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Gold as an Acceptor in Germanium

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Results are presented and discussed concerning the effects of gold in germanium, measured by means of Hall effect, resistivity, photoconductivity, diffusion, heat treatment, and other techniques. It is shown that gold is an acceptor having high-lying states unlike those of the ordinary impurity elements. Evidence is presented to show that each gold atom produces two such levels, one at 0.15 ev above the valence band, the other 0.2 ev below the conduction band. It is assumed that these are brought about through the formation of Au^- and Au^{--}. The implications of this model are discussed. Depending upon the relative proportions of gold atoms and other donors and acceptors, the gold-doped samples may be either high- or low-resistance, *p*- or *n*-type at 77°K. The resistivity may be as high as 10^8 ohm-cm at this temperature. The segregation coefficient, measured from the electrical properties, was about 1.5×10^{-5}. The solubility of gold in germanium is about 10^{16} atoms/cm^3. Photoconductivity studies confirm several features of the model proposed. In particular, gold-doped germanium has been shown to be an infrared photoconductor with response out to about 8 micron. A number of interesting trapping phenomena have been observed with gold-doped germanium. The diffusion coefficient of gold into germanium was measured. It is about 4×10^{-9} cm^2/sec at 900°C, with activation energy of about 2.5 ev, the same as found for other elements. Gold-doped germanium has been studied as a function of heat-treatment (copper diffusion). Several anomalous results are discussed. Gold-doped germanium has also been studied at low temperatures, for the purpose of detecting scattering by doubly charged impurity ions. The results were inconclusive in deciding whether or not doubly charged Au^{--} ions were present. Also results on the scattering of neutral gold atoms were obtained. The Fermi statistics for gold-doped germanium are considered, and theoretical curves have been obtained for the temperature variation of the Fermi level, and of the Hall coefficient, under various conditions of gold-doping. Agreement of experimental and theoretical results was found to be fair. A discussion is also given of the applications of gold-doped germanium to research on other problems.

INTRODUCTION

IT has been known for a number of years that germanium is sensitive in its electrical properties to small traces of impurities.[1] The third column elements, boron, aluminum, and gallium, produce *p*-type (hole-conducting) germanium; whereas phosphorus, arsenic, and antimony produce *n*-type (electron-conducting) germanium. All these elements produce centers in the germanium that require about 0.01 ev for ionization of the carrier at 0°K. The impurity action of these elements is fairly well accounted for by the Bethe "hydrogen-like" model of the impurity center. According to this theory, the ionization energy is just the ionization energy of hydrogen, 13.6 ev, divided by the square of the dielectric constant, which in germanium is 16. In addition, the ionization must be lowered by the ratio of the effective mass of the carrier to the mass of the electron.[1] Since the effective mass from other measurements is of the order $0.2m$, the theoretical result, 0.01–0.02 ev, is in reasonable agreement with the experimental value, in the neighborhood of 0.008–0.01 ev.

Zinc, copper, and platinum[2] also produce acceptor centers in germanium, with energy at about 0.04 ev. These are indicated, along with the energy for the ordinary impurities in Fig. 1.[3] The ionization energy of the zinc-type impurities has not been adequately accounted for, although a "helium-like" model may be partially the answer. In this model, because of the difference of 2 in the valence of the impurity and of germanium, the carriers are assumed to move in the field of a double charge; thus they should be more tightly bound.

The present paper deals with gold,[4] which, as seen in Fig. 1 appears to produce acceptor states high up in the forbidden energy region.† The procedure in the present paper has been to add gold to a germanium melt during the growth of a single crystal, and to study properties of wafers cut from such ingots. The properties have been studied mostly with Hall effect and resistivity measurements.

Following a discussion of the techniques of experimental measurement, the results of Hall and resistivity data are presented. Next some of the time-dependent trapping phenomena that have been discovered are discussed. A theoretical analysis of the electrical properties is given, and a general discussion of the proposed model of the gold center in germanium is given. Application of gold-doping to a number of important research problems is given.

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[1] See for example, W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950).

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

[3] Results on iron, nickel, and cobalt were obtained by Tyler, Woodbury, and Newman, Phys. Rev. **94**, 1419 (1954). Copper and nickel were investigated by Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1954); and copper by J. F. Battey and R. M. Baum, Phys. Rev. **94**, 1393 (1954).

[4] It has been pointed out by W. Kaiser and H. Y. Fan, Phys. Rev. **93**, 977 (1954), that germanium ingots containing gold have been made and studied at Purdue University. Previous publications by the author are Phys. Rev. **90**, 208 (1953); and Phys. Rev. **91**, 1282 (1953).

† *Note added in proof.*—Recently, evidence has been obtained that gold also produces a donor level about 0.05 ev above the valence bond. This evidence and its effect upon observed properties are to be discussed in a forthcoming paper. The validity of the data and interpretations of the present paper are not affected by this discovery, except in the case of "strongly *p*-type" gold-doped specimens.

EXPERIMENTAL

Crystal Growing

The crystals described in the present report were made in a Czochralski furnace of rather conventional design. The melt was contained in a quartz crucible surrounded by a graphite liner, all inside a long quartz envelope. The graphite liner served to equalize inhomogeneities in the thermal flow pattern about the axis of growth. The crystal was withdrawn from the melt by a seed held in a molybdenum chuck, suspended from a drawing head that raised the seed and rotated independently of the raising motion. The heater was a nichrome winding surrounding the envelope, controlled by "Variac" and "Sola" transformers.

Doping was done during the growth of the crystal by adding the impurity, either as the metal, or as an alloy with germanium. The ingot was usually lifted from the melt during doping to allow complete mixing of the impurity.

Most of the crystals studied were grown with the (111) axis along the direction of crystal growth. X-ray examination of a few crystals was made. They were found to be good single crystals, with little evidence of local distortion and inhomogeneity, provided the gold content was well below the solubility limit ($\sim 10^{15}$ atoms/cm^3).

Approximately seventy-five single crystals of gold-doped germanium have been produced. Included were a wide range of relative proportions of the ordinary and gold impurity centers. In many of these crystals, the crystal was doped, either with gold, or gold plus some impurity such as arsenic, five to eight times during growth.

Purity of the Additions

The question of the purity of the additions is a crucial one in such a study as the present one. In addition, the purity of the germanium used as starting material, and the contamination arising in the furnace during growth are important.

Germanium for these studies was generally purified to the intrinsic range by several pre-melts, each of which leads to purification through the normal segregation process. The ultimate resistivity, or rather the ultimate impurity density, is determined by the rate at which impurities enter the melt during the growth process from the furnace. In a few cases, the material had only 5×10^{12} impurities/cm^3, although it cannot be said definitely that this was not the result of compensation.

The gold used came from three sources, and all three varieties of gold led to equivalent results, as far as could be determined. They were (a) cp gold wire from Baker; no chemical analysis was available on this material, (b) gold wire from Handy and Harmon, stated to be 99.96 percent pure; (c) gold ingot procured from Sigmund Cohn, and assayed spectroscopically in the General Electric Research Laboratory. The purity was found to be 99.99 percent or better.

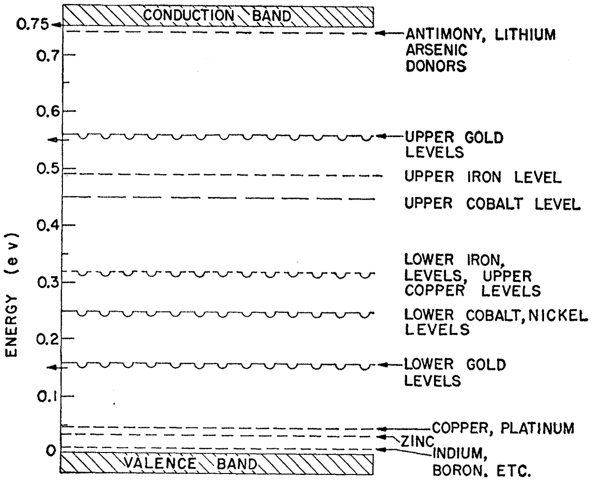

FIG. 1. Energy level diagram for gold and other impurity atoms in germanium.

It was not found to be easy to produce gold-doped germanium to desired specifications in any given run. This would mean specifying both the gold content and the donor (or acceptor) content to perhaps a few percent. The normal segregation process and the possibility of contamination of the furnace both complicate the problem of getting the various types of impurity in their desired proportions. This is found to be especially true for producing high-resistivity n-type germanium, for in this case the donor density must be between n_{Au} and $2n_{\mathrm{Au}}$, where n_{Au} is the gold density in atoms/cm^3. If more donors than this are present, the material stays low resistance at 77°K, and if less than this amount is present, the material is p-type.

Measurements

Most of the data of the present paper were obtained from Hall and resistivity measurements on rectangular plates cut from ingots prepared in the above manner. Mobility was determined from the ratio (R/ρ), in cm^2/volt sec.

The measuring equipment consisted of a low-impedance Rubicon potentiometer, and suitable current supplies, standard resistances, etc. It was found that satisfactory measurements could be made at impedance levels as high as 1–2 megohm in many cases. For higher impedance measurements, a Leeds and Northrup Electronic Amplifier, Model 7673, was used as an impedance transformer. Pickup of stray signals became a severe problem at impedance levels above 20 megohm, and relatively little work was done at higher impedances.

Temperatures ranged from 77°K to 400°K for most of the measurements, although some measurements of scattering were made at temperatures as low as 15°K in a cryostat described in another paper.[2] Most of the measurements were made by cementing the sample to a

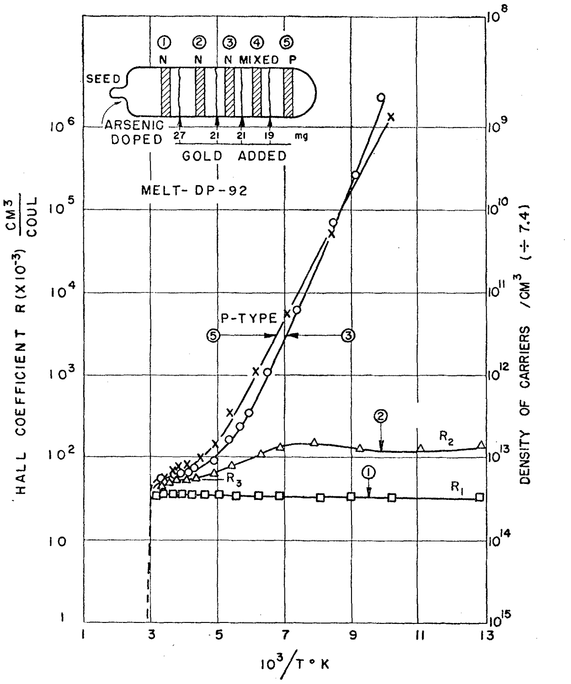

FIG. 2. Hall coefficient and carrier density of *n*-type gold-doped samples made by adding gold in steps to germanium already slightly doped with arsenic.

stainless steel holder mounted in a heavy copper block, in turn mounted in a large Dewar flask. A thermocouple was mounted near the sample. Thermal leakage through the lead wires was minimized since they passed through fine slots in the copper housing. With this equipment temperatures could be kept constant to ±0.1°C during the course of a measurement.

Indium-soldered contacts were used for all samples. For *n*-type samples, the indium was alloyed with small amounts of arsenic to prevent formation of rectifying contacts.

Since some of the samples were extremely photosensitive, precautions had to be taken to keep them in the dark for all measurements.

HALL EFFECT AND CONDUCTIVITY STUDIES OF GOLD-DOPED GERMANIUM

Addition of Gold to *n*-Type Germanium

Figure 2 shows the Hall coefficient and density of carriers of several plates of germanium cut from ingot DP-92. The doping sequence is also shown. To a melt already slightly *n*-type because of the addition of arsenic, gold was added four times, about 25 mg each time. Curve (1) shows the normal variation of the Hall coefficient of a sample of germanium. There is no deionization of these carriers until the temperature is well below 77°K. After addition of 27 mg of pure gold, two effects occur: (1) the room temperature resistivity increases, showing the acceptor effect of the gold, but the sample remains *n*-type; and (2) there is a slope to the Hall curve between 77°K and room temperature. This is a sign of a high-energy donor being present.

With further addition of gold, it is seen that from Curve (3) there are still electrons present, but in still smaller numbers. Here the large activation energy of the "donors" is clear. From the slope of the Hall curve we estimate 0.18 ev for the ionization energy. On further addition of gold, we see that *p*-type germanium is formed, again with a high ionization energy, about 0.15 ev. Sample 4 was not measured because it was mixed *n*- and *p*-type.

Figure 3 shows the resistivities of these samples, and Fig. 4 the mobilities. The room temperature mobilities of gold-doped samples are often low, and so also is the slope of the logμ *vs* log$T$ curve, compared to that for pure undoped samples. However, the mobilities were high enough at the lower temperatures to assure us that few or no barriers were present in the samples.

Addition of Gold to *p*-type Germanium

Figure 5 shows the Hall curves for a series of samples prepared by adding gold to an ingot originally slightly doped with gallium. Now the crystals start out *p*-type, and with each addition of gold the resistivity drops. Here the picture is complicated by the apparent tendency of the furnace to contribute *n*-type contamination, so that the drop in resistivity is not always appropriate to the amount of gold added. Also, the presence of the trace of gallium in the ingot has dis-

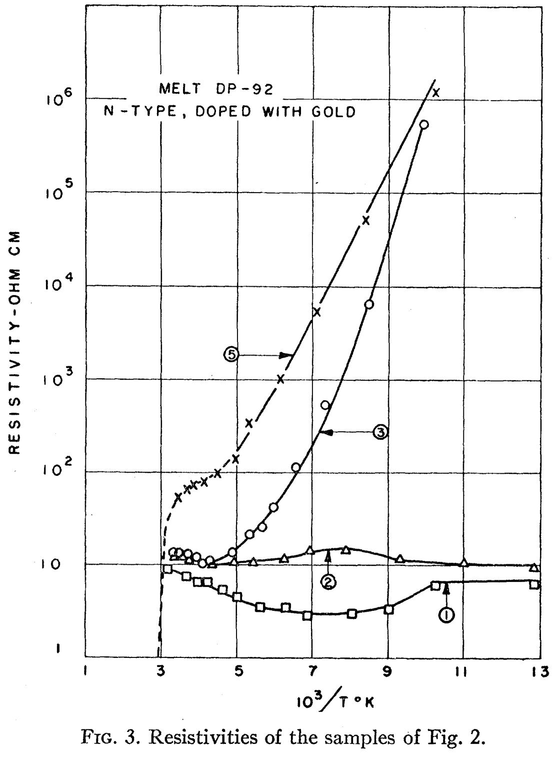

FIG. 3. Resistivities of the samples of Fig. 2.

appeared after the second doping, again presumably because of the effects of contamination by donors. The high-energy gold acceptors now become clearly evident in the high slopes of the Hall and resistivity curves. Figures 6 and 7 show the resistivities and mobilities of these same samples.

Energy Level Scheme for Gold in Germanium

Based upon evidence of the type just discussed, the energy level scheme of Fig. 1 is proposed for gold. The following features of the model are important.

(1) Gold produces two acceptor levels in germanium. However, because the upper acceptor state is so close to the conduction band, the material may act as an *n*-type semiconductor, through excitation of the trapped electrons into the conduction band.

(2) The observed properties are determined by the extent to which the gold states are filled by electrons from donors present. Thus the germanium may be high- or low-resistance, *p*- or *n*-type, depending on the ratio of gold states to the normal impurity states. A further discussion of the theory is given below where the Fermi statistics is discussed.

(3) Because one state is above, the other below the middle of the forbidden band, it is not possible to see ionization from both states in the same Hall or resistivity curve. The ionization of the upper level can only be seen with *n*-type material, and the ionization of the lower state is seen only with *p*-type material.

(4) For reasons to be outlined below, it is suggested that both states are different ionization states of the gold atom, and hence that, when electrons are added to germanium containing neutral gold, the gold first becomes Au^- and then Au^{--}. A corollary of this statement is that the two states cannot properly be listed on the same diagram, in the sense that the upper state when filled destroys the lower state.

(5) Although the values 0.15 ev and 0.20 ev have been quoted, actually there is some variation in ionization energy as determined from the slopes of the Hall curves. This may partly be due to the effect of compensating donors, and partly to short-circuiting influences such as surface conductivity, dislocation conductivity, etc. Also, the degree of occupation of the levels affects the slope, as discussed below under "Fermi statistics."

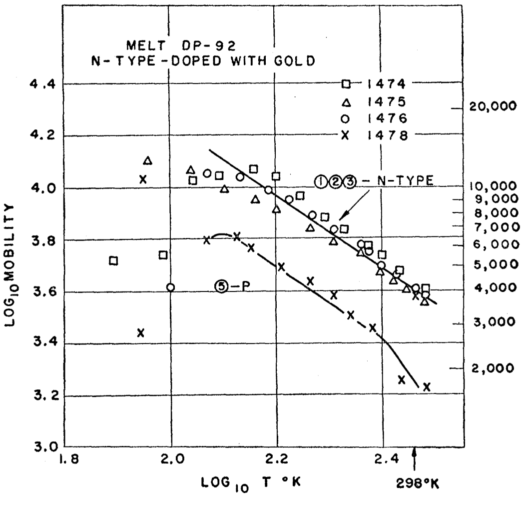

FIG. 4. Mobilities (R/ρ) of the samples of Fig. 2.

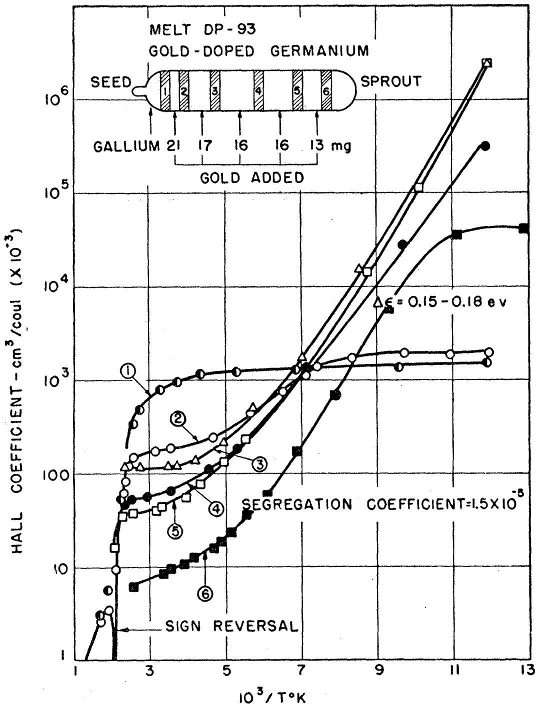

FIG. 5. Hall coefficient *vs* $1/T$ for a series of samples prepared by adding gold to a melt already doped with gallium.

Relative Density of Upper and Lower States

The nature of the model depends on whether we can answer the question as to the equality of the number of upper and lower states introduced. One method for doing this is the following: When gold is added to the crystal, the increase in resistivity after adding gold should tell us the total number of electrons removed from the crystal by the gold atoms. The excitation curve such as that of (1) in Fig. 2 should tell us the number of electrons in upper gold states, which should be half the total. Calculations on this basis show, for DP-92, that this prediction is borne out, to better than 25 percent.

Referring to Fig. 2, we take the Hall coefficients R_1, R_2, and R_3.

(1) R_1 should give the total number of electrons available from arsenic donors.

(2) R_2 gives the number of arsenic electrons remaining, at 77°K.

(3) R_3 gives the number of electrons excited from the upper gold states.

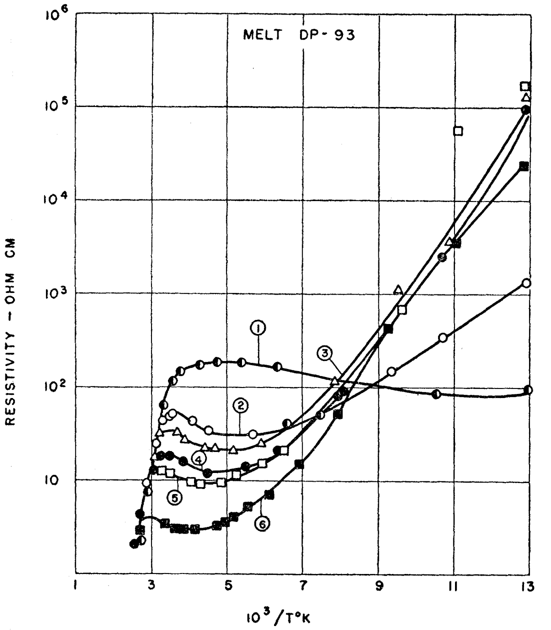

FIG. 6. Resistivities of the samples of Fig. 5.

If N^L is the number of lower gold levels, N^U that of the upper, and if $n_1=7.4\times10^{18}/R_1$, namely the number of carriers at R_1, then

$$N^U=n_3-n_2,$$

$$N^L+N^U=n_1-n_2.$$

Using the appropriate values of the Hall coefficients, we find

$$n_1=20\times10^{13}/\text{cm}^3,$$

$$n_2=6.1\times10^{13},$$

$$n_3=14.8\times10^{13},$$

whence $N^U=8.7\times10^{13}/\text{cm}^3$ and $N^L=6\times10^{13}/\text{cm}^3$, and we conclude that these two numbers are equal to within the experimental error.

This result also depends upon the following assumptions: (a) the samples (1) and (2) were sufficiently close together that normal segregation did not significantly change the arsenic concentration; this assumption is a good one, since the wafers were only a few mm apart and far from the sprout end of the crystal. Also, (b) no additional donors were added along with the gold. This assumption is more difficult to justify.

Other experiments have been done tending to verify the above conclusion. However, the agreement has not always been as good as in this case, and the numbers N^U and N^L have varied as much as a factor 2.

Segregation Coefficient and Solubility

Studies of segregation of gold have been made using radioactive gold 198. However, errors are introduced in this method because of precipitation of tiny droplets of gold, and it is thought that changes in electrical properties are the most reliable method of estimating segregation coefficient.

The segregation coefficient is determined by the ratio of gold concentration in the solid to that in the liquid at equilibrium. From melt DP-92, it was found that 8.2×10^{18} atoms of gold were added to each cm^3 of melt. The density of gold atoms in the solid was $8\times10^{13}/\text{cm}^3$, assuming that each gold atom furnished *two* acceptors. The result, 1.5×10^{-5}, was identical with that obtained from the change in carrier density in *p*-type germanium, assuming *one* acceptor per gold atom in that case. While the degree of agreement is almost certainly fortuitous, it does appear to lend additional weight to the hypothesis that each gold atom furnishes two acceptor states in germanium.

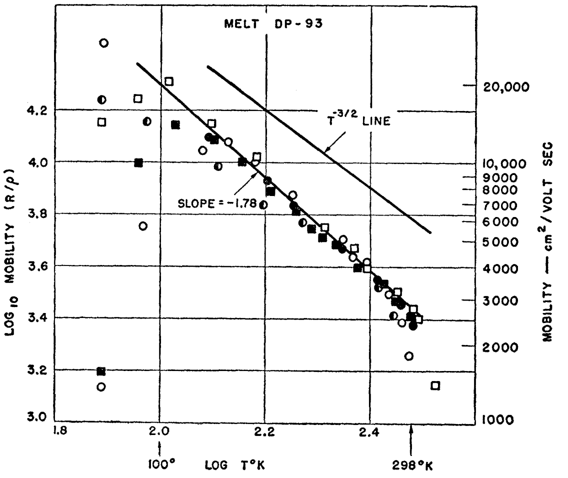

FIG. 7. Mobilities of the samples of Fig. 5.

The lowest resistivity observed in any of the *p*-type ingots was about 1 ohm-cm. It is concluded that the solubility of gold in germanium is about 10^{15} atoms/cm^3 at the melting point. Metallographic examination has been made of some of the gold-doped ingots. It is found that close to the point where the gold content is approaching 10^{15}, the single-crystal character tends to deteriorate—first indications of "lineage," in the form of numerous fine lines in the etched surface appear, and, in a fairly narrow belt, the crystal becomes polycrystalline. Close examination shows a large number of pockets containing metallic gold in this region of the crystal.

Model of the Gold Acceptor States

Figure 8 shows the model assumed to apply to gold in germanium. Gold, on the basis of the previous results, and the diffusion data to be discussed below, is assumed to be substitutional in germanium. The electronic structure of the gold atom is

$$5s^25p^65d^{10}6s^1.$$

Thus, gold is a transition element with the $5f$ shell completely empty in the free atom, and with one valence electron in the 6*s* shell. In its chemical compounds, gold may have a valence of either 1 or 3.

The properties of gold in germanium are best accounted for if gold is assumed to have a valence of two. This would require promotion of one of the 5*d* electrons to form a $6s^2$ structure.

There is at present no reliable evidence regarding the electronic state of gold in germanium. Such information might be obtained by (1) paramagnetic resonance experiments, (2) magnetic susceptibility measurements, (3) measurement of ionic mobility of the gold ion (although measurement at high temperature may be misleading if the electronic state changes with temperature).

Pending determination of this information, it is assumed that gold takes up two electrons, and becomes Au^{--}. It should be remembered that the lower acceptor level is defined by placing an electron upon a neutral gold atom, the upper level by placing an electron upon a singly charged (Au^-) ion. It is further assumed that in this state it has acquired four electrons, and matches the germanium bond structure, as do the 3–5 column impurities. However, it is possible that gold goes in with only the one 6*s* electron, takes up two electrons, and has three electron pair bonds with the germanium.

Figure 8 shows a possible atomic arrangement in the gold center as compared to the similar center containing indium. The first electron is seen being bound to the gold from a germanium lattice atom, whereas the second is made only by trapping electrons from other impurities, since too much energy is required to break a second germanium bond.

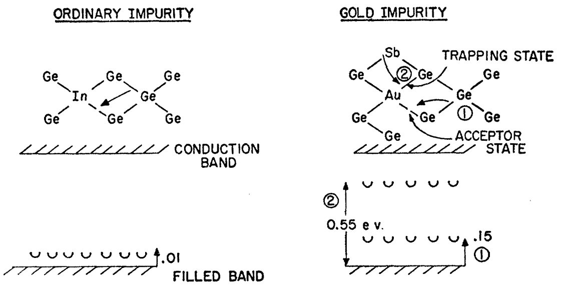

FIG. 8. Model of the gold impurity center in germanium.

Figure 9 shows a possible curve for the potential energy *vs* distance for an electron approaching (a) the neutral gold atom, and (b) the singly charged Au^- ion. The forces of attraction are relatively weak in (a) until the electron is within an atomic spacing or so, at which distances the exchange forces become quite strong. In (b) we see the repulsion at long range arising from the Coulomb forces, and the strong attractive effect if the electron is able, in spite of the Coulomb repulsion, to come within an atomic distance of the ion. The height of the Coulomb barrier was calculated to be of the order 0.1 ev, with a reasonable form for the exchange energy function. However, the nature of the electronic structure about the gold center is sufficiently uncertain that the Fig. 9 should not be considered to have more than semiquantitative validity.

PHOTOCONDUCTIVITY AND TRAPPING PHENOMENA

Soon after the preparation of both the *p*-type and the *n*-type gold-doped germanium, a number of unusual time-dependent effects were discovered, apparently related to the deep-lying levels previously discussed in this paper.

Most prominent of these involve photoconductivity. Gold-doped germanium samples are good photoconductors: (a) the high resistivity at 78°K makes it easy to detect small photocurrents, and (b) because of the relatively small ionization energy, photoconductivity is observed at wavelengths much longer than those of fundamental photoconductivity: out to 8–10 micron.

The photoconductivity of a number of the specimens used in the conductivity studies has been measured by Newman.[5] These studies are of interest particularly because they give a means of checking the location of the energy levels as determined from the Hall and conductivity data. Newman studied both *p*- and *n*-type samples of high-resistivity, and his values for the threshold energy for photoconduction agreed almost identically with those obtained here, namely, 0.15 ev for *p*-type, 0.20 ev for *n*-type samples.

Besides the threshold conductivity effect, Newman noticed a "quench" effect in gold-doped samples. In this effect, the application of infrared radiation in certain narrow bands of wavelength, particularly at 0.66 ev (~2 micron), led to a *decrease* of current flowing through the sample rather than an increase. Since the dark current consists of electrons, it may be presumed that there were trapped holes which permitted passage of these electrons. If the quenching radiation were to excite electrons into the hole traps, the latter would be destroyed, and the dark current would be correspondingly reduced.

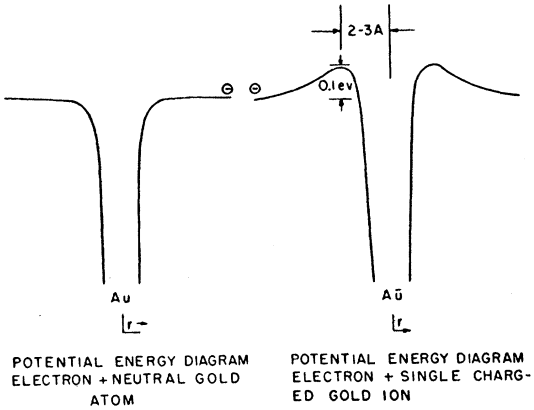

FIG. 9. Potential energy diagrams for electrons in the Au^- and Au^{--} centers in gold-doped germanium.

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[5] R. Newman, Phys. Rev. 94, 278 (1954).

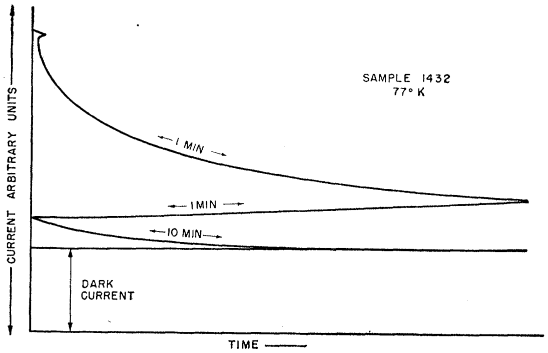

FIG. 10. Time dependence of photoconductivity of gold-doped specimens of germanium.

The existence of the narrow wavelength band is, up to this point, a mystery. It points, in all likelihood, to an internal transition in the gold center as an essential part of the quench process.

The quench effect is found only in *n*-type samples, but it has been found in both high-resistivity and low-resistivity samples. There seems to be a dependence upon gold concentration.

Time Delay of Photoconductivity

Along with the large photoconductivity there is a large time delay that often appears when the sample is illuminated by white and infrared light while at 78°K. Such a recovery curve is shown in Fig. 10. The time constant for the recovery is of the order of 1 minute. As in the quench effect, these slow recoveries were seen only with *n*-type gold-doped germanium.

Pulsing Effects

A number of interesting effects were found when the voltage applied to a sample of *n*-type high-resistivity gold-doped germanium was changed to a new value or reversed. A typical result is that of Fig. 11, which is a copy of a chart made with an *x-y* recorder, plotting the current through the sample at constant applied measuring voltage as a function of time. Just prior to the measurement, the sample had been pulsed with a 100-volt pulse of the sign opposite to that of the measuring voltage, and about 2 sec in duration.

Study of this pulsing effect has indicated that there exist in gold-doped samples regions of space-charge, and that under certain conditions the sample will exhibit polarization voltages of appreciable magnitude, capable, for example, of driving current in the reverse direction through batteries of voltage as high as 1 volt.

Similar effects were observed whenever current was changed—again these effects were found only for *n*-type, high-resistivity samples.

The effect has been found to vary considerably from sample to sample—in some samples, the current after pulsing will start out in the same direction as the pulsing current, then rapidly reverse to the sign of the measuring voltage. In others, it remains of the sign of the measuring voltage throughout. In addition, the effect depends to a considerable extent upon the contacts, and replacement of the contact by a similar but not identical one will usually change the shape, although not the nature of the response. This dependence upon contact has led to the assumption that the effects observed may be the result of current injection of minority carriers into the gold samples, and the effects of the trapping states upon these carriers.

Further work needs to be done on the nature of the polarization effects in gold-doped germanium.

Effect on Recombination Lifetime

A relatively small amount of work has been done on the effect of gold-doping on the lifetime of germanium specimens. Tests have generally been made using the decay of the reverse characteristic of a fused-contact rectifier made on the surface of the specimen. With gold content of the order 10^{14} atoms/cm^3, lifetimes of the order 1 microsecond were generally observed.[6] No quantative estimates of cross sections have been made.

HEAT TREATMENT STUDIES

In the previously described studies on gold-doped germanium, evidence for two sets of levels has been obtained on different samples containing relatively different proportions of gold and ordinary impurities such as arsenic or gallium. Similar evidence can be obtained on a single specimen by heat treatment, that is, by maintaining a uniform gold content and by varying the content of an acceptor such as copper, which diffuses rapidly, and which can be easily spread through the crystal.

A typical study was carried out with Sample 1531. It was first soaked for a few minutes in copper nitrate solution, in order to coat it with a thin layer of copper. Then the sample was heated to 800°C in argon for two hours and cooled rapidly to room temperature. The

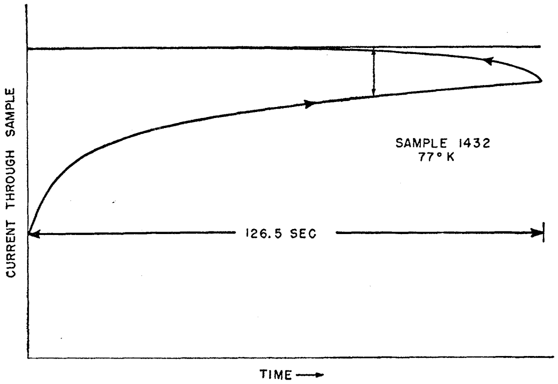

FIG. 11. Pulsing effect in gold-doped germanium. The trace shown was obtained by applying a 100-volt pulse for ~2 sec in the opposite direction to that of the small measuring voltage.

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[6] E. M. Pell (private communication, to be published).

sample was thus converted from high-resistance *n*-type to low-resistance *p*-type. The temperature curve of the Hall effect and resistivity was taken at various times of annealing at 450°C, until the sample had been restored almost identically to its original condition.

Results of the Hall curves are shown in Fig. 12. The most surprising thing about the results is that after the quench there is no evidence for the 0.15 ev lower gold states, which should show up as a slope of the Hall curve between 200° and 300°K. This behavior has been checked with similar samples, and the same results have been found in almost all cases. It is possible that there is an interaction between the gold and copper centers, which changes the electronic structure of the impurity centers. This would be plausible if the copper tended to diffuse preferentially to locations near the gold atoms, and it is also possible that both the gold and copper atoms occur preferentially near imperfections in the lattice.

On annealing, the slope of the Hall curve increases, until the value is of the order 0.13 ev, comparable to that obtained with the doped crystals.

On further annealing, the properties return to the original ones; namely, *n*-type germanium, with the high ionization energy, 0.20 ev, characteristic of *n*-type gold-doped material.

Repetitions of this series of tests have been carried out on six or seven samples, not always with uniform results. In several cases the *p*-type states have been visible in the Hall curve after quenching, while in others there has been only the same flat portion seen in Fig. 12.

DIFFUSION OF GOLD IN GERMANIUM

Study of diffusion has been found to be quite helpful in the evaluation of new materials as doping agents in germanium and silicon. In particular, the order of magnitude of the diffusion is useful in determining the nature of the impurity—whether it is interstitial or substitutional in germanium.

Diffusion coefficients have been measured both by the *p-n* junction technique,[7] and the radioactive tracer method.[7] In the *p-n* junction method, the sample is coated with the unknown, and heated. The penetration of the impurity converts the material from one type to the other, and the boundary is determined by a thermoelectric or a rectification probe.

The diffusion coefficient of gold was determined using *n*-type samples of 5–10 ohm-cm resistivity, and coated with gold by immersing the sample for about 5 sec in 1 percent $AuCl_3$ solution. The samples were then sealed in quartz tubes, in an atmosphere containing 15 cm Hg of pure dry argon. Heating was accomplished in accurately controlled ovens.

In order to prevent heat treatment effects from interfering with results, all samples were annealed 4–8 hours at 575°C following the diffusion heating. This guaranteed that the base germanium returned to its level at 5–10 ohm-cm *n*-type.

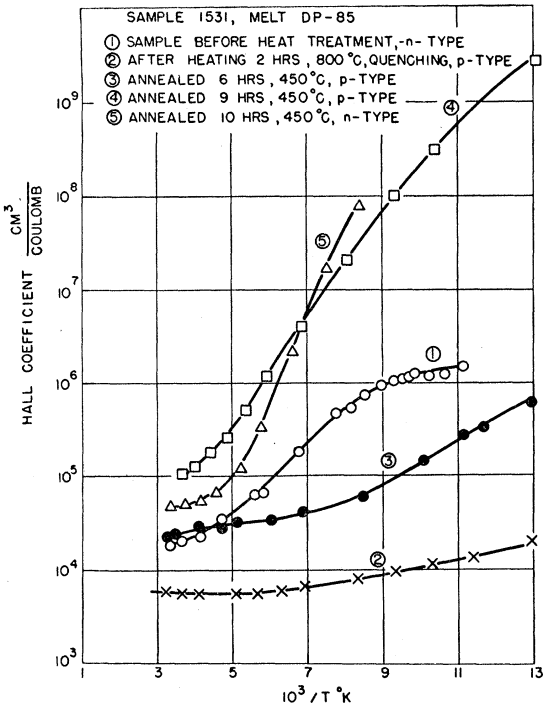

FIG. 12. Hall curves on gold-doped specimens quenched from 800°C and annealed various times at 400°C.

Because of the limited solubility of gold in germanium (assumed 3×10^{15} for all temperatures), the constant-source solution previously used is no longer valid. Instead the "step-function" solution is used; this leads to higher values of diffusion coefficient than the other method of calculation.

Results on diffusion of gold are shown in Fig. 13. Also shown are previously published results on antimony. It is at first noteworthy that gold diffuses more rapidly than antimony, the most rapidly diffusing of the donor elements. All the ordinary acceptors such as indium and gallium diffuse much more slowly than antimony. On the other hand, gold, though diffusing more rapidly than antimony, is much less rapidly diffusing than copper[8] or lithium.[9]

The activation energy for diffusion of gold is almost identical with that for antimony; namely, 2.5 ev, or 57000 cal./mol. This similarity makes it appear that both these elements diffuse by the same mechanism, and thus that they are both substitutional in germanium. The rapid diffusion of gold is inconsistent with the previous picture that gold acquires two electrons to become Au^{--} in the lattice. It is probable that at

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[7] See for example, W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954).

[8] Fuller, Struthers, Ditzenberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

[9] C. S. Fuller and J. A. Ditzenberger, Phys. Rev. **92**, 846 (1953); J. C. Severiens and C. S. Fuller, Phys. Rev. **92**, 1322 (1953).

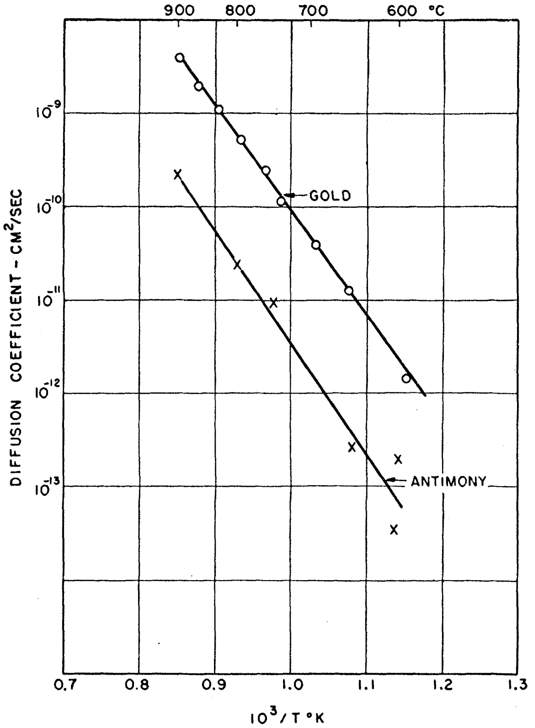

FIG. 13. Diffusion coefficient of gold in germanium, determined by the depth of penetration of the *p-n* junction. Also shown for comparison is the diffusion curve for antimony.

elevated temperatures both electrons are lost, and that the gold actually diffuses as a neutral atom, or even as a positive ion. This conclusion is similar to that recently arrived at in the case of copper.[10]

IMPURITY SCATTERING IN GOLD-DOPED GERMANIUM

Gold-doped germanium containing various relative proportions of gold and arsenic-type impurities offers the means for obtaining new information on impurity scattering. It also makes possible an independent check on the hypothesis previously made, that gold can acquire two electrons to become Au^{--}. By proper control of the concentration of ordinary donors and acceptors, it should be possible to study the scattering by doubly charged ions, singly charged ions, and by neutral impurities. Data have been taken in the temperature range 15°–300°K for all these cases, but the results have not been conclusive.

The difficulties stem from several sources:

(1) The solubility of gold is limited to about 3×10^{15} atoms/cm^3, and this density is not sufficient to make impurity scattering easily observable except at the very lowest temperatures, say below about 50°K.

(2) The experimental accuracy of the method is such that it is difficult to distinguish between the scattering between doubly-charged and singly-charged impurity ions. Although an examination of the theory shows that doubly-charged ions should scatter 4 times as strongly as singly-charged ones, still only half as many would be present, so that the scattering would be only 2 times as great, and this difference is not great enough for easy detection since there are natural differences between samples arising from differences in crystal structure, impurity distributions, etc.

The most suitable procedure for producing doubly-charged ions in samples for scattering measurements is to add gold, and also sufficient arsenic to just fill all the gold levels. This requires, on the basis of the present model, an arsenic concentration that is equal to twice the gold concentration. Thus the added impurity scattering produced by the arsenic must also be taken into account.

Scattering by neutral ions is studied after adding gold to pure germanium containing no other impurities. On going to low temperatures, one should find scattering due only to neutral impurities.

Figure 14 shows mobility data on various samples of germanium, both with and without gold, in the temperature range between 15° and 300°K. Several comparison specimens are included of both *n*- and *p*-type. It is found that in general the mobility of gold-doped specimens is considerably lower than that for specimens

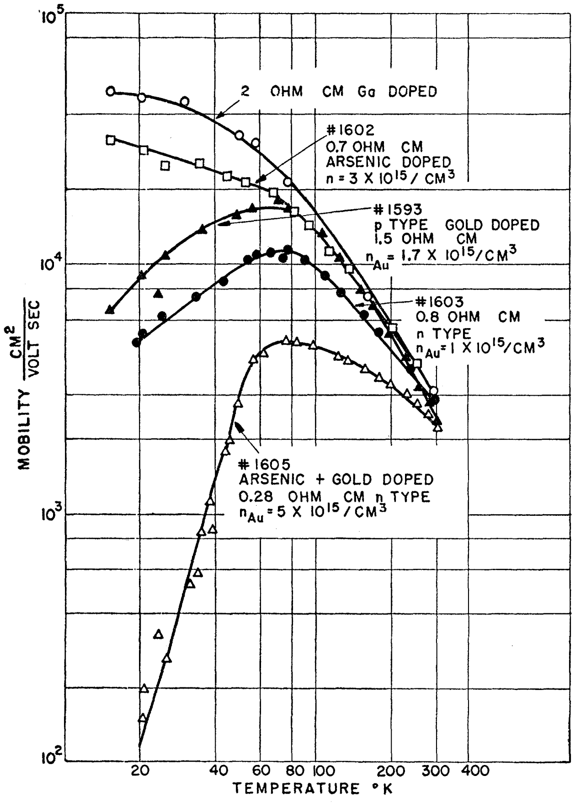

FIG. 14. Mobility of various samples of gold-doped germanium at low temperatures, in the impurity scattering range.

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[10] See reference 8, and J. C. Severiens and C. S. Fuller, Phys. Rev. **94**, 750 (1954).

containing the equivalent charge density of arsenic or other ions. It is not possible, however, to conclude that evidence is found for the existence of the doubly charged Au^{--} ion. In particular, the possibility that the gold introduces structure defects or space charge barriers with temperature sensitivity similar to that for impurity scattering cannot be overlooked.

FERMI STATISTICS FOR GOLD-DOPED GERMANIUM

General

In this section we discuss the determination of the theoretical Hall curves for gold-doped germanium containing different amounts of both gold and normal-type donors and acceptors. Although both the gold states are acceptors, we adopt here a viewpoint toward these levels that is somewhat broader than usually used.[11,12]

It is possible to set up the statistics of trapping levels on a fairly general basis, based upon the calculation of the partition function. However, in the present discussion, no attempt at a formalism that covers all cases is made. Instead, we shall examine several particular cases, and show how the Fermi level is determined in each case.

A general analysis is complicated by the fact, previously mentioned, that the upper state is the energy level for an electron in the field of the Au$^-$ ion, and when an electron is in this state, the lower state no longer exists. Here again, we can avoid the difficulty by dealing with situations in which we need regard only one of the two levels at a time.

A major simplification is attained in the present analysis because the ionization energy of the gold is large in comparison both to kT and to the ionization energy of the ordinary donors and acceptors. In the first instance, we can use Boltzmann statistics in practically every case of interest. In the second, we can neglect the statistical effect of the ordinary impurity states and regard them as part of the conduction or valence bands. In carrying out the calculations, a partly graphical method has been employed. From the calculated Fermi level as a function of temperature, the Hall coefficient curves have been derived.

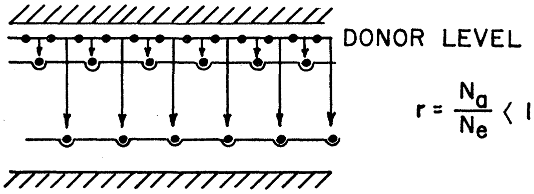

FIG. 15. Energy diagram showing the filling of states in "strongly *n*-type gold-doped germanium."

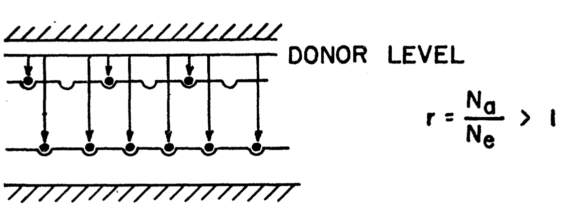

FIG. 16. Energy level diagram for weakly *n*-type (high resistivity) *n*-type gold-doped germanium.

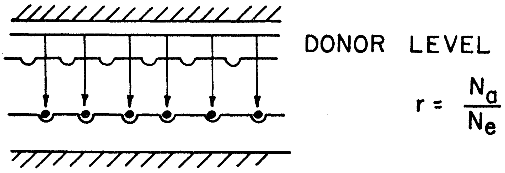

FIG. 17. Energy level diagram for intrinsic gold-doped germanium.

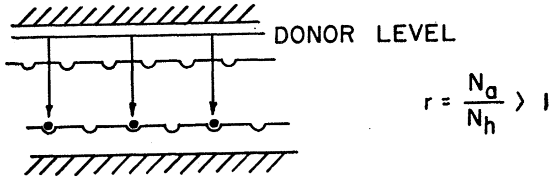

FIG. 18. Energy level diagram for weakly *p*-type (high-resistivity) gold-doped germanium.

The relative concentration of gold and other impurities is defined here by the "trapping ratio." This quantity, r, is defined as the ratio of the number of acceptor (gold) states to the number of electrons available (in the upper gold states, the donor levels, and the conduction band).

We discuss next five important situations ranging from strongly *n*-type through intrinsic to strongly *p*-type.

In Fig. 15 we see the situation at 0°K for a strongly *n*-type sample, for which $r \sim 0$. Here there are many more donor atoms than gold atoms, all the gold states are filled, and the material is low-resistivity at all temperatures. However, the presence of the upper gold state will still be seen in the ionization of electrons from the upper gold level, at a temperature somewhere between 77° and 300°K. The smaller the trapping ratio, the higher the temperature at which this ionization becomes appreciable, since the greater is the tendency of the conduction electrons to refill the gold state.

In Fig. 16 we see the situation where there are not enough electrons to completely fill all gold states at 77°K, with the result that the material is of *n*-type, but high-resistivity at 77°K. The trapping ratio is greater than 1. This is the case of rapidly varying resistivity, since all the electrons will be emptied from the upper gold levels at room temperature.

In Fig. 17 we see the intrinsic situation where $r \to \infty$, since there are just as many electrons as lower gold states, and the number of available electrons is ~ 0.

Figure 18 shows the case of weakly (high-resistivity) *p*-type material, where the number of electrons is only sufficient partly to fill the lower gold states. At 77°K there will be no appreciable number of holes excited to

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[11] See reference 1, Chap. 11.

[12] Several of the results quoted here were taken from a report by J. K. Bragg and M. H. Hebb, General Electric Research Laboratory Report RL-468, December, 1950 (unpublished).

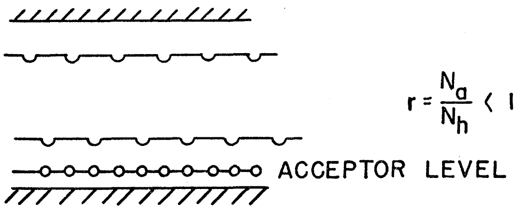

FIG. 19. Energy level diagram for strongly p-type gold-doped germanium.

the gold states from the valence band because of the high ionization energy. The trapping ratio r is defined now by $r = N_a/N_h$, where N_h is the number of available holes (those in the lower gold level, any additional normal acceptor level, and the valence band). In this situation the trapping level is greater than 1.

In Fig. 19 we see the case of strong p-type material.§ Where there are additional acceptor levels of the usual kind, there are carriers present at lower temperatures, and thus the material is of low resistivity. The trapping ratio is less than unity.

In all the above cases, there can be mixtures of ordinary donor and acceptor levels in many proportions. To a first approximation, however, the results are determined only by the number of gold states and by the trapping ratio. This follows from our neglect of the statistical effect of the normal impurity levels, which are much closer to the conduction bands than to the gold level or to the Fermi level, under most conditions.

It is seen that there is a high degree of symmetry between the situations for n- and for p-type material. Ignoring the difference in mass between holes and electrons, and in the ionization energies of the upper and lower states, there is almost complete symmetry.

Examination of all the practical cases shows that in none of them do we have to deal with both levels in the same problem. The upper level is important only for n-type material (Fermi level in the upper half); and the lower for p-type (Fermi level in the lower half).

Normalization Process in Fermi Statistics

The Fermi distribution f has the form

$$f = \frac{1}{1+\exp[(E-\zeta)/kT]}, \tag{1}$$

where E is the energy of any particular energy state, and ζ is the Fermi level. The downward direction is assumed negative, and the zero is taken at the bottom of the conduction band. Similarly the distribution function for holes is f_h:

$$f_h = 1 - f = 1 - \frac{1}{1+\exp[(E-\zeta)/kT]} = \frac{1}{1+\exp(\zeta - E/kT)}. \tag{2}$$

If we transform coordinates so that $E' = -E - E_g$, $\xi = -\zeta - E_g$, then

$$f_h = \frac{1}{1+\exp[(E'-\xi)/kT]}, \tag{3}$$

where E_g is the energy gap between the conduction and valence bands, and ξ may be considered the Fermi energy for holes in the new energy coordinate system.

The density of energy states is assumed to be

$$N_e = 4\pi(2m/h^2)^{\frac{3}{2}} E^{\frac{1}{2}}, \tag{4}$$

where we take the effective electron mass to be the electron mass. Consequently, the number of electrons in the conduction band is

$$n_c = \int_0^\infty \frac{N_e}{1+\exp[(E-\zeta)/kT]} dE = 4\pi\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{E^{\frac{1}{2}} dE}{1+\exp[(E-\zeta)/kT]}. \tag{5}$$

Because the upper gold level, and thus also the Fermi level, is in units of kT, far away from the conduction band, the Boltzmann approximation to the Fermi statistics is justified and Eq. (5) becomes

$$n_c = 4\pi\left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int E^{\frac{1}{2}} \exp[-(E-\zeta)/kT] dE = 2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} e^{\zeta/kT}. \tag{6}$$

Also, if N_a is the number of acceptor states in the upper acceptor level, then the density of electrons in this level is given by

$$n_1 = N_a / \{1+\exp[-(\Delta E_1 + \zeta)/kT]\}, \tag{7}$$

where ΔE_1 is the energy gap between the upper acceptor level and the bottom of the conduction band.

Similarly, the density of states at the top of the valence band is taken to be:

$$N_v = 4\pi(2m/h^2)^{\frac{3}{2}} E'^{\frac{1}{2}}, \tag{8}$$

and the hole concentration is found to be

$$n_v = 2(2\pi mkT/h^2)^{\frac{3}{2}} e^{\xi/kT}. \tag{9}$$

Also, the density of holes in the acceptor levels is given by

$$n_2 = N_a / \{1+\exp[-(\Delta E_2 + \xi)/kT]\}, \tag{10}$$

where ΔE_2 is the energy gap between the gold level and the valence band.

Let us now take up the normalization for electrons in n-type samples. The basic condition for electrical neutrality is:

$$N_e = n_c + n_1,$$

which states that the total number of excess electrons

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§ *Note added in proof.*—Recent evidence indicating a donor state 0.05 ev above the valence bond may require revising the point of view toward the statistics of strongly p-type gold-doped germanium. This point will be discussed in a forthcoming paper.

(above that number required to fill acceptor levels) is equal to the number in the conduction band and in the donor levels. Now, in the case of gold-doped germanium, we consider the upper acceptor level as a donor level, for statistical purposes. However, we ignore the lower acceptor level in this calculation, since it cannot furnish electrons to the conduction band, being below the middle of the band.

Then

$$N_e=2\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}e^{\zeta/kT}+\frac{N_a}{1+\exp[-(\Delta E_1+\zeta)/kT]}. \quad (11)$$

Letting $\eta=\zeta/kT$, Eq. (11) can be solved for e^η, yielding:[12]

$$e^\eta=\frac{N_e}{2B}\left[-\frac{B}{N_e}e^{-x_1}-r+1+\left(\frac{B^2}{N_e^2}e^{-2x_1}+\frac{2B}{N_e}(r+1)e^{-x_1}+(r-1)^2\right)^{\frac{1}{2}}\right], \quad (12)$$

where we have $B=2(2\pi mkT/h^2)^{\frac{3}{2}}$, $x_1=\Delta E_1/kT$. Again, r is the trapping ratio N_a/N_e. Evaluation of e^η for different T yields the Fermi level in the ionization region of n-type gold-doped germanium. This we shall do graphically in the next section.

In the region of intrinsic conduction, the normalization condition is:

$$N_e=n_c-n_v. \quad (13)$$

This expression leads to the following equation for e^η in the approach to intrinsic conduction:

$$e^\eta=\frac{N_e}{2B}\left[1+\left(1+\frac{4B^2}{N_e^2}e^{-K_0}\right)^{\frac{1}{2}}\right], \quad (14)$$

where $K_0=E_g/kT$. The final region of consideration is the saturation region, which, fortunately in the case of gold in germanium, is reached well before the intrinsic range is reached. Thus the n_1 term becomes negligible before the n_v term assumes any importance. That this is so is best seen by making a few sample calculations.

The identical calculations are made for p-type samples: the normalization condition for the ionization region is:

$$N_h=n_v+n_2,$$

where again N_h is the number of "active" holes in the system (those in the valence band and in additional acceptor levels plus those in the lower acceptor level). This normalization leads to the formula:

$$e^\gamma=\frac{N_h}{2B}\left[-\frac{B}{N_h}e^{-x_2}-r+1+\left(\frac{B^2}{N_h^2}e^{-2x_2}+\frac{2B}{N_h}(r+1)e^{-x_2}+(r-1)^2\right)^{\frac{1}{2}}\right], \quad (15)$$

where $\gamma=\xi/kT$ and $x_2=\Delta E_2/kT$. Again the trapping ratio is $r=N_a/N_h$.

Determination of the Fermi Levels *vs* Temperature

Although Eqs. (12) and (15) can be used directly for the calculation of the Fermi level for particular cases, graphical solutions are required for most Fermi level calculations. We write the normalization expression in the form:

$$e^\eta=\frac{N_e}{B}\left[1-\frac{r}{1+e^{-x-\eta}}\right]. \quad (16)$$

The graphical method involves plotting the right and the left hand sides separately as functions of η, and determining the η value of the point of intersection. For depicting the course of the results, all plots are made on semilog paper, and a coordinate transformation is made so that calculations for a variety of temperatures can be shown on the same sheet of paper.

Figures 20 and 21 show the results for both n- and p-type samples containing 10^{14} atoms gold/cm³, and for various temperatures and trapping ratios r. The straight lines are, essentially, simply the function e^η, but shifted to the left by the amount the curves would normally have been shifted to the right for the various T's.

For very low temperatures, the Fermi level is located at the value

$$\eta=\zeta/kT=-\ln(r-1)+(\Delta E_1/kT), \quad (\text{for } r>1). \quad (17)$$

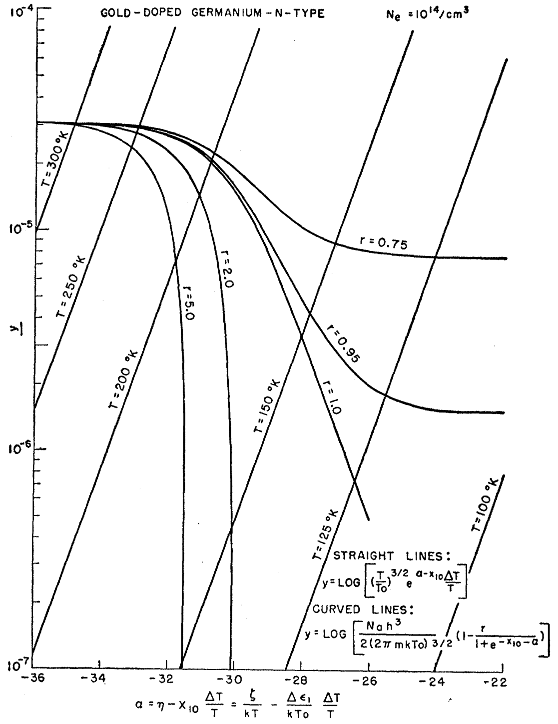

FIG. 20. Graphical solution for the Fermi level of gold-doped, n-type germanium containing 10^{14} gold atoms/cm³ and various concentrations of donors, determined by the trapping ratio r.

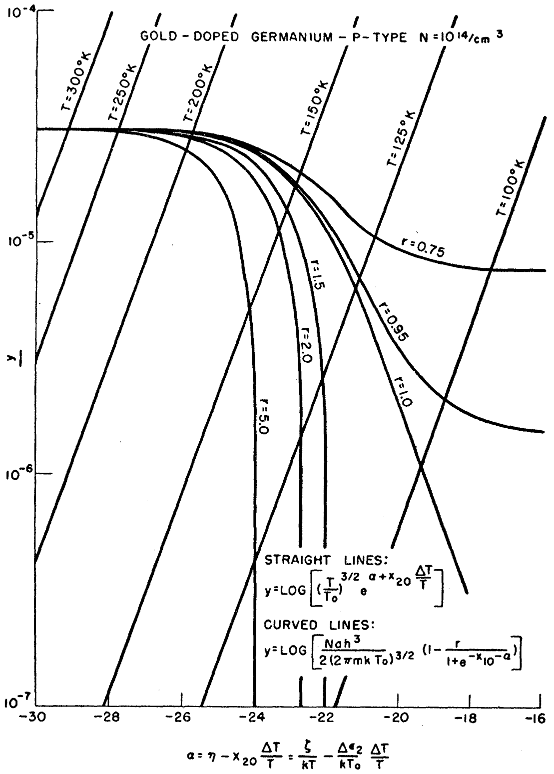

FIG. 21. Graphical solution for the Fermi level for *p*-type gold-doped germanium.

As the temperature rises, for large *r*, the Fermi level remains nearly constant until the saturation region is approached, at which state the point of intersection begins to move around the corner at *A*. For higher temperatures, the intersection gives constant values of η, which means that the Fermi level is increasing (negatively), and moving back down toward the middle of the forbidden energy gap.

As is expected, for low *r*, $r<1$, the Fermi level remains closer to the conduction band for all temperatures than for the larger *r*.

Figures 22 and 23 show the course of the Fermi level itself plotted *vs* temperature. Indicated also are the gold level and the middle of the forbidden energy band. As the temperature rises, the Fermi level moves to the middle of the band neglecting the term of the order *kT* arising from the different effective masses of holes and electrons.

Comparison of Theoretical and Experimental Hall Curves

The Hall coefficient is easily determined from the Fermi level, and thus it is easy to compare predicted shapes of the Hall curve for various trapping ratios with those actually observed.

The density of conduction electrons (for the *n*-type case) is given by

$$n_c = 2(2\pi mkT/h^2)^{\frac{3}{2}} e^{\zeta/kT}, \tag{18}$$

and since the Hall coefficient is given by

$$R = (3\pi/8e)(1/n_c), \tag{19}$$

then we have the Hall coefficient for *n*-type material:

$$R = (3\pi/8eB)e^{-\zeta/kT}, \tag{20}$$

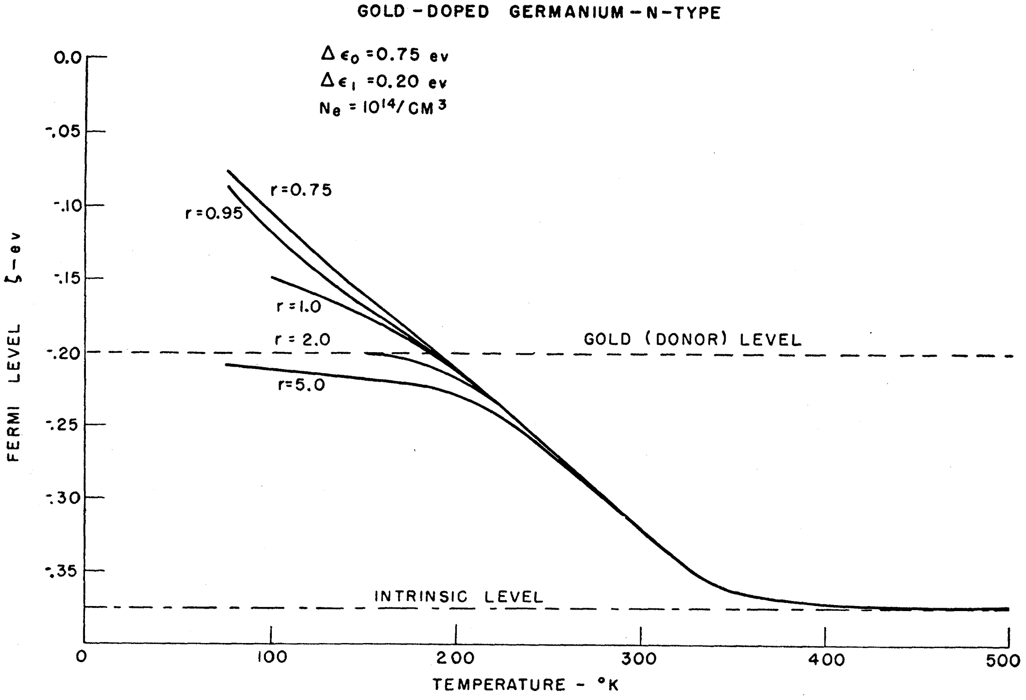

FIG. 22. Fermi level of *n*-type gold-doped germanium, plotted *vs* temperature.

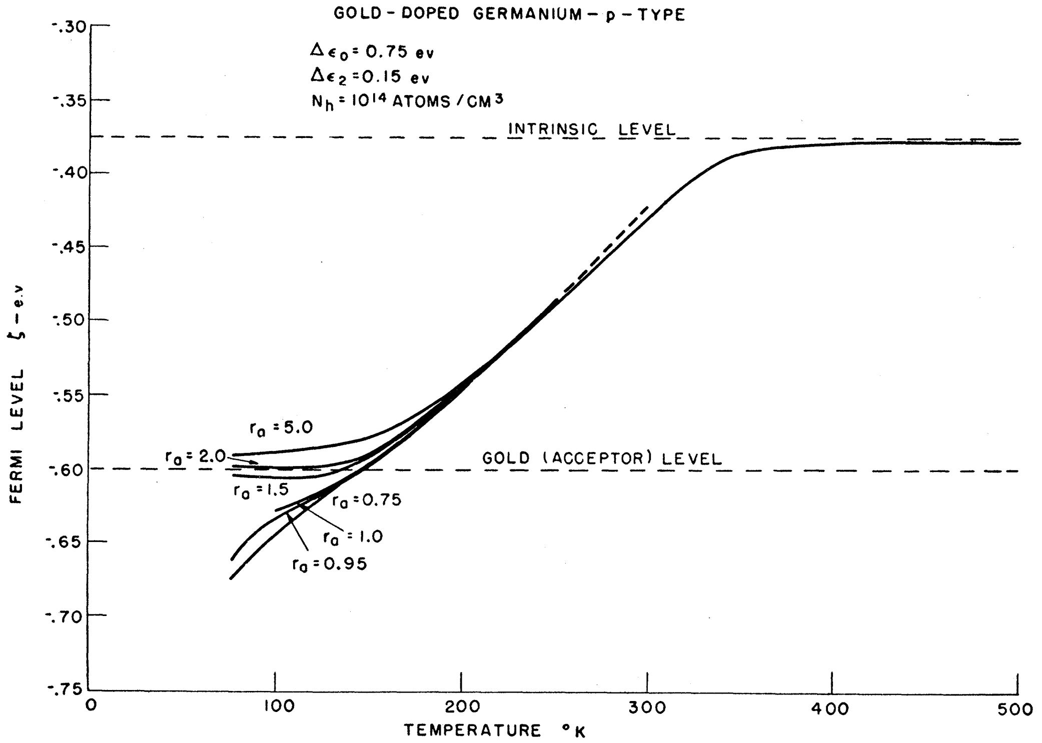

FIG. 23. Fermi level of *p*-type gold-doped germanium.

and for *p*-type material:

$$R = (3\pi/8eB)e^{-\xi/kT}. \qquad (21)$$

Figures 24 and 25 show theoretical Hall curves for *p*- and *n*-type material respectively. Results are plotted for various trapping ratios. Of particular interest is the fact that for $r \sim 1$, linear curves are obtained which could lead to erroneous values of ionization energy if not correctly interpreted.

Included in Fig. 25 are experimental points for two *n*-type samples of various trapping ratios. The experimental points apply for samples with nearly, but not exactly 10^{14} gold states. The trapping ratio of the measured samples is not known exactly, because of the presence of a small number of donors arising from contamination in the furnace. The trapping ratio can probably be estimated reasonably well from these plots. The agreement between the experimental and theoretical curves appears to be quite good. This agreement appears to lend additional weight to the validity of the present model.

APPLICATIONS OF GOLD-DOPED GERMANIUM

We have shown that gold-doped specimens having a wide range of properties can be produced. In the present discussion, we shall deal with applications of these special properties that have been made, or which may be made, in various research fields. These applications are based upon the following special characteristics: (1) high resistivity, (2) high ionization energy, (3) effects characteristic of gold, (4) studies of trapping phenomena.

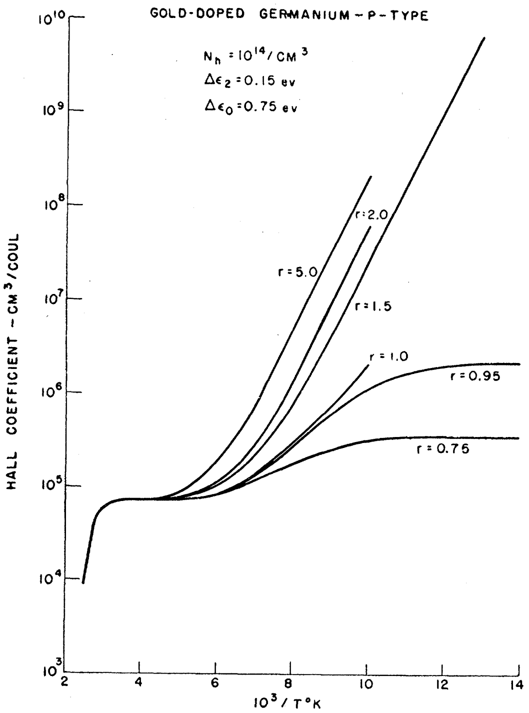

FIG. 24. Plot of Hall coefficient of *p*-type gold-doped germanium, for various values of trapping ratio, as determined theoretically.

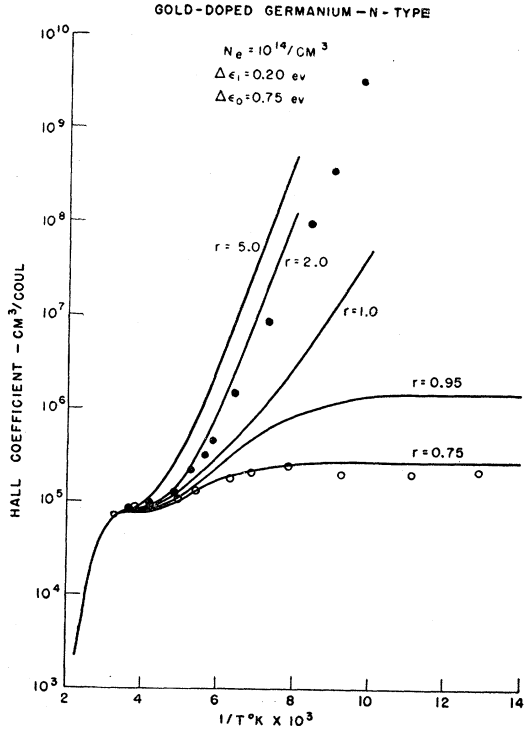

FIG. 25. Plot of Hall coefficient of *n*-type gold-doped germanium for various *r*. Also shown are experimental results on two samples.

(1) Studies made possible by the high-resistivity of gold-doped germanium. As indicated previously, the high ionization energy of gold in germanium makes possible the doing of experiments that were difficult in the past with the available material, which would have required the use of liquid helium, or liquid hydrogen. Since it is possible to obtain resistivities of the order 10^8 ohm-cm at liquid nitrogen temperatures, with gold-doped, and even higher with copper and iron-doped material, many such experiments can be more easily done. Among these are:

(a) Measurement of the dielectric constant and studies of dielectric properties of germanium in general. Availability of gold-doped germanium made possible the first direct measurements of the dielectric constant of germanium.[13] Previous measurements had been done at infrared and microwave frequencies only. The average value for K obtained with the gold-doped germanium, namely 15.8, was in good agreement with the value 16.0 found for example, by Briggs from infrared measurements, and by Benedict and Shockley from microwave studies.

(b) Studies on optical absorption are simplified by the use of gold-doped germanium. Kaiser and Fan,[4] for example, have used gold-doped germanium for investigating absorption under conditions where the free-carrier absorption would not have to be corrected for.

(c) Gold-doping is useful in eliminating the conductivity from certain regions of the sample. For example, Tweet[14] has used gold-doped germanium for the study of the conductivity in grain boundaries. By making gold-doped bicrystals of germanium, he was able to freeze out the bulk conductivity and measure the conductivity along the grain boundary for various angles of the bicrystal.

This technique is useful for other similar purposes, where the other source of conductivity has an activation energy smaller than that of the gold itself. Attempts to study the surface conduction of germanium by using gold-doped germanium have not been very successful, apparently because under the conditions of the experiment, the surface conduction layers had an activation energy comparable to that of the gold, and at low temperatures, not enough differences could be seen with various surface treatments to make valid measurements.

(d) Similarly, the gold-doping has been found useful in determining possible acceptor action of some very insoluble elements in germanium, such as silver. Since the carrier concentration of gold-doped germanium is only about 10^7/cm³ at 78°K, if an element with a solubility of only 10^{10} atoms/cm³ were dissolved, and if the ionization energy of the acceptors formed was considerably less than 0.15, then a great difference in conductivity would show up at 78°K; whereas the change would be negligible if attempted with ordinary germanium containing perhaps 10^{13} carriers/cm³.

Similar applications have been made in the study of effects of particle bombardment[15] and mechanical deformation.[16] In these cases the same situation applies, namely that lower energy acceptors are produced by the action say of electrons, or of mechanical bending, than of the gold, so that large changes of conductivity are produced when the material is studied at liquid nitrogen temperature.

(2) The use of gold is of advantage in the study of the ionization region of semiconductors, again because the temperatures of study are removed from the inconvenient helium-hydrogen range, to that of liquid nitrogen to room temperature. Such problems as those of the comparison of the statistics with experimental results of Hall measurements already discussed are of interest.

(3) Of particular importance are the many problems involving the nature of the gold states and the interaction of the gold atom with the lattice. These studies may be approached by measurements of photoconductivity and Hall coefficient, the optical properties, magnetic susceptibility, the dependence of the resistivity upon pressure, and by other techniques. It is to

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[13] W. C. Dunlap, Jr., and R. L. Watters, Phys. Rev. **92**, 1396 (1953).

[14] A. G. Tweet, Phys. Rev. **96**, 828 (1954).

[15] Pepper, Klontz, Lark-Horovitz, and MacKay, Phys. Rev. **94**, 1410A (1954).

[16] C. J. Gallagher and A. G. Tweet, Phys. Rev. **96**, 834 (1954).

be hoped that results from such investigations may answer many of the questions raised in the present work.

(4) The use of gold permits the introduction in reasonably large quantities ($>10^{15}/\text{cm}^3$), of electron traps located at a definite level. These have already been shown to be involved, in all probability, in various trapping phenomena. Further studies should add considerably to knowledge of secondary photoconduction and other phenomena but poorly understood up to the present time.

(5) Gold-doped germanium has particular promise as a photoconductor for the long-wavelength infrared region because of its response out to about 8 microns. In this respect it is much superior to both lead telluride and lead selenide, whose long wavelength response dies out at about 6 and 4 microns respectively. Of course, gold-doped germanium has to be cooled sufficiently that deionization of the carriers can take place, and that sensitivity be increased and dark current reduced.

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Molecular Field in the Spherical Model*

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The Heisenberg model of ferromagnetism is replaced by a classical model in which the interaction between a pair of neighboring atoms is $-2JS(S+1)\boldsymbol{\varepsilon}_i\cdot\boldsymbol{\varepsilon}_j$, where S is the spin of any atom, J is the exchange integral, and the $\boldsymbol{\varepsilon}_i$ are classical unit vectors. The spherical model is then used to evaluate the molecular field acting on any atom i. This effective field is found to have the generalized Weiss form, $H+W(T)M+W'(T)M'y_i^\pi$, where H is the magnetic field, M the magnetization, and M' the antiferromagnetic order (in units of magnetization). The coefficient y_i^π changes sign from one sublattice to another. The "Weiss" coefficients $W(T)$ and $W'(T)$ are slowly temperature-dependent and obey $dW/dT>0$; $dW'/dT>0$.

A phase transition is found in three dimensions, but not in one or two dimensions. For spin $\frac{1}{2}$ lattices of simple cubic, body-centered cubic, and face-centered cubic type, the ferromagnetic transition temperature T_c in units kT_c/J is found to be 1.98, 2.87, and 4.45, respectively. Corresponding values for the simple cubic case due to P. R. Weiss and V. Zehler are 1.85 and 1.93 respectively. The susceptibility and the paramagnetic temperature θ are found for the three lattices. The ratio θ/T_c is found to be independent of spin with the values 1.52, 1.39, and 1.34 for the s.c.c., b.c., and f.c.c. lattices respectively. Corresponding results for the transition temperatures, susceptibility, etc., are obtained for the antiferromagnetic cubic lattices.

1. INTRODUCTION

THE treatment of dielectric and magnetic phenomena has often been facilitated by the use of appropriate effective fields. Some typical examples are the Lorentz electric field in nonpolar cubic crystals, the Weiss molecular field treatment of ferromagnetism, and the Van Vleck[1] sub-lattice treatment of antiferromagnetism.

The effective field method usually asserts that the behavior of a single member of an assembly of interacting particles can be treated as if it stood alone in a modified field. The modified or effective field differs from the applied field (if any) because it includes the average effects of all other members of the assembly (computed holding the particle in question fixed).[2]

These remarks may be made more definite by considering a classical system[3] described by the (vector) parameters $\boldsymbol{\varepsilon}_1, \boldsymbol{\varepsilon}_2, \cdots \boldsymbol{\varepsilon}_N$, the energy $U=U(\boldsymbol{\varepsilon}_1,\cdots \boldsymbol{\varepsilon}_N)$ and the partition function,

$$Q=\int \exp(-U/kT)d\boldsymbol{\varepsilon}_1\cdots d\boldsymbol{\varepsilon}_N. \tag{1.1}$$

The distribution function $Q(\boldsymbol{\varepsilon}_j)$ for the single particle can be obtained by integrating (i.e., averaging) over all other particles:

$$Q(\boldsymbol{\varepsilon}_j)=\int \exp(-U/kT)d\boldsymbol{\varepsilon}_1\cdots d\boldsymbol{\varepsilon}_N/d\boldsymbol{\varepsilon}_j. \tag{1.2}$$

There is, of course, no guarantee that the distribution function of a single particle in an effective field has the same form as $Q(\boldsymbol{\varepsilon}_j)$ but the two can usually be made to coincide by permitting the effective field to be a sufficiently complicated function of temperature and $\boldsymbol{\varepsilon}_j$.

In practice, the effective field is often estimated by intuitive procedures (as, in the Bragg-Williams treat-

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[1] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

[2] Compare with the definition that arises naturally in M. Lax, Phys. Rev. **85**, 621 (1952).

[3] The succeeding remarks can be translated into quantum mechanics by replacing integrations of the Boltzmann factor over phase space by traces of the corresponding Boltzmann operator.