

## Electrical and Optical Properties of Amorphous Germanium\*

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Measurements of density, optical absorption, resistivity, photoconductivity, and Hall effect have been made on amorphous Ge films ranging in thickness from 1 to 23  $\mu$ . The density was found to be  $3.9 \pm 0.4$  g/cm<sup>3</sup>. The absorption coefficient (measured at room temperature) was found to be exponential from 0.6 to 1.1 eV with a slope of 0.14 eV. Resistivity was determined to be 300  $\Omega$  cm at room temperature with an activation energy of 0.15 eV. The activation energy at 30°K was about 0.02 eV. The spectral response of dc photoconductivity (measured at 4.2°K) showed a maximum at 1.5 eV, which may correspond to intrinsic transitions. The Hall measurement gave a value for carrier concentration (at room temperature) of  $10^{18}$  cm<sup>-3</sup> and a Hall mobility of  $10^{-2}$  cm<sup>2</sup>/V sec. The sign of the Hall constant was negative. The optical measurements (both in this study and the work of Glass and Tauc *et al.*) suggest that much of the band structure is retained in the amorphous phase. There is an apparent contradiction, however, in that the resistivity and Hall measurements suggest transport via localized states, whereas the absorption data of Tauc *et al.* indicate bands of nonlocalized states.

### I. INTRODUCTION

THE band structure and transport properties of disordered materials have been subjects of increasing interest in recent years (for reviews and bibliographies, see Gubanov<sup>1</sup> and Cusack<sup>2</sup>). Unfortunately, much experimental work has been done on relatively complicated systems (e.g., oxides, chalcogenides) where interpretation is difficult. For this reason, a study of amorphous Ge was undertaken. The vast literature available on properties of the Ge crystalline state makes a ready source for comparison. Furthermore, there is evidence (see below) that amorphous Ge corresponds more closely to our concept of an "ideally" disordered system (i.e., composed of random atomic spacings).

This paper will consist of a brief review of some theoretical and experimental work, details of sample preparation, description of experiments, and discussion. The properties measured were density, optical absorption, resistivity, dc photoconductivity, and Hall constant.

### II. REVIEW OF SOME THEORETICAL AND EXPERIMENTAL WORK

#### Band Structure of Disordered Systems

The band structure of one-dimensional and three-dimensional disordered systems has been treated by Gubanov<sup>1</sup> (see also Moorjani and Feldman<sup>3</sup>). In one dimension, the spacing between neighboring atoms is written as

$$a(1 + \epsilon\gamma), \quad (1)$$

where  $a$  is the crystalline spacing,  $\epsilon$  a small number

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<sup>1</sup> A. Gubanov, *Quantum Electron Theory of Amorphous Conductors* (Consultants Bureau, New York, 1965).

<sup>2</sup> N. Cusack, *Rept. Progr. Phys.* **26**, 361 (1963).

<sup>3</sup> K. Moorjani and C. Feldman, *Rev. Mod. Phys.* **36**, 1042 (1964).

characterizing the degree of the disorder, and  $\gamma$  a random variable with a Gaussian distribution. The change in potential  $V(x)$  upon disordering is arbitrarily divided into two parts: (1) The maxima and minima of  $V(x)$  will shift in a random fashion; (2) random fluctuations in the magnitude of  $V(x)$  will be introduced.

The first change in  $V(x)$  is treated by transforming to a distorted coordinate system, where the chain becomes periodic. This transformation gives back the original Schrödinger equation, plus some perturbing terms. Gubanov<sup>1</sup> has solved this problem (in both one and three dimensions), and he finds that the essential features of the band structure are retained, although the forbidden gap is narrowed by the perturbing terms.

We expect the fluctuations in  $V(x)$  to be Gaussian in distribution, although not necessarily symmetrical. In fact, there should be an inherent asymmetry in the problem because there is a limit as to how close two atoms may come together, where as in principle there could be separation of many "lattice" spacings. These fluctuations in potential will give rise to localized states. In particular, states near the band edges will be perturbed into the gap and form donor and acceptor states. Because we expect an asymmetry in favor of "vacancy-like" defects, however, this should give rise to a predominance of acceptor states.<sup>4</sup> (It is not possible at present to say whether these "vacancy-like" defects will be discrete vacancies as found in crystals, or whether they will form a continuum.) Assuming no discrete vacancies, then, a simple band picture for an amorphous semiconductor would be as shown in Fig. 1.

#### Electron Transport in Disordered Systems

Before discussing possible transport mechanisms, we should check on the validity of the Boltzmann equation, because we intuitively expect that the disordered material will have a low mobility. The electron wavelength in a semiconductor at room-temperature is

<sup>4</sup> J. Corbett, General Electric Research Laboratory, Report No. 65-RL-3782(B)M, 1965 (unpublished).

about  $10^{-6}$  cm. Assuming that a wave packet should live for at least one oscillation before being scattered (if it is to have any essence as a wave), this implies a mean free path of  $10^{-6}$  cm. For a free-electron effective mass, this gives a mobility of  $100 \text{ cm}^2/\text{V sec}$ . Thus, we should be suspicious of mobilities below this value.

There may be an empirical criterion, however, more important than the validity of the Boltzmann equation. This is the existence of nonlocalized states in the band structure. The existence of such states would make it difficult to justify a complete reversion to  $X$  space, where one considers hopping of the electrons between localized states.

Assuming that transport is via nonlocalized states, the first scattering mechanism which comes to mind is phonon scattering. As pointed out by Gubanov,<sup>1</sup> the major contribution to phonon scattering in covalent semiconductors comes from the very long-wavelength acoustic phonons. Such phonons average over large numbers of atoms, and so (to first approximation) they should not be sensitive to the disorder. Thus, we would expect mobility arising from phonon scattering to be of the same order of magnitude in the amorphous phase as in the crystal.

A more important mechanism is liquid (or disorder) scattering. An approximate value of the mean free path for this process has been calculated by Moorjani and Feldman<sup>3</sup>:

$$\Lambda_{\text{liquid}} \approx a/\epsilon^2. \quad (2)$$

(A more rigorous treatment is given by Gubanov,<sup>1</sup> but his expression involves unknown matrix elements.)

### Amorphous Germanium

If Ge is vapor-deposited onto substrates whose temperature is less than  $400^\circ\text{C}$ , an amorphous film is formed. X-ray studies of amorphous Ge have been made by Richter and Fürst.<sup>5</sup> They find the same spacing for the first two or three coordination rings as in crystalline Ge. Assuming a density 20% less than the crystalline value, they find that the coordination numbers of the first and second rings, respectively, are four and twelve (the same as crystalline Ge). From their data, one can estimate that  $\epsilon \approx 0.2$ .

Transmission-electron microscopy studies have been made by Richter and Fürst,<sup>5</sup> and Balluffi and Parsons.<sup>6</sup> Their results show that if crystallites are present, they are less than  $100 \text{ \AA}$  in size (such extremely small crystallites would be indistinguishable from a purely random distribution with respect to measurements involving macroscopic averages<sup>7</sup>).

The most extensive work on electrical and optical properties of amorphous Ge has been done by Grigoro-

<sup>5</sup> H. Richter and O. Fürst, *Z. Naturforsch.* **6a**, 38 (1951).

<sup>6</sup> J. Parsons and R. Balluffi, *J. Phys. Chem. Solids* **25**, 263 (1964).

<sup>7</sup> A. Clark, thesis, Cornell University, 1966 (unpublished).

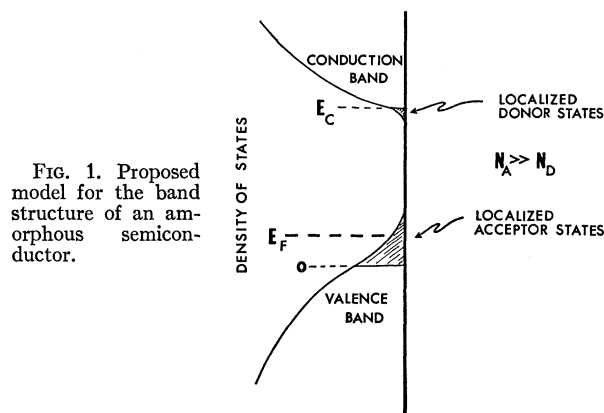


FIG. 1. Proposed model for the band structure of an amorphous semiconductor.

vici, Croitoru, Tauc, *et al.*<sup>8-10</sup> They find a resistivity of  $10^2 \Omega \text{ cm}$  at room temperature, and an intrinsic transition above room temperature with activation energy of  $0.55 \text{ eV}$ .<sup>9</sup> Junctions of amorphous Ge with crystalline Ge have been made,<sup>8,9</sup> and the amorphous phase is found to be  $p$  type. By measuring the barrier capacitance of the junction, a value of  $p = 10^{17} \text{ cm}^{-3}$  at  $300^\circ\text{K}$  and at  $100^\circ\text{K}$  was obtained.<sup>9</sup>

Optical-absorption measurements<sup>10</sup> from  $0.6$  to  $1.8 \text{ eV}$  indicate indirect transitions between parabolic bands, and reflectivity measurements<sup>10</sup> show that some structure due to the Van Hove singularities is retained. Both of these measurements would indicate that a great deal of the band structure is retained in the transition to the amorphous phase. Furthermore, parabolic bands indicate quasifree electrons whose wave functions must be nonlocalized at least to some extent.

Optical absorption has also been measured by Glass<sup>11</sup> as part of a study of the effects of grain size on absorption-edge broadening. His results will be presented with those of the author.

To the author's knowledge, all measurements on amorphous Ge have been made on films  $1 \mu$  or less in thickness (one exception is the work of Glass,<sup>11</sup> which was a  $5\text{-}\mu$  film). Naturally one would like to work with the thickest possible films in order to have confidence that one is measuring bulk properties and not those characteristic of the thin films.

### III. SAMPLE PREPARATION

The amorphous Ge films in this study were prepared from  $40\text{-}\Omega \text{ cm}$  material in a standard vacuum system using an MRC electron-beam evaporator. Complete details are given in the author's thesis.<sup>7</sup> The ambient pressure in the system was typically  $1 - 2 \times 10^{-6} \text{ mm Hg}$ .

<sup>8</sup> N. Croitoru and N. Marinescu, *Rev. Roumaine Phys.* **9**, 201 (1964).

<sup>9</sup> R. Grigorovici, A. Dévényi, and E. Teleman, in *Proceedings of the International Conference on Semiconductors, Paris, 1964* (Academic Press Inc., New York, 1964), p. 423.

<sup>10</sup> J. Tauc, A. Abraham, L. Pajasova, R. Grigorovici, and A. Vancu, in *Conference on Non-Crystalline Solids, Delft, 1964*, p. 606 (unpublished).

<sup>11</sup> A. Glass, *Can. J. Phys.* **43**, 1068 (1965).

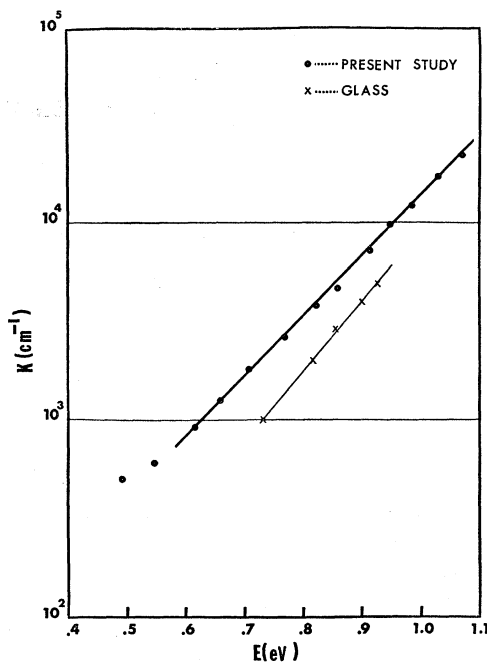


FIG. 2. Optical absorption—amorphous germanium.

The substrates were either tin-oxide coated Pyrex, plain Pyrex, or LiF. The conducting substrates were initially used in order to produce a sandwich arrangement. When it was found that the resistivity of the amorphous Ge was quite low, however, (see next section) the sandwich arrangement was abandoned, and the films were deposited on insulating substrates. Substrate dimensions were  $\frac{5}{8}$  in.  $\times$   $\frac{5}{8}$  in.  $\times$   $\frac{3}{32}$  in. The majority of the films were of circular shape,  $\frac{5}{16}$  in. in diameter. The Hall samples were of the standard geometry as shown in Fig. 5.

The Pyrex substrates were cleaned in a glass-cleaning solution, followed by distilled water. They were then placed in an ultrasonic cleaner containing absolute alcohol, and then rinsed with absolute alcohol. The LiF substrates were polished on SiC paper followed by metallurgical polishing wheels. They were then immersed in absolute alcohol followed by ether.

Water cooling was supplied to the substrate holder during evaporation. It was found, however, that films greater than about  $4 \mu$  in thickness tended to shatter with the water on. Thus, the majority of the films were produced with no substrate cooling. As a check, however, films in the  $4\text{-}\mu$  range were produced both with and without water-cooling. No differences in electrical properties were observed.

By using a relatively low evaporation rate (about  $1 \mu/\text{h}$ ), films of amorphous Ge up to  $23\text{-}\mu$  thick were produced (although the thicker films were quite prone to shatter, and could not be produced consistently). After evaporation, dry nitrogen was bled through a desiccant into the chamber (it was found that initial

exposure to the atmosphere tended to produce shattering in the thicker films).

Film thicknesses were measured using a Zeiss interference microscope. It is estimated that the error was within 5% for films greater than  $5 \mu$ , and within 10% for the thinner films.

Electron diffraction patterns and micrographs were made using a  $500\text{-}\text{\AA}$  film and a  $10\text{-}\mu$  film which had been thinned for transmission. The results agreed with those of Parsons and Balluffi<sup>6</sup> (i.e., no structure was observed, and the limit of resolution was about  $100 \text{\AA}$ ).

#### IV. EXPERIMENTS

##### Density Determination

The determination of coordination number by Richter and Fürst<sup>5</sup> was admittedly circular in that they assumed a density 20% less than the crystalline value. In order to check this, a density measurement was made on scraps of film which had shattered from the substrates. A Mettler microbalance was employed, and the films were weighed in air and in Dow-Corning No. 704 silicone oil (this liquid has an extremely low vapor pressure). The reproducibility of the measurement was about 10%, and the density determined was  $3.9 \pm 0.4 \text{ g/cm}^3$ . This is a 28% decrease from the crystalline value of  $5.35 \text{ g/cm}^3$ .<sup>5</sup> Note that the decrease in density supports the argument concerning predominance of vacancy-like disorder.

##### Optical Absorption

Optical absorption was measured at room temperature from 0.5 to 1.1 eV using a Perkin-Elmer Model 99 monochromator. Transmission curves were measured for 8 different samples, ranging in thickness from 2 to  $23 \mu$ . The absorption coefficient was calculated using pairs of films of different thickness, thus eliminating the effects of substrate and interfaces. The thicker films were opaque at the shorter wavelengths, whereas the thinner films were transparent at longer wavelengths. Nevertheless, there were regions of overlap between different pairs, and a composite curve was made with an accuracy of about 10%. This is shown in Fig. 2, along with the results of Glass.<sup>11</sup> Part of the discrepancy between the curves may be due to the fact that Glass normalized his curve at long wavelengths and neglected spectral variation of absorption in the substrate and reflection at the two interfaces.

The absorption coefficient measured in this study is exponential (within experimental error) with a slope of 0.14 eV. This does not agree with the shape found by Tauc *et al.*,<sup>10</sup> although a calculation of absorption coefficient at 1.0 eV from their curve agrees with the value reported here to within 15%. It is not clear, however, what accuracy should be attributed to their data below 1.0 eV.

### Resistivity

Resistivity was measured on films 1 to 6  $\mu$  in thickness from 325 to 25°K. One of two electrode materials was deposited onto the samples—gold or gold plus 0.5% gallium (this latter material was chosen because it is recommended for making ohmic contact to *p*-type Ge<sup>12</sup>). Currents were measured using a Keithley 610B electrometer. They were observed to be ohmic with both types of electrodes up to fields of 4000 V/cm (the highest measured). Although a majority of the measurements were made using a simple two-electrode arrangement, resistivity was also checked on the 6-probe Hall samples down to 200°K. The results were the same.

Results of the resistivity measurement are shown in Fig. 3. All samples gave a curve of the same shape versus  $1/T$ , although a fluctuation of about 50% in magnitude was observed for different samples. There did not appear to be any systematic variation with film thickness, type of substrate, or the presence or absence of water-cooling during preparation. One could attribute at most 20% error to measuring physical dimensions of the film, and the electrical measurements were made to within 2%. The curve in Fig. 3 has an activation energy of about 0.15 eV at room temperature and 0.02 eV at 30°K.

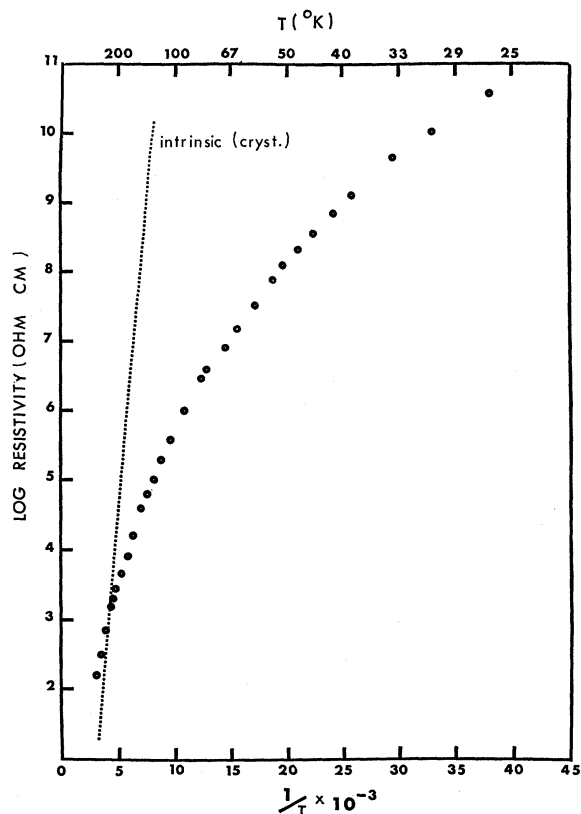


Fig. 3. Resistivity—amorphous germanium.

<sup>12</sup> E. Putley, *The Hall Effect and Related Phenomena* (Butterworths Ltd., London, 1960).

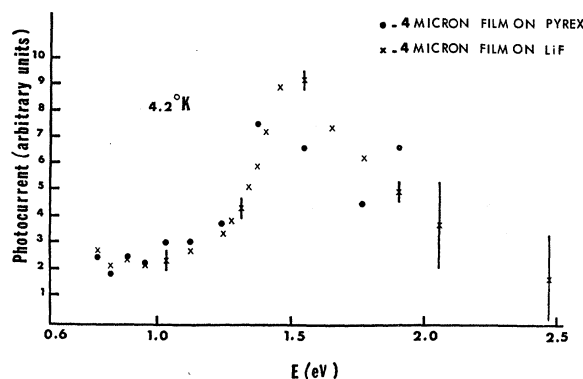


Fig. 4. Photoconductivity—amorphous germanium. Corrected for relative intensity, reflectivity, and absorption.

### Thermally Stimulated Currents

One might anticipate that a disordered material would contain traps, perhaps in addition to those localized states which give rise to impurity conduction. A reasonable amount of time was spent searching for thermally stimulated currents arising from such traps, cooling samples to 77°K, irradiating with various types of light and then warming. No stimulated currents were observed. In retrospect this is not too surprising, since it is now felt that the carrier concentration in amorphous Ge is the order of  $10^{17}$ – $10^{18}$   $\text{cm}^{-3}$  (see the work of Grigorovici<sup>8</sup> and the results of the Hall measurement). The presence of traps in concentrations much lower than this would not be detected.

### Photoconductivity

Photoconductivity in amorphous Ge was observed to be extremely low. Using the collected light from a 300-W incandescent source, no change in dc conductivity as measured with the Keithley 610B could be observed at room temperature. At 77°K, the change was about 1% (although some of this change is thought to be due to heating of the sample). Finally, at 4.2°K where the dark current was essentially zero, photocurrents the order of  $10^{-13}$ – $10^{-12}$  A were observed with fields up to 4000 V/cm. The photocurrents were ohmic up to this value of field (the highest employed).

The spectral response of the photoconductivity was measured using a Bausch & Lomb IR-I monochromator. Measurements were made with a 4- $\mu$  film on pyrex and then repeated for a 4- $\mu$  film on LiF. The relative spectral output of the light source, monochromator, and associated optics was measured using the Perkin-Elmer model 99 monochromator, in which the spectral response of the PbS detector cell was obtained from a curve supplied by the manufacturer. Results are shown in Fig. 4. Reflectivity corrections were made using the data of Tauc *et al.*,<sup>10</sup> while the absorption correction used data from the present work (Fig. 2).

TABLE I. Results of Hall-effect measurement.

Sample	$T$ ( $^{\circ}\text{K}$ )	Constant	$R$ ( $\text{cm}^2/\text{C}$ )	$n$ ( $\text{cm}^{-3}$ )	$\mu_H$ ( $\text{cm}^2/\text{V sec}$ )
No. 80 ( $4.3 \mu$ )	300	5 kG	$-4.13 \pm 4.55$	$(1.5 \pm 1.7) \times 10^{18}$	$(1.4 \pm 1.5) \times 10^{-2}$
No. 83 ( $5.75 \mu$ )	300	5 kG	$-7.93 \pm 2.14$	$(7.9 \pm 2.1) \times 10^{17}$	$(2.6 \pm 0.7) \times 10^{-2}$
No. 83	300	$20 \mu\text{A}$	$-7.35 \pm 3.16$	$(8.5 \pm 3.7) \times 10^{17}$	$(2.5 \pm 1.1) \times 10^{-2}$
No. 83	233	5 kG	$-16.2 \pm 28.8$	$(3.9 \pm 6.9) \times 10^{17}$	$(1.0 \pm 1.8) \times 10^{-2}$
No. 85 ( $2.2 \mu$ )	300	5 kG	$-5.77 \pm 3.06$	$(1.1 \pm 0.6) \times 10^{18}$	$(1.9 \pm 1.0) \times 10^{-2}$
No. 85	300	$5 \mu\text{A}$	$-4.83 \pm 6.0$	$(1.3 \pm 1.6) \times 10^{18}$	$(1.6 \pm 2.0) \times 10^{-2}$

### Hall Effect

In an attempt to determine carrier concentration and mobility in amorphous Ge, a dc Hall measurement was made. The circuit used for the measurement is shown in Fig. 5. The input impedance of the Keithley 610B is  $10^{14} \Omega$ . This was deemed sufficiently high as the resistance across the Hall probes was never greater than  $10^8 \Omega$ . The IR drop across the Hall probes was balanced out, using the zero adjustments on the electrometer.

The Hall voltages generated were very small (a few microvolts) compared to the total voltage generated by the magnetic field (the order of  $100 \mu\text{V}$ ). By repeating the measurement about 10 times, however, and then by taking appropriate sign combinations of the current and magnetic field, the unwanted effects were eliminated and a Hall voltage could be measured to within an accuracy of about 100%. Values of Hall voltage were measured as a function of current and field, and a least-squares fit was made to the data in order to obtain the Hall constant.

Because it was necessary to remain at a constant temperature for a day or two in order to get reasonable statistics, most of the measurements were made at room-temperature. Some data were taken at liquid Freon 22 ( $-40^{\circ}\text{C}$ ) and Freon 13 ( $-80^{\circ}\text{C}$ ), but the total voltage generated by the magnetic field was greater than at room temperature ( $300\text{--}700 \mu\text{V}$ ), and this made the averaging used to obtain the Hall voltage even more uncertain.

Table I shows the results of the Hall measurement. The carrier concentration was calculated using the simple, one-carrier relationship:

$$R = 1/ne. \quad (3)$$

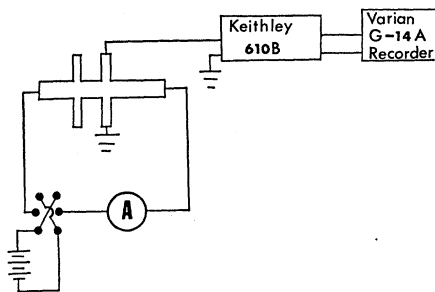


Fig. 5. Circuit used for Hall measurement.

(The simplest expression is used here, as we only expect an order-of-magnitude understanding at this stage.) The errors shown are 90% confidence limits.

## V. DISCUSSION

### Optical Absorption

A simple interpretation of an exponential absorption edge in an amorphous material is given by Lanyon.<sup>13</sup> We assume an exponential tail on the valence band:

$$n = N e^{-E/\Delta}. \quad (4)$$

If the shape of the conduction-band density of states is neglected, the absorption coefficient will be proportional to the integrated density of states in the tail (assuming constant transition probabilities):

$$K(\hbar\omega) \sim \int_{E_c - \hbar\omega}^{E_F} N e^{-E/\Delta} dE \sim e^{\hbar\omega/\Delta}. \quad (5)$$

Thus, we would conclude that the slope of 0.14 eV measured by absorption corresponds to the slope of the tail. The problem is considerably more complicated, however. First, the Fermi function should be folded into the integrand. This will contribute to the edge broadening, although it will not be a simple " $kT$ " broadening because of degeneracy. Secondly, if we assume a parabolic conduction band, the shape of this band does make a contribution to the energy dependence, and the absorption coefficient is no longer exponential.<sup>7</sup>

### Resistivity

Assuming the validity of the band picture for amorphous Ge, one can attempt to estimate the scattering mechanism. The mobility of pure crystalline Ge at room temperature is greater than  $1000 \text{ cm}^2/\text{V-sec}$ . This mobility is determined by phonon scattering, and if the argument in Sec. II is valid, phonon scattering in the amorphous material should be the same. We can estimate the mean free path for liquid scattering using Eq. (2) and the results of Richter and Fürst.<sup>5</sup> From their data, we estimate a nearest-neighbor distance of  $2.5 \text{ \AA}$ , and

<sup>13</sup> H. Lanyon, Phys. Rev. **130**, 134 (1963).

$\epsilon=0.2$ . From this we calculate

$$\Lambda_{\text{liquid}} \approx 60 \text{ \AA}, \quad (6)$$

which gives

$$\begin{aligned} \mu &\approx 60 \text{ cm}^2/\text{V sec}; & m^* &= m \\ \mu &\approx 200 \text{ cm}^2/\text{V sec}; & m^* &= 0.1m. \end{aligned} \quad (7)$$

So to order of magnitude, we expect a mobility of 100  $\text{cm}^2/\text{V-sec}$  arising from liquid scattering, and 1000  $\text{cm}^2/\text{V-sec}$  from phonon scattering. Thus, we would expect the liquid scattering to dominate at room temperature and below.

If the mobility is constant, then a change in carrier concentration must account for the resistivity change from room temperature to 25°K (a change of about 9 orders of magnitude). In order to obtain an idea of the validity of such thinking, a calculation was made of the hole concentration arising from the distribution of localized states shown in Fig. 1. Computer calculations were made for total "impurity" concentrations of  $10^{18}$  and  $10^{19} \text{ cm}^{-3}$ . Details and results are presented in the Appendix. The important result, however, is that the hole concentration changed by less than one order of magnitude in both cases as temperature changed from 300°K to about 50°K.

Clearly such a model cannot hope to explain the resistivity curve shown. This situation will be discussed in more detail in connection with the Hall data.

#### Photoconductivity

As is seen in Fig. 4, the spectral response of the photoconductivity contains relatively little structure (note that the scale is linear). There clearly is a peak at about 1.5 eV. This may correspond to intrinsic transitions which were reported by Grigorovici *et al.*<sup>8</sup> They found an activation energy for (dark) conduction of 0.55 eV at high temperatures. This implies an intrinsic gap of 1.1 eV.

The other noteworthy feature of Fig. 4 is the absence of the exponential edge below 1.0 eV, which was observed in the optical absorption. As has been mentioned, one expects a large number of localized states near the band edges, with an asymmetry in favor of acceptor states. If the absorption is due to transitions between localized states, one would not expect this process to give rise to photoconductivity. If the transition is from the tail of the valence band to nonlocalized states in the conduction band, then one might expect photoconductivity. There is always the question of lifetime, however. The recombination time for the above-mentioned process might be considerably less than that for intrinsic processes.

#### Hall Effect

First we note that the sign of the Hall constant indicates electrons [assuming the simple interpretation

of Eq. (3)], while the results of Grigorovici *et al.*<sup>9</sup> with *p-n* junctions indicate that amorphous Ge is *p* type. This is not the first instance where the sign of the Hall constant is in disagreement with other measurements on amorphous semiconductors.<sup>14</sup> The value of the carrier concentration (the order of  $10^{18} \text{ cm}^{-3}$ ) is in reasonable agreement with results of barrier capacitance measurements on *p-n* junctions<sup>9</sup> ( $10^{17} \text{ cm}^{-3}$ ). Unfortunately the temperature dependence of this parameter could not be measured with the present technique. The value of Hall mobility ( $10^{-2} \text{ cm}^2/\text{V-sec}$ ) is considerably lower than that expected for disorder scattering, and furthermore is of such low value that one must seriously question the validity of the Boltzmann equation (this corresponds to a mean free path of 0.01 Å).

There is always the possibility that the Hall constant results from a two-carrier effect, with a high-electron mobility accounting for the negative sign. An order-of-magnitude estimate, however, shows that the electron mobility would have to be 4 orders of magnitude greater than the hole mobility.<sup>7</sup> This is not impossible, but seems unlikely. One should also estimate the size of the Ettingshausen voltage in the present case, as it might be comparable to the Hall voltage. This was done using the standard formulas,<sup>12</sup> and it is estimated to be of the order of  $10^{-13} \text{ V}$ .

This being the situation, we are led to consider the possibility that transport is via hopping amongst localized states. This would explain the high-carrier concentration and low mobility, again assuming that the simple interpretation of the Hall effect is valid. The theory of the Hall effect in impurity conduction is not completely developed,<sup>15,16</sup> and the situation may actually be quite complicated.<sup>17</sup>

If it seems reasonable from the results of the Hall data and resistivity to assume transport via localized states, we have the problem of deciding where these localized states will fit into the band picture. The calculation in the Appendix shows that the exponential tail is very closely coupled to the valence band (i.e., almost all the states are ionized, producing a large number of holes). If the optical data (Ref. 9) are being interpreted correctly, these hole states in the valence band are nonlocalized, and should have a mobility corresponding to disorder scattering (i.e., the order of  $100 \text{ cm}^2/\text{V-sec}$ ). Thus, these states should contribute most to conduction.

<sup>14</sup> B. Kolomiets and T. Nazarova, *Fiz. Tver. Tela* **2**, 395 (1960) [English transl: *Soviet Phys.—Solid State* **2**, 369 (1960)].

<sup>15</sup> T. Holstein, *Phys. Rev.* **124**, 1329 (1961).

<sup>16</sup> L. Bányai and A. Aldea, *Phys. Rev.* **143**, 652 (1966).

<sup>17</sup> It is interesting to note that a simple argument put forth by Mott and Twose [N. Mott and W. Twose, *Advan. Phys.* **10**, 107 (1961)] would predict a negative Hall constant for impurity conduction. The basic point is that the unoccupied localized state differs from a hole in that it always moves in a direction opposite to the electron, even in a magnetic field.

There is the possibility of localized states lying deep within the forbidden region (perhaps discrete vacancy states), which are not strongly coupled to the non-localized bands. The difficulty with this hypothesis is that one would expect to see more structure in the absorption curve (Fig. 2) from such states.

## VI. CONCLUSION

The goal of this study was to construct a model (consistent with all the experimental results) describing band structure and transport properties of amorphous Ge. As is clear from the discussion, this goal was not achieved. The following conclusions are drawn:

(1) Amorphous Ge is a well-defined phase. The structural and electronic properties determined in this study are in essential agreement with other work (see Sec. II). This implies that history of preparation does not have a serious effect on the properties of the material.

(2) The density measurement confirms the predominance of vacancies or of vacancy-like defects, although it is not possible at present to distinguish between the two.

(3) The existence of a band structure in a disordered material (confirmed both theoretically and experimentally) is apparently not sufficient to insure that transport will be governed by the nonlocalized states in the bands. This conclusion is reached because of an inability to reconcile the results of optical measurements with those of conductivity and Hall effect.

*Note added in proof.* A more recent paper by Tauc *et al.* [Phys. Status Solidi 15, 627 (1966)] describes an absorption band below the main absorption edge. These states are interpreted to be excitons associated with vacancies, and thus they could be the localized states which determine the transport properties.

## ACKNOWLEDGMENTS

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## APPENDIX: CALCULATION OF THE HOLE CONCENTRATION ARISING FROM AN EXPONENTIAL DISTRIBUTION OF ACCEPTOR STATES

Let the distribution of acceptor states be written as

$$N_A = N e^{-E/0.14}, \quad (\text{A1})$$

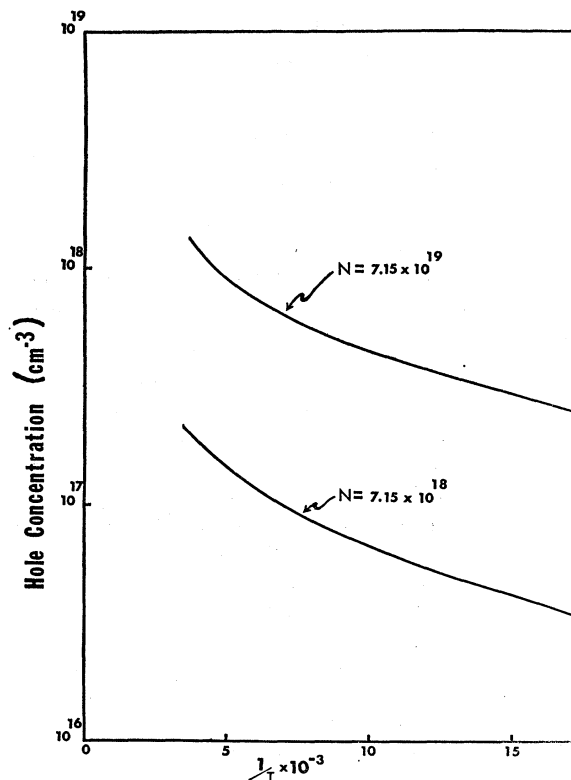


FIG. 6. Theoretical hole concentration for exponential distribution of acceptor states  $N_A = N_{\text{exp}} e^{-E/0.14}$  ( $m_h^* = 0.1m$ ).

where the value 0.14 eV is taken from the optical absorption measurement (see Fig. 2). The density of states in the valence band is

$$g_h(E) + N. \quad (\text{A2})$$

The  $N$  is necessary for continuity (see Fig. 1), and

$$g_h(E) = \frac{1}{2\pi^2} \left( \frac{2m_h}{\hbar^2} \right)^{3/2} (-E)^{1/2}. \quad (\text{A3})$$

The condition which determines the carrier concentration is charge neutrality<sup>18</sup>:

$$p + N_d^+ = n + N_a^-, \quad (\text{A4})$$

where  $p$  is the hole concentration in the valence band,  $n$  the electron concentration in the conduction band,  $N_d^+$  the concentration of ionized donors, and  $N_a^-$  the concentration of ionized acceptors. We assume no donor states, and furthermore that  $n$  will be reduced below the intrinsic value by compensation. Our charge neutrality condition becomes:

$$p = \int_{-\infty}^0 \frac{[g_h(E) + N] dE}{1 + e^{(E_F - E)/kT}} = N_a^- = \int_0^{\infty} \frac{N e^{-E/0.14} dE}{1 + e^{(E - E_F)/kT}}. \quad (\text{A5})$$

<sup>18</sup> C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956), 2nd ed.

We may solve this problem numerically (assuming a value for  $N$  and  $m_h$ ) by finding the value of  $E_F$  which makes the integrals equal. This was done by computer, assuming  $m_h=0.1m$  (the crystalline value) and choosing two values of  $N$  corresponding to a total "impurity" concentration of  $10^{18}$  and  $10^{19}$   $\text{cm}^{-3}$ . This is determined

simply by

$$\text{total impurity concentration} = \int_0^{\infty} N e^{-E/0.14} dE. \quad (\text{A6})$$

Five values of temperature were used, ranging from 290 to 58°K. The results are shown in Fig. 6.

## ***p*-Type Photoelectric Behavior in CdS Dominated by a High-Resistivity Region near the Anode\***

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It is observed, using the Franz-Keldysh effect, that certain very pure CdS crystals show a high-field layer close to, but well separated from, a hole-injecting anode (Au). Inversion of an infrared quenching spectrum into a similar infrared excitation spectrum is observed at an applied voltage where this high-field layer becomes "visible." The data are tentatively interpreted in terms of a model with a current-controlling *p*-type region adjacent to the anode and produced by hole injection, followed by a *p-n* junction identified with the observed high-field region, followed by the normal *n*-type region occupying most of the bulk.

### I. INTRODUCTION

CADMIUM sulfide at room temperature has always been observed to be *n* type,<sup>1-6</sup> and it is not yet possible to dope CdS in such a way that it becomes *p* type. However, there are some indications that the ratio of hole to electron concentration in CdS can be increased by injection of holes from the anode. The observation of green electroluminescence has been attributed to such an injection mechanism.<sup>7-10</sup> If this injection is strong enough, one may obtain regions of the crystal with predominant hole concentration close to the anode. The material here can become *p* type. In this region, the electron density is strongly reduced because of an enhanced recombination. In a transition region between *n*-type and *p*-type material, the lowest carrier concentration will be observed. This region will

act essentially as a *p-n* junction caused by a minority-carrier injection and will present a layer of highest resistivity, and thereby highest field strength, in the crystal. Under certain conditions, this junction may control the current through the crystal.

There exist some theoretical investigations into similar double-injection phenomena which show that characteristic deviations of the current-voltage characteristic occur when the injection becomes marked.<sup>11,12</sup>

However, up to now, there was no direct experimental evidence for such a single-injection-produced *p-n* junction. Therefore, the Franz-Keldysh effect<sup>13,14</sup> has been used to look for these high-field layers associated with the *p-n* junction. After observing such layers in certain crystals, the influence of visible and infrared illumination and applied voltage was studied. The results of this work are reported in this paper.

### II. EXPERIMENTAL METHOD

Thin CdS single-crystal platelets, grown by sublimation in an  $\text{N}_2\text{-H}_2\text{S}$  atmosphere at about 1100°C, were prepared with evaporated Au electrodes, covered with an evaporated film of Cr (for mechanical protection). The electrodes were deposited at a pressure of  $10^{-6}$  Torr onto opposite sides of the crystal with a spacing of about 1.5 mm. Any heat treatment which

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<sup>1</sup> *p*-type conductivity in heavily Cu-treated CdS reported earlier (Refs. 2, 3) has recently been shown (Refs 4-6) to be due to precipitation of copper compounds and cannot be attributed to CdS.

<sup>2</sup> J. Woods and J. A. Champion, *J. Electron. Control* **7**, 243 (1959).

<sup>3</sup> D. C. Reynolds, L. C. Green, R. G. Wheeler, and R. S. Hogan, *Bull. Am. Phys. Soc.* **3**, 111 (1956).

<sup>4</sup> A. Dreeben, *J. Electrochem. Soc.* **111**, 174 (1964).

<sup>5</sup> N. I. Vitrikhovskii and M. V. Kurik, *Fiz. Tver. Tela* **7**, 3676 (1965) [English transl.: *Soviet Phys.—Solid State* **7**, 2969 (1966)].

<sup>6</sup> H. Sturmer and C. E. Bleil, *Appl. Opt.* **3**, 1015 (1964).

<sup>7</sup> R. Smith, *Phys. Rev.* **105**, 900 (1957).

<sup>8</sup> K. W. Böer, H. J. Hänsch, and H. Obernik, *Phys. Status Solidi* **1**, 352 (1961).

<sup>9</sup> H. Yamashita, S. Ibuki, M. Yoshizawa, and H. Komiya, *J. Phys. Soc. Japan* **15**, 2366 (1960).

<sup>10</sup> G. Diemer, *Phillips Res. Rept.* **9**, 109 (1954).

<sup>11</sup> M. A. Lampert, *Phys. Rev.* **125**, 126 (1962).

<sup>12</sup> C. W. Litton and D. C. Reynolds, *Phys. Rev.* **133**, A536 (1964).

<sup>13</sup> W. Franz, *Z. Naturforsch.* **13a**, 484 (1958).

<sup>14</sup> I. V. Keldysh, *Zh. Eksperim. i Teor. Fiz.* **34**, 1138 (1958) [English transl.: *Soviet Phys.—JETP* **6**, 788 (1958)].