceptor impurity could have been present in just the right amount to make a possible donor level appear as an acceptor level. However, the striking similarity of the optical properties of germanium doped with these elements indicates that these levels are basically the same. And it would be extremely fortuitous if these elements all had impurities that would just compensate a donor-type level.

In addition to these elements, germanium has also been doped with vandium in a manner similar to that described above for manganese. Five vandium-doped crystals were grown with no observable effect on the resistivity or on the room-temperature lifetime. Lineage markings appeared on the crystal when the concentration of the vanadium in the germanium melt became approximately one-half of one percent with a pulling rate of approximately 2 cm/hr. Hall measurements from room temperature to 25°K were made on *n*-type and *p*-type vanadium-doped samples whose type was controlled by counterdoping. From analysis of these data, we can put an upper bound on the number of states introduced by the vanadium and thus on an effective distribution coefficient. This upper bound will depend on the energy of the assumed state. Assuming that each vanadium atom introduced either an acceptor or a donor hydrogen-like level, than the distribution coefficient for vanadium in germanium must be less than $3\cdot10^{-7}$ unless such levels were accidentally compensated by impurities in the vanadium. On the other hand, on the assumption that each vandium atom introduces a deep level, i.e., a level in the forbidden band greater than approximately 0.1 ev from either band, then the Hall measurements show that it is necessary that the distribution coefficient for vanadium in germanium be less than $2\cdot10^{-8}$. Hall mobilities were calculated and showed typical temperature dependent characteristics for undoped germanium. To account for the above facts, it is concluded that either vanadium is soluble in germanium but is electrically inactive, or that the solubility of vanadium in germanium is appreciably less than that of the other transition metals that have been studied.[9]

The optical properties of Mn-doped germanium crystals[6] are similar to those reported for Fe-,[1] Co-,[2] and Ni-[3] doped crystals. These impurities all introduce double-acceptor sites which may be made doubly charged by proper counterdoping during the crystal preparation. The presence of doubly-charged negative sites is the basis for hole trapping and the consequent high photosensitivity and quenching effects observed in *n*-type samples. The double acceptor model has also proven adequate for a qualitative understanding of the Hall coefficient studies of optically excited carriers,[7] studies of charged impurity scattering, and transient measurements.

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[8] J. A. Burton, Physica **20**, 845 (1954).

[9] In addition to these observations, negative results are obtained when germanium is doped with the fourth column elements, tin and lead. On the basis of the reported value of 0.02 for the distribution coefficient of tin (see reference 8), crystals have been prepared containing more than 10^{18} tin atoms/cc. The presence of tin at this concentration has no observable affect on lifetime, resistivity, or mobility and it is concluded that tin is electrically inactive in germanium. These results were obtained using "C. P. Baker's Analyzed" tin. When "commercial high-purity" tin was used, *n*-type impurities were introduced into the germanium from impurities in the tin.