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Electrical Properties of Plastically Deformed Germanium

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Samples of Sb-doped (10 ohm-cm *n*-type) and Au-doped (20 ohm-cm *p*-type) Ge have been plastically deformed at 550°C–620°C. The deformation created a large concentration of acceptor centers distributed inhomogeneously throughout the deformed sections of the samples. These acceptors lie near the valence band and converted the Sb-doped specimens to *p*-type. Hall coefficient measurements have been made as a function of temperature to determine the energies of these acceptors. Upon annealing at temperatures above 750°C from 30 minutes to $1\frac{1}{2}$ hours, the acceptor levels near the valence band disappear, leaving only the acceptors probably associated with edge dislocations. It is postulated that the annealable acceptors may be due to the presence of vacancies.

I. INTRODUCTION

THERE has been considerable study recently of the electrical properties of plastically deformed Ge.[1–5] The experimental investigations have all indicated that plastic deformation at temperatures between 500°C and 700°C produces acceptor centers in the Ge, but there has been some disagreement as to whether or not the material can be converted to *p*-type by this treatment.

It has been indicated[4] that acceptor centers with energies less than 0.15 ev from the valence band are created during the plastic deformation of Au-doped Ge. The work reported here comprised a somewhat more extensive examination of this effect. It also included an investigation of certain annealing effects observed in the deformed material at elevated temperatures.

II. EXPERIMENTAL

A. Procedure

Bars of Sb-doped Ge (∼10 ohm-cm, *n*-type) and Au-doped Ge (∼20 ohm-cm, *p*-type) $\frac{7}{8}$ in.$\times\frac{1}{8}$ in.$\times\frac{1}{32}$ in. have been bent to a radius of curvature of $\frac{1}{4}$ in. on a quartz form in an atmosphere of 99.9 percent N_2 at temperatures between 550° and 620°C, as read on a Chromel-Alumel thermocouple. The bars were etched and cleaned with KCN to remove Cu before insertion in the bending apparatus, which was given the same KCN treatment. In order to simplify the experimental arrangements, the bars were also straightened in the same apparatus before proceeding with the electrical measurements. (Separate experiments indicated no qualitative difference between the electrical properties of the bent and straightened bars and those of the bars which were simply bent.)

Indium contacts were fused to the samples, and the Hall coefficient measured as a function of temperature in a permanent-magnet Hall effect apparatus.[6] Some Hall measurements were also made by using pressure contacts of phosphor bronze tinned with In. There was no appreciable difference between the results of measurements by the two methods, indicating that preferential diffusion of the In down the dislocations[7] very probably did not occur.

Other samples which had been bent and straightened were treated with KCN and annealed for various lengths of time at temperatures above 600°C in a 99.9 percent N_2 atmosphere. Hall coefficient measurements were then made on these annealed specimens as a function of temperature, by using fused tin contacts.

B. Results

Figure 1 shows the Hall coefficient, R, in cm³/coulomb plotted *vs* the reciprocal of the temperature for two sections of a sample of Au-doped Ge. Both sections were *p*-type, both before and after the deformation, with a room temperature hole concentration of $\sim 10^{14}/\mathrm{cm}^3$. The inset identifies the two sections, one of which has been plastically deformed. Note that the contacts are arranged for Hall effect measurements only. The straight line portion of Curve A is of the form $e^{+\varphi/kT}$, where $\varphi=0.15$ ev, characteristic of the lower Au acceptor state in Au-doped Ge.[8] In Curve B the straight line portion of the plot has a φ of 0.10 ev. These data are representative of data taken on several similar samples, which show a spread in φ from 0.08 ev to 0.12 ev.

Figure 2 is a Hall coefficient *vs* $1/T$ plot for a sample of plastically deformed Sb-doped Ge. Again two sections of the sample have been measured; both were in the deformed region in this case. Before deformation, the sample was uniformly 10 ohm-cm *n*-type, whereas after deformation both sections were *p*-type with a room temperature hole concentration of $2\times 10^{14}/\mathrm{cm}^3$. These data show quite strikingly the extreme inhomogeneity which is usually observed in bent specimens. The slope of the straight line portion of Curve A, which is of the form $e^{+\varphi/kT}$, yields $\varphi=0.10$ ev. Again this is

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[1] C. J. Gallagher, Phys. Rev. **88**, 721 (1952).
[2] W. C. Ellis and E. S. Greiner, Phys. Rev. **92**, 1061 (1953).
[3] Pearson, Read, and Morin, Phys. Rev. **93**, 666 (1954).
[4] C. J. Gallagher and A. G. Tweet, Phys. Rev. **96**, 834 (1954).
[5] W. T. Read, Phil. Mag. **45**, 775 (1954).
[6] A. G. Tweet, this issue [Phys. Rev. **99**, 1182 (1955)].
[7] D. Turnbull and R. E. Hoffman, Acta Metallurgica **2**, 419 (1954).
[8] W. C. Dunlap, Jr., Phys. Rev. **91**, 1282 (1953).

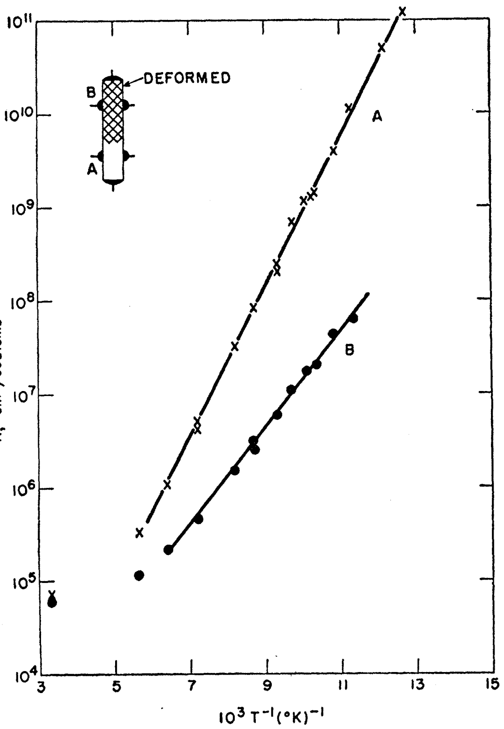

FIG. 1. Hall coefficient *vs* $1/T$ plots for plastically deformed (B) and undeformed (A) sections of a bar of Au-doped Ge. Both sections are p-type. Straight line portion of each curve is of the form $e^{\varphi/kT}$. $\varphi_A=0.15$ ev, characteristic of lower Au acceptor level in Ge; $\varphi_B=0.10$ ev, representative of acceptor levels introduced in Ge by plastic deformation.

characteristic of slopes observed on many such plots, which show a spread in φ from 0.08 ev to 0.12 ev. The data for Curve B are too meager to justify the assignment of a slope.

The reason for the relatively low resistance section shown in Curve B (Fig. 2) is not known. Such sections were found on roughly half of the samples investigated. In a few Au-doped samples, the entire bent region was of relatively low resistance, and it was possible to obtain data down to much lower temperatures. In these cases, the slopes of the log$R$ *vs* $1/T$ plot yielded a φ of $\sim$0.04 ev. (This is equal to the energy reported for the low-lying acceptor level due to Cu in Ge.[9] However, the unbent ends of these samples gave no evidence of Cu contamination.)

Figure 3 is a Hall coefficient *vs* $1/T$ plot for two specimens from one ingot of Sb-doped Ge which were bent, straightened and annealed. Two control specimens cut from adjacent sections of the same ingot were annealed with the deformed ones and are also plotted for comparison. The two deformed specimens, which converted from n- to p-type upon deformation, reverted to n-type during annealing. The control samples remained $\sim$10 ohm-cm n-type during annealing. Curve A is for a plastically deformed sample which was heated $\frac{1}{2}$ hour at 800°C followed by $1\frac{1}{2}$ hours at 600°C. Curve B is for a similar sample which was annealed at 750°C for 1 hour followed by 1 hour at 600°C. Curves A' and B' are for the control specimens which were given the same heat treatment as samples A and B, respectively. The dotted line is a plot of data of Pearson, Read, and Morin[3] on deformed n-type Ge.

Prior to annealing, the Hall coefficients of the deformed specimens were measured using pressure contacts and were found to be similar to those shown in Fig. 2 in their temperature dependence.

The annealing process reduced macroscopic sample inhomogeneity in the deformed samples very considerably, and it was possible to make fairly reliable Hall mobility measurements. In Fig. 4 are plotted mobility data on the four samples of Fig. 3, with the curves labeled as on Fig. 3. The mobility in the deformed and annealed specimens seems to be approximately proportional to the temperature, as predicted by Dexter and Seitz[9] on the basis of a deformation potential scattering mechanism. However, the magnitude of the scattering indicated by the experiments is very much larger than that predicted for the dislocation densities present in our samples.

Read[10] has calculated the effects of scattering by charged dislocations upon Hall mobility in semiconductors. This approach seems to be well-suited to dis-

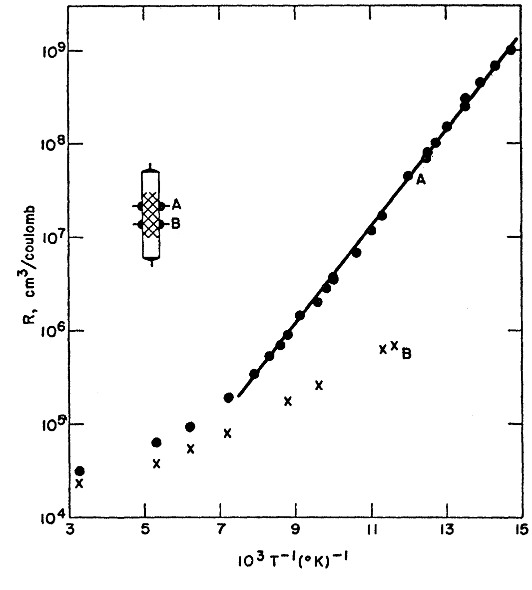

FIG. 2. Hall coefficient *vs* $1/T$ plot for two sections of a bar of plastically deformed Sb-doped Ge, 10 ohm-cm n-type before deformation, p-type after deformation. Straight line portion of Curve A is of the form $e^{\varphi/kT}$, $\varphi=0.10$ ev. This behavior is representative of the effects of acceptor levels introduced in Ge by plastic deformation. Note the inhomogeneity, characteristic of most of the samples investigated.

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

[9] D. L. Dexter and F. Seitz, Phys. Rev. **86**, 964 (1952).

[10] W. T. Read, Jr., Phil. Mag. **46**, 111 (1955).

location scattering below room temperature in the n-type Ge samples of Figs. 3 and 4.

Annealing effects have also been observed on deformed Au-doped Ge samples. In this case, annealing eliminated the behavior of the Hall coefficient in the deformed region shown in Curve B (Fig. 1), so that the carrier density now follows Curve A (Fig. 1) over the entire sample.

III. DISCUSSION

The experimental results described above are consistent with the idea that plastic deformation of Ge introduces, in addition to the array of edge dislocations required by the geometry of the deformation, some other crystalline defect which can be annealed out of the crystal at elevated temperatures. The shapes of the $\log R$ *vs* $1/T$ curves for the deformed samples indicate that these additional defects introduce at least one kind of isolated localized acceptor level. The isolated nature of these acceptors must be contrasted with the strongly interacting acceptors postulated by Read[5] as being associated with edge dislocations in Ge. The latter, of course, yield an entirely different shape for the curve of R *vs* $1/T$.

It is believed that the annealing heat treatment of the deformed Ge, while removing the acceptors near the valence band, perhaps by removing the defects giving rise to them, does not result in an appreciable diminution in the density of dislocations in the material. It is doubtful that a significant rearrangement of the dislocations occurs in the time and at the temperature of annealing to which the deformed specimens in these experiments were subjected.[11] Probably some annihilation of the two opposite signs of edge dislocations put in by the bending and straightening of the sample occurs, but the results of the experiments in which the samples were only bent do not differ qualitatively from those for the samples which were straightened as well. Consequently, it is believed that the R *vs* $1/T$ data for the annealed samples shown in Fig. 3 confirm the acceptor action of dislocations in Ge reported by Pearson, Read and Morin.[3,12] Read[5] has advanced the following explanation for the shape of the curves in Fig. 3. As the temperature decreases, the electrostatic repulsion of the charge already trapped by the dislocation line tends to prevent other carriers from accumulating there, and the charge concentration on the line soon becomes insensitive to further decrease in temperature.

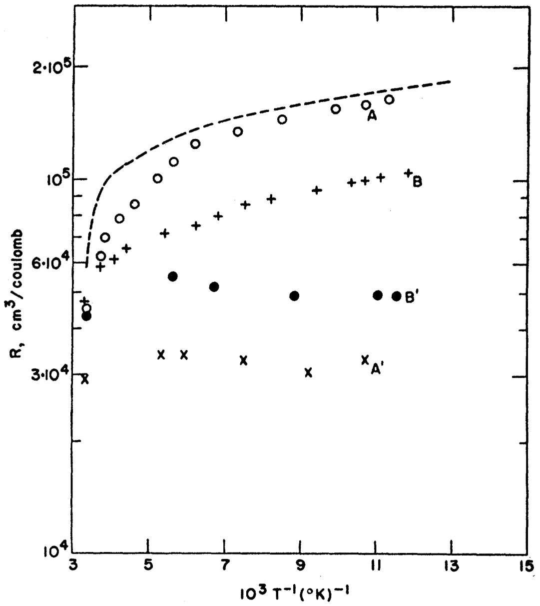

FIG. 3. Hall coefficient *vs* $1/T$ plot for two samples of plastically deformed Sb-doped Ge (A and B) and two control samples (A' and B') which were annealed at temperatures above 600°C for various times (see text). The deformed samples reverted to n-type during annealing. Prior to this they were similar in properties to the samples shown in Fig. 2.

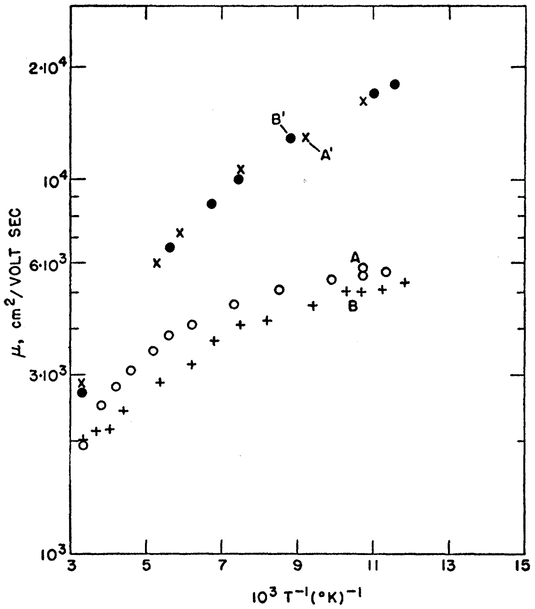

FIG. 4. Hall mobility *vs* $1/T$ for the annealed samples of FIG. 3. Curve labels are as in Fig. 3.

The proper identification of the annealable acceptors, on the other hand, is a much more complicated task. There is evidence that lattice vacancies give rise to acceptor action in Ge. Electron bombardment experiments on Ge have been interpreted[13] in terms of the acceptor behavior of vacancies introduced in the crystal lattice by the bombardment.

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[11] F. L. Vogel, Jr., Acta Metallurgica 3, 95 (1955).

[12] W. T. Read has stated that the temperature at which the samples reported on in reference 3 were deformed was probably somewhat above the 650°C noted there. Considering the relatively light deformation (5-cm radius of curvature) employed by Pearson, Read and Morin, it seems quite likely that their samples were annealed during bending.

[13] Fan, Kaiser, Klontz, Lark-Horovitz, and Pepper, Phys. Rev. 95, 1087 (1954).

It is well known[14] that under appropriate circumstances the movement of dislocations through a crystal, as in plastic deformation, can result in the creation of rows of vacancies and interstitials. Hence it is possible that the annealable acceptors investigated in the present experiments are vacancies. These might be present singly, in clusters, or in combination with other kinds of lattice defects. An investigation of the kinetics of the annealing process would probably help elucidate this important point.

ACKNOWLEDGMENTS

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[14] F. Seitz, Advances in Phys. 1, 43 (1952).

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Permanent Magnetic Moments of a Superconducting Sphere

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The magnetic flux retained by a polycrystalline sphere of pure tin has been studied by two experimental methods. It is shown that the amount of flux retained by the superconducting sphere exhibits a reproducible dependence on the temperature at which the transition is allowed to occur. The specimen shows a 99.9% Meissner effect for transitions well below the critical temperature, but near to T_c the percent of residual flux increases several hundred-fold. The residual flux is constant as long as the temperature of the specimen is constant, but the flux is not necessarily conserved when the temperature is perturbed.

INTRODUCTION

SIGNIFICANT experiments on superconductivity must now be high-precision measurement on details of the mechanism. The experiments reported here cover several years' work and thousands of data points from two independent experimental methods and are directed toward an investigation of the departures from a complete Meissner effect. In particular, does the residual flux behave as a reproducible function of the path by which the state is reached, or is it subject to random fluctuations?

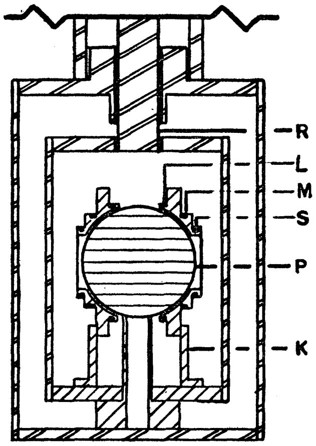

Fig. 1. Drawing of the coil and sphere arrangement. Rotating rod *R* spins the coil forms *K* about the sphere *P*.

The results suggest that the residual flux is a reproducible function in a particular sample, but that it may change when the temperature is changed, even well within the superconducting region.

EXPERIMENTAL ARRANGEMENTS

Two arrangements have been used to obtain the results to be described. The first of these was a torsion pendulum which detected the magnetic moment of a superconducting sphere by means of the torque on the sphere in a small external field. The second apparatus measured the frozen flux by means of a set of flip coils located very close to the superconducting sphere.

The torsion pendulum equipment was described in connection with studies of the gyromagnetic ratio of a superconductor done in this laboratory several years ago.[1] A plot of the reciprocal square of the period against the external field gave a curve whose slope could be used to calculate the effective dipole magnetic moment of the sphere. A small departure from a straight line was attributed to a slight ellipsoidal form of the sphere, but the slope at zero field was independent of this effect.

The torque on the sphere was also measured by observing the change in the equilibrium position as a function of the applied field. For these measurements the sphere was turned so that the axis of the magnetic moment was perpendicular to the external field.

A detail of the flip coils used in the second method is

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[1] Pry, Lathrop, and Houston, Phys. Rev. 86, 905 (1952).