

Properties of Zinc-, Copper-, and Platinum-Doped Germanium*

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Hall effect and resistivity measurements have been made on a number of samples of single-crystal germanium containing additions of zinc, platinum, and copper. All three were found to be acceptors with energy of ionization 0.029, 0.040, and 0.036-eV electron volt, respectively. Measurements were made in the temperature range 15°K to about 400°K. All the Hall and resistivity curves showed a tendency to flatten out at the lowest temperatures, rather than to continue on an exponential curve. Possible explanations include (a) surface conductivity with low activation energy, (b) traces of low-ionization energy acceptors, (c) internal leakage due to imperfections or dislocations. Studies were made looking for acceptor states in the upper part of the forbidden band, such as have been found for gold. Evidence was found for a platinum acceptor level 0.2 eV below the conduction band and for a copper acceptor level just below the middle of the forbidden band.

INTRODUCTION

A NUMBER of studies have recently been made of acceptors in germanium not in the third column of the periodic table. First of these was zinc,¹ which was found, by low-temperature resistivity measurements, to be an electron acceptor in germanium with an ionization energy of the carrier equal to about 0.03 eV. Copper has also been studied, both by doping of the crystal during growth,² by diffusion methods,³ and by the study of heat-treated specimens.⁴ An ionization energy was found in the vicinity of about 0.04 eV. The equality of values found for heat-treated as compared to diffused specimens has been one important piece of evidence for the theory that traces of copper account for all the main heat-treatment phenomena of germanium.

In the present work, a new low-temperature cryostat for the measurement of Hall coefficient and resistivity of semiconductor specimens was designed and built. The first work carried out with this new equipment was done on zinc-doped specimens. It was considered desirable to extend the previous resistivity measurements to determine the ionization energy from Hall measurements. Following this study, Hall measurements were made to study heat-treated samples and thus to extend the previous resistivity measurements of DeSorbo and Dunlap. Studies have also been made with platinum-doped germanium. Unlike the other agents studied, this is apparently the first work done with platinum. Besides determination of the acceptor action and the ionization energy of platinum, estimates were made of the segregation coefficient ($\sim 10^{-6}$), and the solubility ($\sim 10^{14}$ atoms/cm³) of platinum in germanium as determined from the properties of the grown crystals.

Of particular interest in the study of new doping

agents in germanium is the possibility of second states of the impurity center. Such states were first found with gold,⁵ and more recently Tyler, Woodbury, and Newman⁶ have found evidence for such states with iron and cobalt. Burton *et al.*⁷ have also indicated that copper might possess a second ionization level just below the middle of the forbidden region. The investigation of this possibility for the three elements zinc, copper, and platinum formed a chief object of the present study.

EXPERIMENTAL

Preparation of Samples

Single crystals were grown especially for this work, with a Czochralski furnace of essentially conventional design. The melt was contained in a quartz crucible surrounded by a $\frac{1}{2}$ -in. thick graphite liner used to improve axial thermal symmetry. The furnace consisted of a quartz jar containing a viewing window, and surrounded by a nichrome furnace winding. The heating current was controlled manually by a Variac auto-transformer. Crystals were generally grown from (111) seeds, held in a stainless steel chuck. The pulling head provided independent lifting and rotating motions. The rotation speeds were, generally, 3–4 revolution/sec, the pulling speed generally 1–2 in. per hour. Forming gas (nitrogen +10 percent hydrogen) was used as the atmosphere.

Addition of the desired impurity was made by insertion of a small funnel into the top of the furnace. The metallic impurity was then added in the form of one or two weighed pellets. The seed was withdrawn during this process and the melt allowed to stand a few minutes so that uniform distribution of the impurity might more easily take place.

In many of the melts, the original crystals contained appreciable quantities of arsenic or antimony impurities.

* Presented in preliminary form at the Michigan meeting of the American Physical Society, March, 1954 [Phys. Rev. **94**, 1419 (1954)].

¹ W. C. Dunlap, Jr., Phys. Rev. **85**, 945 (1952).

² F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

³ Fuller, Theurer, and Van Roosbroeck, Phys. Rev. **85**, 678 (1952).

⁴ W. DeSorbo and W. C. Dunlap, Jr., Phys. Rev. **83**, 869, 879 (1951).

⁵ W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).

⁶ Tyler, Woodbury, and Newman, Phys. Rev. **94**, 1419 (1954).

⁷ Burton, Hull, Morin, and Severiens, J. Phys. Chem. **57**, 853 (1953).

In others, the original crystal was nearly intrinsic in resistivity. All samples designed to show the direct effect of the impurities contained negligible quantities of other impurities.

The samples used were rectangular plates, sawed out of the ingots in planes normal to the axis of growth. The six connections for measurement were made by soldering techniques, in most cases. Indium was found to be a satisfactory solder for low-temperature work with *p*-type specimens, while arsenic-doped indium was used for soldering contacts to *n*-type specimens.

Measurement Methods

The methods of measurement were quite conventional. The cryostat involved a few new features and is shown in Fig. 1. The metal Dewar contained an inner can of stainless steel from which hung a 9-in. copper bar, $\frac{3}{4}$ in. in diameter. The inner can also contained carbon black, which, when pumped on, aided cooling by the energy of desorption. The sample was cemented inside this copper bar, the leads and thermocouple passing up through the center of the copper bar and through a stainless steel tube extending up through the inner can and out the top of the Dewar. A heater coil was wound around the copper bar between the sample and the inner can, which could be filled either with liquid helium or hydrogen. With hydrogen in the can, the temperature of the sample could be easily controlled between 15°K and 65°K, and temperatures above this range caused no problem. Two liters of liquid hydrogen were sufficient to cool the system from 77°K, and to maintain it at 20°K for 6–8 hours.

The copper bar was surrounded by a radiation shield at 78°K and an outer brass case, total diameter about $1\frac{3}{4}$ in., although the thickness of the main part of the Dewar was about 10 in. The sample thus could be mounted in a permanent magnet with a field of 1500 gauss. Rotation of the magnet served to reverse the magnetic field.

Temperature was measured by means of copper-constantan thermocouples, calibrated against the Ohio State gas thermometer. Thermocouples were indium-soldered to the samples. The thermal emf's were measured with a Type B Rubicon potentiometer. Thermal emf's in the potentiometer and associated circuit often caused errors, at 20°K, of a few microvolts. Consequently, a calibration was usually made at 20°K with the sample maintained at liquid hydrogen temperature. It was assumed that the extraneous few microvolts would remain constant during a run. The few times this was checked by repeat calibrations this was found to be so. It is estimated that temperatures measured are accurate to about 0.2°C in the worst part of the range, between 15 and 20°K.

The samples themselves were used as the measure of the constancy of temperature for each measurement. To obtain a given temperature, it will be remembered

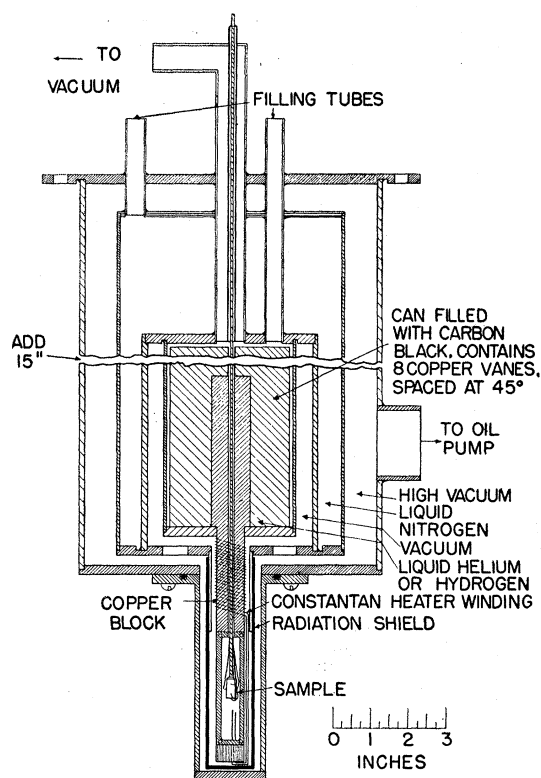


FIG. 1. Diagram of cryostat and sample connections.

from the above, the flow of heat into the hydrogen can was compensated by the heater between the sample and the can. The heating current was adjusted until the potential drop across the sample was constant during the time needed for Hall and resistivity measurements. This was often not easy because of the extreme sensitivity of some of the samples to temperature variation in the temperature range 15–78°K. In most cases, the temperature had to be held constant to less than 0.01°K during the time of measurement.

Purity of the Doping Agents

In experiments such as the present ones, purity of the doping agents can be a critical problem. This is particularly true of elements with a very small segregation coefficient—defined as the ratio of the concentration of the element in the solid to that in the liquid. If the element should be contaminated with a very small percentage of an element, such as arsenic, with a much larger segregation coefficient (about 0.1 for As), the results can be completely erroneous. The best check on this problem is to obtain the purest possible materials, with 99.99-percent purity a minimum, and to make many repetitions of the growth of crystals with material from several sources.

All the impurity agents used in the present work were 99.99 percent or better in purity, and consistent results were obtained.

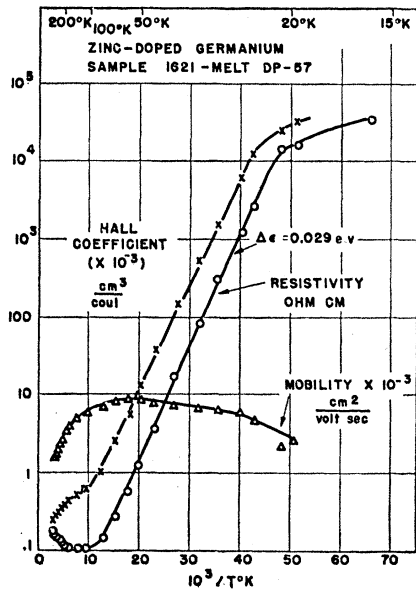


FIG. 2. Conduction properties of a *p*-type zinc-doped specimen of germanium. Room temperature resistivity was 0.2 ohm cm, the carrier density about 10^{16} cm^{-3} . Hall coefficient, resistivity, and Hall mobility (R/ρ) are shown in the temperature range between 300°K and 15°K.

RESULTS

Zinc

Figure 2 shows typical results on zinc. Hall coefficient, resistivity, and mobility are all plotted on the same chart. The ionization energy found from the relation

$$n \sim 1/R \sim n_0 \exp(-\Delta E/kT),$$

was about 0.029 eV. This is to be compared with the value 0.031 eV previously found by the author from resistivity measurements on other samples. The agreement is quite satisfactory.

The room temperature resistivity of this particular sample was about 0.2 ohm cm. Other samples have been made with resistivities as low as 0.05 ohm cm. No direct information on solubility of zinc in germanium has been sought. The above facts indicate, since samples of less than 0.05 ohm cm have not been found even in heavily doped melts, that the solubility is about 10^{17} atoms/ cm^3 .

Likewise, good values of segregation coefficient have been somewhat difficult to obtain, primarily because of the high vapor pressure of zinc at the melting point of germanium, 940°C. Burton has estimated 0.01 for the segregation coefficient, and our results are not inconsistent with this figure.

The Hall coefficient and resistivity tend to flatten out at temperatures below 40°K. This is a phenomenon that has been observed with many widely different samples of germanium and other semiconductors. The nature of the effect is not clear and may arise from a number of possible sources, such as traces of ordinary

acceptors such as indium or boron, surface conductivity, a conductivity associated with dislocations, or other effects. Because the effective number of centers required to produce these effects is so small relative to the 0.03-zinc state, they do not appear to be related to any state of the zinc atoms.

The mobility of zinc-doped specimens tends to be somewhat less than that for most *p*-type specimens of comparable resistivity. In the present case, the Hall mobility at 25°C was 1506 $\text{cm}^2/\text{volt sec}$, whereas indium-doped specimens of the same resistivity are usually in the range 2400–2600 $\text{cm}^2/\text{volt sec}$.

No evidence has been found that zinc produces any acceptor levels in the upper half of the forbidden band, such as are found for gold. The methods of investigating this point are discussed more fully in the section on platinum.

Platinum

The purity of the platinum used is a critical part of the study, since the segregation coefficient is about 5×10^{-6} . Platinum of claimed 99.999-percent purity obtained from Sigmund Cohn was used. Because of the large segregation, amounts of the order 25–50 mg were added to melts of the order 100 g weight. In all tests made using this and other platinum samples, evidence for acceptor action was found. Twenty platinum-doped melts were made.

Figure 3 shows the low-temperature Hall and resistivity data for a sample of platinum-doped material made by adding 41-mg platinum during growth of an ingot with 75-g germanium. The resistivity before the platinum was added was 40 ohm cm *n* type, afterwards

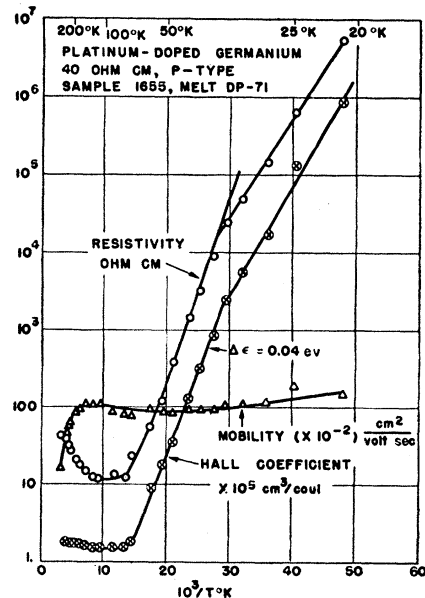


FIG. 3. Conduction properties of a platinum-doped specimen of germanium. The platinum content was about 10^{14} atoms/ cm^3 , the room temperature resistivity 40 ohm cm.

40 ohm cm *p* type. The segregation coefficient calculated from the change in electrical resistivity was 5×10^{-6} . Since the minimum resistivity (*p* type) found with any of the ingots prepared in these studies was about 10 ohm cm, it is presumed that the solubility is about 2×10^{14} atoms/cm³.

The slope of the Hall coefficient curve gives an ionization energy of 0.04 ev. This is taken from the higher temperature range, since it can be seen that the curve apparently breaks into a section of smaller slope. Rather than ascribe any significance to this low-temperature portion, we shall tentatively classify it with the corresponding result in the zinc case and assume that it results from an extraneous effect.

Because of the similarity in many respects between platinum and gold, an intensive search was made for high-lying acceptor states in platinum-doped germanium. The procedure was to start with low-resistivity *n*-type material and add platinum in steps, about 30-40 mg each, until 150-200 mg had been added. Samples were cut from each successive section, and tested for evidence of acceptor states in the upper half of the band. Figure 4 shows results on several samples. One of these went to high resistance, with a slope indicating an ionization energy of 0.18 ev. The other, while of low resistivity, showed a "hump" in the Hall and resistivity curves that indicated an ionization energy of 0.22 ev. Thus it is concluded, contrary to the preliminary findings, that there is a second acceptor level in Pt-doped Ge, at about 0.2 ev below the conduction band. This is at the same level as for gold. It is presumed that the second level is associated with the Pt⁻ ion, although

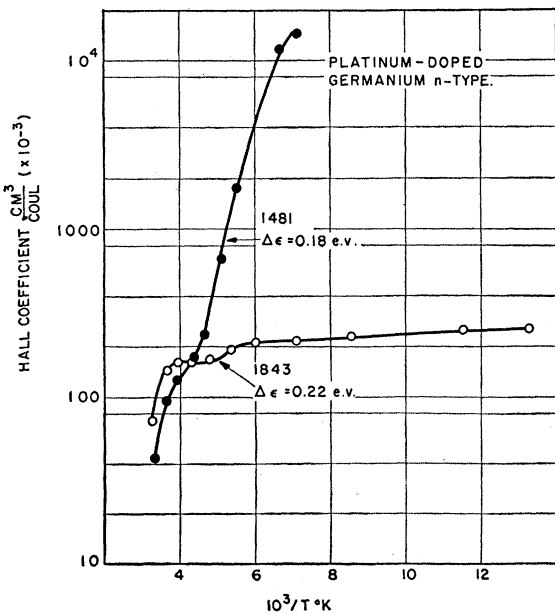


FIG. 4. Experimental results indicating high-lying acceptor levels in Pt-doped germanium. The ionization energy for the high-resistivity sample was obtained directly from the slope, while a more extended analysis was needed for the other case.

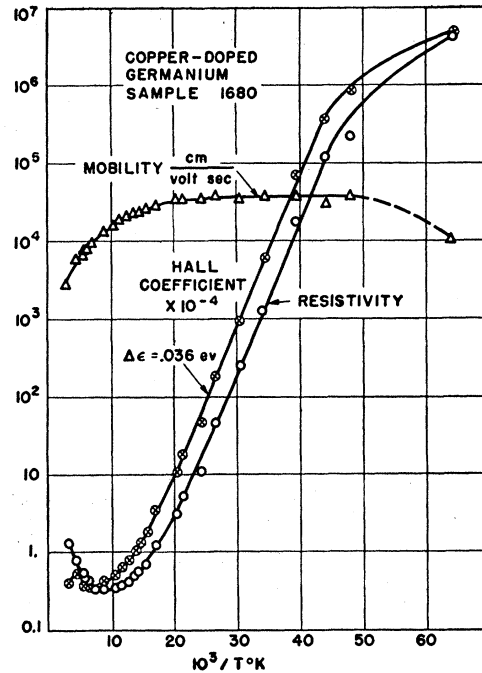


FIG. 5. Conduction properties of *p*-type copper-doped germanium specimen.

it is quite possibly associated with a lattice defect accompanying the Pt center.

Copper

A number of copper-doped melts were prepared, using 99.999-percent pure copper, kindly put at our disposal by Dr. D. Turnbull of this laboratory. The problem of doping with copper is complicated by the large diffusion coefficient of copper, and sectional doping, as described above, is ineffective.

Figure 5 shows the properties of one copper-doped specimen. The ionization energy from the slope of the Hall curve was about 0.036 ev.

Evidence for additional copper states was sought. Some evidence was found of an acceptor state close to the center of the forbidden region, as suggested by Burton *et al.* Figures 6 and 7 show results on several samples of germanium close to the intrinsic region. In all samples of Cu-doped Ge, the Hall and resistivity curves break down into the intrinsic line at temperatures lower than that for ordinary samples, shown in both Figs. 6 and 7 for comparison. These results are consistent with the presence of acceptor states close to the middle of the band. The number of such states, and their exact energy level, is difficult to estimate from such experiments as these.

By annealing such samples, or by doping in such a way that the Fermi level is close to the middle of the band, even at low temperature, one can see the upper copper states more directly. Results are shown in Fig. 8. The slope increases continually on annealing, until the

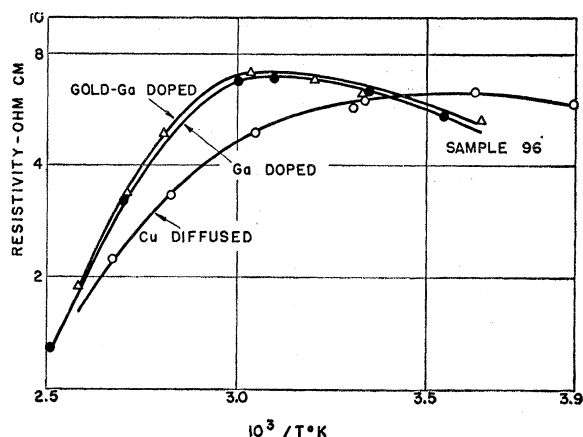


FIG. 6. Resistivity of copper-doped specimen (p type) compared with that of several ordinary samples of p -type germanium with about the same resistivity. Resistivity reaches a peak and begins to approach the intrinsic value at temperatures considerably lower for the Cu-doped specimen than for the Ga-doped specimen. This is evidence for the copper acceptors below the middle of the forbidden band.

slope indicates an ionization energy in the range 0.20–0.25 ev.† Up to this point the homogeneity has remained acceptable, as indicated by the mobility value. Further annealing led to drastic drop in mobility, evidence of p - n junctions being formed in the sample.

DISCUSSION

Ionization Energies

The hydrogen-like model⁸ has been moderately successful in accounting for the ionization energies of third and fifth column impurities in germanium. To obtain agreement with experiment, it is necessary to assume that the effective mass of the carriers is in the range 0.2–0.3 of the electron mass. However, these values are consistent with effective mass values obtained by other means, such as the variation of mobility with resistivity,⁹ and the cyclotron resonance effect.¹⁰

In the case of the elements zinc, copper, and platinum, theoretical correlation is likely to be somewhat more difficult. The closest simplification is that of the helium-like model. In this model, two valence electrons move in a field of the doubly charged impurity ion. The effect of the germanium lattice is taken account of through the reduction of all energy levels, relative to the ionization limit, by the square of the dielectric constant ($K=16$).¹¹

† Note added in proof.—A more exact determination of this level has been made by J. F. Batten and R. M. Baum [Phys. Rev. **94**, 1393 (1954)], who find $\Delta\epsilon=0.32$ ev above the valence band.

⁸ First discussed by H. A. Bethe. See, for example, W. Shockley, *Electrons and Holes in Semiconductors* (D. Van Nostrand Company, Inc., New York, 1950), p. 224.

⁹ P. P. Debye and E. Conwell, Phys. Rev. **93**, 693 (1954).

¹⁰ Dresselhaus, Kip, and Kittel, Phys. Rev. **92**, 827 (1953).

¹¹ H. B. Briggs, Phys. Rev. **77**, 287 (1950); a new low-frequency value of 15.8 is given by W. C. Dunlap, Jr., and R. L. Watters, Phys. Rev. **92**, 1396 (1953).

Since the first ionization potential of helium is 24.5 ev, the ionization energy ΔE for carriers with an effective mass of 0.2 the electron mass is

$$\Delta E = (24.5/K^2)(m^*/m) = 0.02 \text{ ev.}$$

This figure is in reasonable agreement with the value for zinc, but the agreement becomes progressively worse for copper and platinum. It is probable that the details of the binding between ion and lattice, and of such effects as screening, must be calculated more closely to obtain better agreement. It is doubtful, also, whether the effective mass for free carriers is exactly the same as that for bound carriers moving about an impurity atom, and the value of the effective mass may very easily depend upon the nature and strength of the binding forces. We conclude that the helium-like model is, at best, only a very crude approximation.

Diffusion Coefficients

Studies have been made upon the diffusion of zinc¹² and copper¹³ into germanium, although no such work has yet been done using platinum. Although the electrical properties of zinc- and copper-doped germanium are similar in some respects, the diffusion properties are completely different. Zinc diffuses very slowly, and copper very rapidly in germanium. For Zn, D at 900°C is about 10^{-11} cm²/sec, and the activation energy for diffusion is about 2.5 ev. These values are quite comparable to those for indium, gallium, and other acceptors in germanium. Copper, on the other hand, has a diffusion coefficient of $\sim 10^{-5}$ cm²/sec

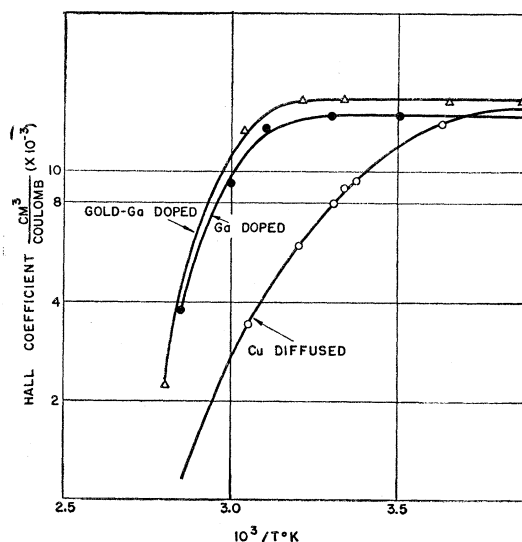


FIG. 7. Hall coefficient data for the samples of Fig. 5.

¹² See reference 1. Also, W. C. Dunlap, Jr., Phys. Rev. **86**, 615 (1952); C. S. Fuller, Phys. Rev. **86**, 136 (1952); and W. C. Dunlap, Jr., Phys. Rev. **94**, 1531 (1954).

¹³ Fuller, Struthers, Ditzemberger, and Wolfstirn, Phys. Rev. **93**, 1182 (1954).

at 600°C, and the apparent activation energy is 0.2 ev or less.

These discrepancies can be accounted for if it is assumed that at room temperature both zinc and copper are substitutional acceptors and that, furthermore, at higher temperatures copper leaves its substitutional sites, presumably by losing one or more electrons, and becomes interstitial. Only a relatively small fraction of the copper ions need to do this in order that one may account for the observed effects. Zinc, on the other hand, retains its electrons even at high temperatures, and remains substitutional. Here, again, the lack of better understanding of the coupling between impurity and the lattice prevents closer correlation of these ideas. A pertinent contradiction, perhaps, is that the tetrahedral radius of copper is 1.35 Å, that of zinc only 1.30 Å. A change in electronic state of copper is probably needed to reduce its size to the point where it can become interstitial, and evidence of Fuller *et al.*¹³ does indicate that copper does diffuse as a *positive*, rather than a negative ion.

SUMMARY¹⁴

The present work shows that several elements besides the "3-5" elements are active in germanium. With other recent work, there are now eight or ten such active elements. Many others may be found, provided they are sufficiently soluble that electrical effects can be seen. Silver, for example, can be seen in germanium from autoradiographs, but the solubility is apparently too small for there to be a direct effect on conduction properties.¹⁵

From the present work it is also seen that crystal-growing and diffusion experiments are both valuable in the study of unknown elements in germanium. Diffusion may be especially useful in the study of

¹⁴ The results obtained with all the present materials have applications to the question of "electrical forming" of germanium rectifiers. Zinc and copper are constituents of most brasses and bronzes, and platinum is a widely used whisker material, either pure, or alloyed with ruthenium. It is clear that if any of the three is present in a whisker material, and the whisker is pulsed with high currents, or "formed," there will be a tendency for *p*-type action because of the alloying of the whisker material with the germanium. The copper will have a further action because of its fast diffusion. The diffusion effect of zinc and platinum is relatively small, but may not be negligible.

¹⁵ W. C. Dunlap, Jr. (to be published).

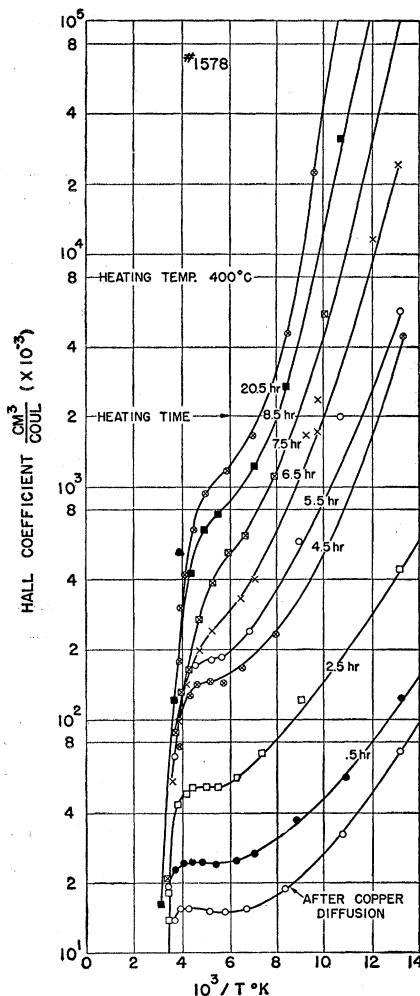


FIG. 8. Hall coefficient for an *n*-type sample that had been quenched, then annealed in stages at 400°C. The increase in slope with annealing shows the existence of high-lying acceptor states, probably at about 0.25 ev.

insoluble elements, since their solubility is often much greater at 700° or 800° than at the melting point.

There remains a large field in the interpretation of such data as have been presented here. The correlation between atomic properties of the impurity, and the band structure of germanium so as to obtain the correct value of ionization energy, and diffusion coefficient has not yet been made.