Coltman, and Redman[18] that cold-worked single-crystal copper does not show a resistance minimum. Insofar as grain boundaries are a further type of lattice imperfection, and low angle grain boundaries may perhaps be regarded as an array of dislocations, it is difficult to understand how grain boundaries, *per se*, can be the origin of the resistance minimum in pure copper. On the other hand, we have suggested how grain boundaries may be of importance *in the presence of certain impurity atoms*.[14] Alternatively, the presence of certain heterovalent and transition metals as impurities may *alone* be sufficient to give rise to a resistance minimum, and we have now observed a resistance minimum in *single-crystal* copper containing iron and tin as impurities.

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# Properties of Germanium Doped with Cobalt

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Measurements of the temperature dependence of electrical resistivity in $n$- and $p$-type cobalt-doped germanium crystals indicate that cobalt introduces acceptor levels in germanium at $0.31\pm0.01$ ev from the conduction band and $0.25\pm0.01$ ev from the valence band. Ionization energies deduced from infrared photoconductivity studies at 77°K are in good agreement with the values obtained from resistivity measurements. $N$-type samples show higher intrinsic photosensitivity than $p$-type samples and demonstrate quenching effects.

## I. INTRODUCTION

THIS paper presents information concerning the properties of germanium single crystals doped with cobalt. A preliminary account of this work has been given.[1] The properties of iron-doped germanium, which are in many respects similar to those of cobalt-doped germanium, are described in detail elsewhere.[2,3] A brief review of the literature relating to deep impurity levels in germanium is given in reference 2.

## II. PREPARATION OF SAMPLES

The method of crystal growth and doping was similar to that described for iron-doping.[2] The concentration of cobalt in the melt just after doping was between 0.05 and 0.1 atomic percent. Lineage developed on the crystals at about the same concentration of impurity in the melt (0.3 percent) observed in the case of iron-doping. Samples used for experimental work were approximately 2 mm$\times$3 mm$\times$9 mm, cut from transverse sections of the crystals above the regions of observable lineage. After heavy etching in 80 percent $HNO_3$, 20 percent HF, contacts were fused to the samples in a hydrogen atmosphere. For $n$-type samples, contacts were of tin or tin, 1 percent arsenic; for $p$-type samples, contacts were of indium. Heavy etching after fusing on contacts was necessary, particularly for $p$-type samples.

The cobalt used for most of the doping experiments was cut from a second generation cobalt single crystal[4] grown from high purity sponge cobalt obtained from the Johnson Matthey Company. Later doping experiments were made using Johnson Matthey Company electrolytic cobalt. As in the case of iron-doping, the effective distribution coefficient of cobalt in germanium is low and the presence of high distribution coefficient impurities in the cobalt would be serious. Spectroscopic analysis[5] failed to detect the presence of boron in either source of cobalt. Traces of arsenic and antimony were observed in each source at about the same concentration. Aluminum and gallium were detected in the electrolytic cobalt but not in the single crystal cobalt. The concentration of each of these impurities detected is probably a few parts per million or less. The doping experiments indicate that both sources of cobalt behave similarly and are sufficiently pure that results are probably not dominated by impurities in the cobalt.

## III. EXPERIMENTAL RESULTS

### A. Resistivity, Mobility, and Lifetime Measurements

Both $n$- and $p$-type cobalt-doped crystals which show high resistivity at 77°K have been prepared. Doping pure germanium with cobalt from either source yields high resistivity $p$-type samples. Because there is no

[1] Tyler, Woodbury, and Newman, Phys. Rev. **94**, 1419 (1954).
[2] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954).
[3] R. Newman and W. W. Tyler, Phys. Rev. **96**, 882 (1954).
[4] We are indebted to Eric Asp of the General Electric Research Laboratory for providing us with the single crystal cobalt.
[5] We are indebted to L. B. Bronk of the General Electric Research Laboratory for spectroscopic analyses.

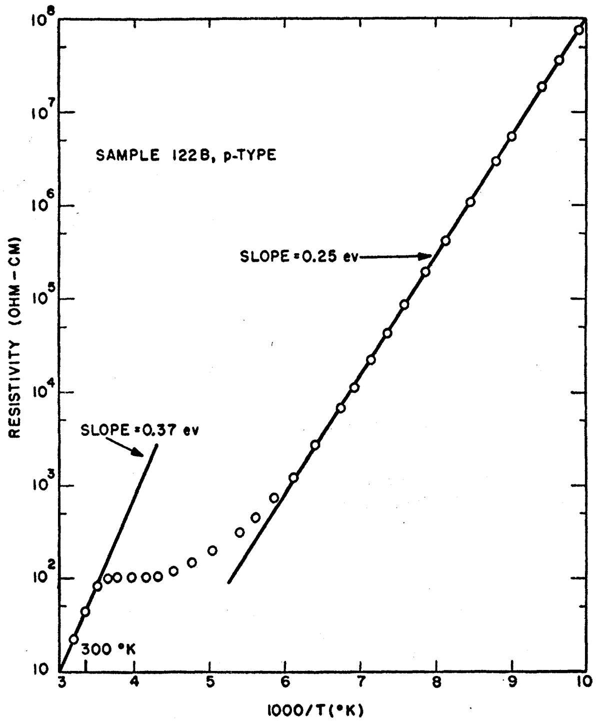


FIG. 1. Resistivity *vs* reciprocal temperature for a $p$-type, Co-doped Ge crystal (sample 122B).

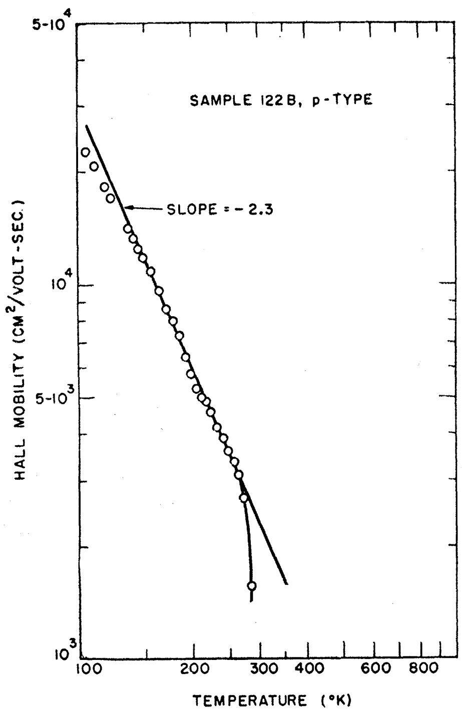


FIG. 2. Hall mobility *vs* temperature for a $p$-type, Co-doped Ge crystal (sample 122B).

evidence for impurities in the cobalt sources which might contribute acceptor states in the crystals comparable in concentration to the cobalt, it is assumed that cobalt acts as an acceptor in germanium. By careful doping of the melt with small amounts of antimony in addition to the cobalt, $n$-type samples have been obtained which show high resistivity when cooled, indicating that cobalt must contribute at least two acceptor states, one below and one above the center of the band. The effective distribution coefficient of cobalt in germanium, estimated from the resistivity measurements is about $10^{-6}$ in agreement with the value reported by Burton *et al.*[6] obtained from radioactive tracer measurements. As in the case of iron-doping, there is evidence that the amount of cobalt in the crystal is not exactly proportional to the amount in the melt.

Measurements of resistivity *vs* temperature for cobalt-doped samples which go to high resistivity when cooled to nitrogen temperature, indicate ionization energies of $0.25\pm0.01$ ev for $p$-type samples and $0.31\pm0.01$ ev for $n$-type samples. These ionization energies are obtained directly from the slopes of $\ln p$ *vs* $1/T$ plots without correction for the difference in the temperature dependence of the mobility for $n$- and $p$-type samples. The 0.01 ev uncertainity quoted represents internal consistency of the data. Measurements were made on $p$-type samples from four crystals, two doped with the single-crystal cobalt and two with the electrolytic cobalt. Three high resistivity $n$-type crystals were studied, two doped with single-crystal cobalt and one with the electrolytic cobalt. Figure 1 shows the dependence of resistivity on temperature for a typical $p$-type cobalt-doped sample. Figure 2 shows the dependence of mobility on temperature for the same sample. Figures 3 and 4 show similar curves for an $n$-type cobalt-doped sample. General features of these curves are similar to those reported for iron-doped crystals. Plots of $\ln\mu$ *vs* $\ln T$ give approximately linear regions with slopes from $-2.1$ to $-2.3$ for $p$-type samples and from $-1.5$ to $-1.6$ for $n$-type samples. The mobility for $p$-type samples show an $H$ field dependence similar to that reported by Harman *et al.*[7] whereas the mobility for $n$-type samples is considerably less dependent on $H$ field up to 4000 gauss. All mobility data reported were measured using a field of 4000 gauss.

Measurements of carrier lifetime at 300°K were made on the cobalt-doped crystals. Lifetime values fell from somewhere in the range 200 to 400 $\mu$sec before doping to values from 10 to 20 $\mu$sec after doping. Lifetime values for samples before doping are decreased to some extent by diffusion of cobalt up the crystal and are in general lower than values obtained in undoped crystals. For the cobalt-doped samples as well as iron-doped samples studied previously,[2] resistivities are intrinsic or

[6] Burton, Kolb, Slichter, and Struthers, J. Chem. Phys. **21**, 1991 (1953).

[7] Harman, Williamson, and Beer, Phys. Rev. **94**, 1065 (1954).

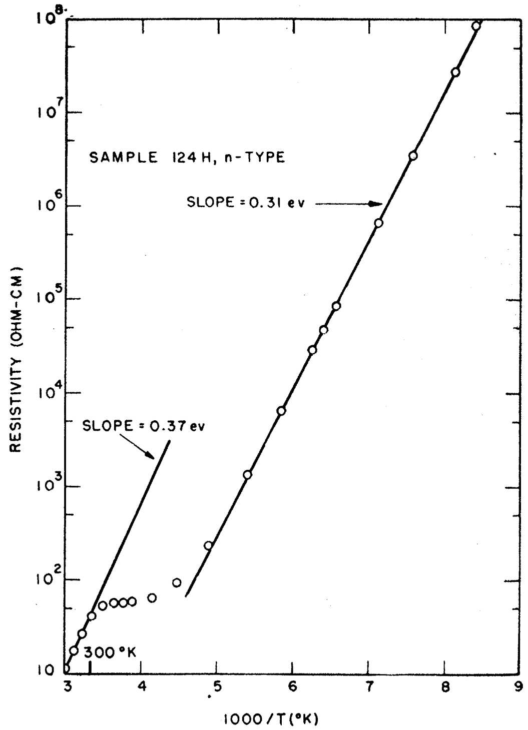


FIG. 3. Resistivity *vs* reciprocal temperature for an *n*-type, Co-doped Ge crystal (sample 124H).

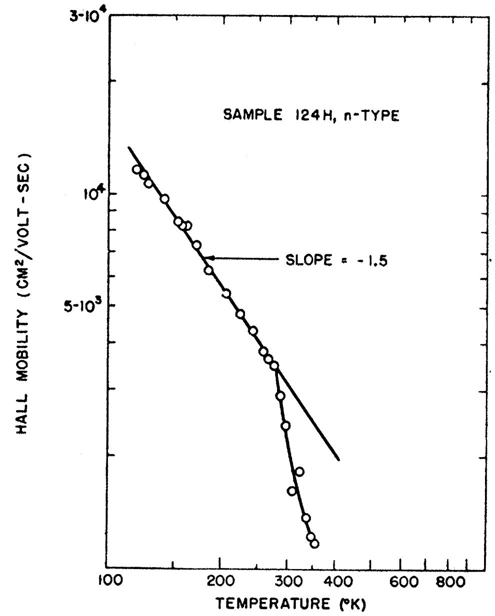


FIG. 4. Hall mobility *vs* temperature for an *n*-type, Co-doped Ge crystal (sample 124H).

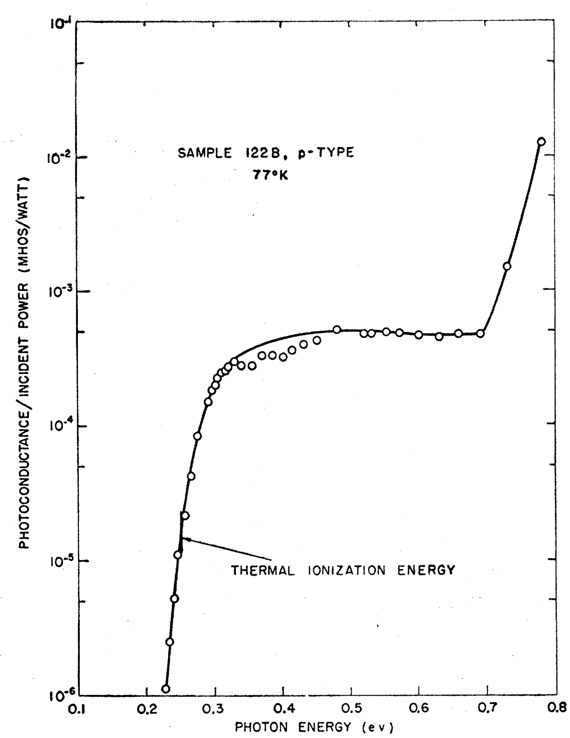


FIG. 5. Photoconductive spectrum of a *p*-type, Co-doped Ge crystal at 77°K (sample 122B).

near intrinsic at 300°K. No attempt has been made to determine limiting values of $\tau_{n0}$ and $\tau_{p0}$ for cobalt in germanium as have been reported by Burton *et al.*[8] for nickel and copper in germanium.

Photoconductivity decay measurements were made on several *n*- and *p*-type high-resistivity cobalt-doped samples at 77°K. Recovery times in most cases were less than several milliseconds and could not be measured accurately due to the decay time of the light source used.[2] One *n*-type cobalt-doped sample showed slow photoconductivity decay and high photosensitivity comparable to *n*-type iron-doped samples.[2] However, this sample showed anomalous mobility behavior, injection effects and nonlinearity and is not considered representative of *n*-type cobalt-doped crystals. The possibility exists that well behaved, *n*-type cobalt-doped crystals showing higher photosensitivity and long decay times might be obtained by properly controlling trapping ratios.[2,3*]

### B. Photoconductivity

Figures 5 and 6 show spectral response of impurity photoconductivity in *p*- and *n*-type cobalt-doped samples at 77°K. Intrinsic photoconductivity begins to dominate at about 0.7 ev. The measurements were made with equipment described elsewhere.[3,9] The sample was exposed to unmodulated light from the

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

* *Note added in proof.*—Recent studies of time decay of photoconductivity in high-resistivity *n*-type Fe-doped crystals, using filtered light, indicate that the long decay times reported (see reference 2) may in part be due to surface effects. Studies of photoconductivity decay in high resistivity Ge crystal sdoped with Fe, Co, and Ni are in progress.

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

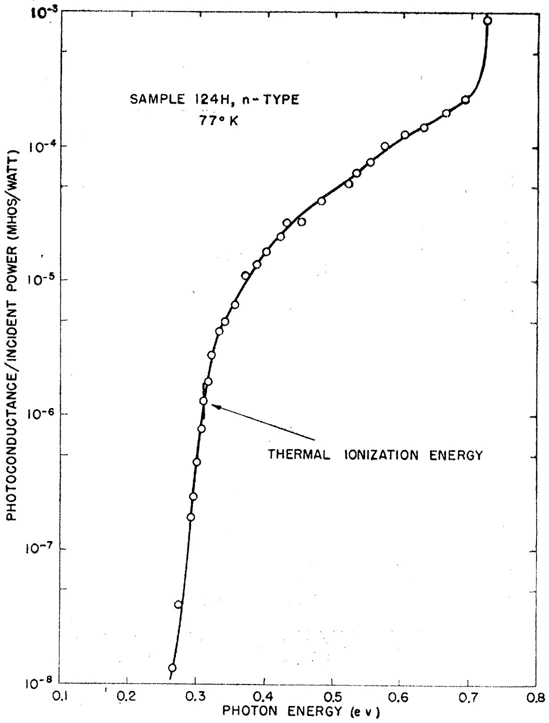


FIG. 6. Photoconductive spectrum of an $n$-type, Co-doped Ge crystal at 77°K (sample 124H).

Perkin-Elmer spectrometer. Photocurrents of the order of $10^{-10}$ ampere were measured in a series circuit consisting of sample, six-volt battery, and load resistor. Spectral response curves shown are typical of results for $p$-type samples from 5 different crystals and $n$-type samples from 3 different crystals. $P$-type samples give a flatter spectral response and sharper cut-off than do $n$-type samples. Optical threshold energies are in reasonable agreement with thermal ionization energies obtained from resistivity data.

In two of the $n$-type samples, quenching effects were observed. Quenching had been observed previously in $n$-type gold-doped[9] and iron-doped[3] germanium crystals. Figure 7 shows a quench spectrum for an $n$-type cobalt-doped sample. The technique used for this measurement has been described.[9,3] In neither of the cobalt-doped crystals in which the effect was obtained was the quenching as pronounced as for gold- and iron-doped crystals and it was not easy to separate the effects of normal intrinsic photoconduction and quenching. Quenching effects seem to maximize at a photon energy of about 0.32 ev.

## IV. SUMMARY

Two acceptor levels in germanium crystals have been identified with the presence of cobalt in the melt from which the crystals were grown. From measurements of the temperature dependence of resistivity, these levels have been located at 0.25±0.01 ev from the valence band and 0.31±0.01 ev from the conduction band. Hall coefficient measurements indicate that high resistivity cobalt-doped crystals show temperature dependence of mobility which is in agreement with previous measurements of mobility in high purity $n$- and $p$-type germanium crystals. The effective distribution coefficient for cobalt in germanium is about $10^{-6}$. Deep states introduced by cobalt in germanium are effective as recombination centers at 300°K.

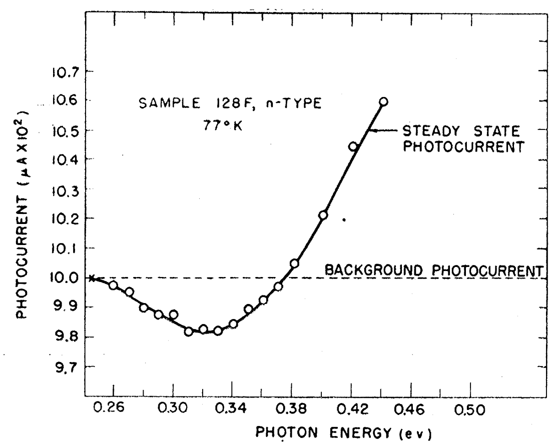


FIG. 7. Quench spectrum of an $n$-type, Co-doped Ge crystal at 77°K (sample 128F).

Impurity photoconductivity studies in $n$- and $p$-type cobalt-doped germanium crystals yield optical threshold energies which are consistent with thermal ionization energies. In agreement with results of gold- and iron-doped crystals, $n$-type cobalt-doped crystals have higher intrinsic photosensitivity than $p$-type samples and show quenching effects. Both of these observations suggest the presence of hole traps and are in accord with the model[2,3] that doubly charged negative impurities sites act as hole traps in germanium.

## ACKNOWLEDGMENT

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