

Absorption of Infrared Light by Free Carriers in Germanium

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The absorption of infrared light associated with the presence of free carriers in germanium has been measured by injecting these carriers across a $p-n$ junction at room temperature. The absorption is found to be proportional to the concentration of carriers. The absorption as a function of wavelength shows the same rather sharp maxima previously observed in normal p -type germanium. These bands are found to change with temperature. An explanation of this absorption is offered in terms of a degenerate energy band scheme.

THE presence of donor or acceptor impurities in germanium has been found to cause additional absorption of infrared light of wavelengths greater than the fundamental absorption limit of two microns.¹⁻³ Some such absorption would be expected according to the classical Drude-Zener⁴ theory of the optical properties of the free carriers, which in this case are the holes and electrons released by the ionized impurities. However, the observed absorption is two to three orders of magnitude higher than the Drude-Zener theory would predict.¹⁻³ In addition for p -type germanium, the absorption has structure³ instead of increasing uniformly with the square of the wavelength as the Drude-Zener theory predicts for this wavelength range. These observations have led us to perform two additional types of experiments. First, in order to show that the additional absorption, particularly in p -type germanium, is really caused by the free carriers, we have measured the excess absorption caused by free carriers which have been *injected* into the germanium. Second, the absorption by p -type germanium in thermal equilibrium has been measured as a function of temperature.

EXPERIMENTAL METHOD

The first experiment depends upon the injection of free carriers across a $p-n$ junction when the junction is biased in the forward, or low resistance, direction.⁵ If the light, whose absorption is to be measured is allowed to pass through the sample in a narrow beam parallel and near to the junction, the injected carriers will cause an increase in absorption which can be measured.⁶

A single crystal of germanium containing a junction between 2.0 ohm-cm, p -type (gallium doped) and 5.5 ohm-cm, n -type (arsenic doped) was finished in a rectangular block 1.5×1.0×0.4 cm, the plane of the junction being perpendicular to the long dimension.

¹ H. Y. Fan and M. Becker, *Proceedings of Reading Conference* (Butterworths Scientific Publications, London, 1951), pp. 132-147.

² H. B. Briggs, *Phys. Rev.* **77**, 727 (1950); M. Becker and H. Y. Fan, *Phys. Rev.* **76**, 1531 (1949).

³ H. B. Briggs and R. C. Fletcher, *Phys. Rev.* **87**, 1130 (1952).

⁴ E.g., see F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 639.

⁵ W. Shockley, *Bell System Tech. J.* **28**, 435-489 (1949).

⁶ This type of absorption was first suggested to one of us by R. L. Wallace, August 30, 1949. Similar suggestions have been published: K. Lehovc, *Proc. Inst. Radio Engrs.* **40**, 1407 (1952).

The sides exposed to the light were finished plane parallel and polished.

The germanium block fitted in a groove in a Bakelite mount (Fig. 1). The attachments S_1S_2 are opaque shields with 0.5-mm apertures which limited the light beam to a narrow region in the germanium. The germanium block could be moved with respect to the apertures with a calibrated screw. P_1 and P_2 are voltage probes positioned 0.75 mm apart at each edge of the aperture in S_1 and making contact with the germanium, and I_1I_2 are current leads making pressure contacts with the gold-plated ends of the germanium block. Sample and mount were supported in front of the entrance slit of a Perkin-Elmer spectrometer, the plane of the junction being parallel to the slit.

The increased absorption caused by the injected carriers was determined by modulating the voltage applied across the junction with a 10 cps rectangular wave obtained from a motor driven commutator and detecting the rectangular wave of transmitted light with either a lead sulfide photocell or a thermocouple followed by an amplifier and rectifier. This signal was compared with the signal obtained by eliminating the modulation voltage across the junction and inserting a light chopper, driven by the same motor as the commutator at the same frequency, and using the same

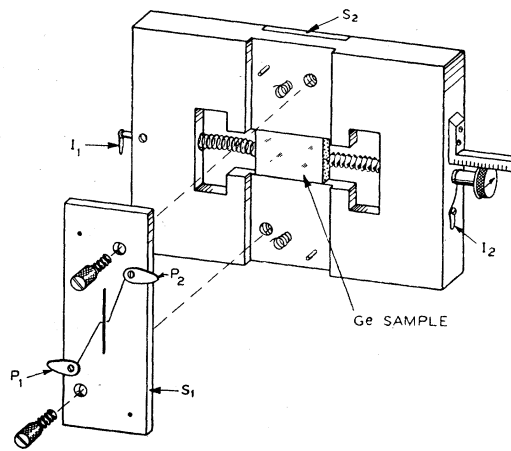


FIG. 1. Experimental arrangement for measuring infrared light absorption by injected carriers; I_1I_2 are the current leads to the $p-n$ junction, P_1P_2 are the voltage probes, and S_1S_2 is the light shield in which the illuminating slit is cut.

detection scheme. If the ratio of the first signal (voltage modulation) to the second signal (light modulation) is called r , the absorption coefficient attributable to the injected carriers, α_i , is given by

$$\alpha_i = -\frac{1}{d} \ln\left(\frac{1}{1-r}\right),$$

where d is the thickness of the sample traversed by the light. This formula neglects changes in multiple reflections caused by α_i , an approximation which introduces an error of less than 4 percent in the experiments to be described. This method of measuring α_i is not subject to errors in determining the reflection coefficient or to the errors introduced by changed light paths which are normally encountered in measuring absorption coefficients.

The concentration of added carriers attributable to hole or electron injection was determined from measurements of voltage across the probes P_1P_2 and current

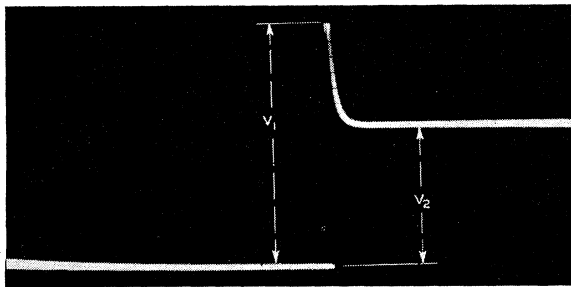


FIG. 2. A photograph of the oscilloscope trace of the voltage across the probes P_1P_2 as a function of time after the forward voltage is applied across the $p-n$ junction. The initial deflection V_1 is associated with the conductivity of normal germanium before the injected carriers arrive. The steady-state value of V_2 is associated with the increased conductivity of the injected carriers added to the normal conductivity.

through the sample. The voltage across P_1P_2 was displayed on an oscilloscope screen through a balanced input amplifier. A photograph of a typical oscilloscope pattern is shown in Fig. 2. The initial rise V_1 , arises from the conductivity of normal germanium before the injected carriers arrive at the probes. The sharp drop to an intermediate position is caused by the arrival of the injected carriers, so that V_2 arises from the combination of the conductivity of the normal germanium plus that associated with the injected carriers. For every injected carrier added, there must also be an extra carrier added of the type normally present in order to preserve neutrality. Thus, for an n -type sample, if σ_n and σ_i represent the normal and increased conductivities, respectively, and n and p_i equal the concentrations of the normal and injected carriers, respectively,

$$\begin{aligned} \sigma_n &= ne\mu_n, \\ \sigma_i &= ne\mu_n + p_i e(\mu_n + \mu_p), \end{aligned}$$

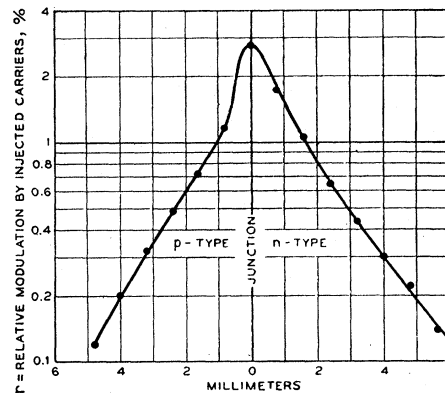


FIG. 3. Modulation of infrared light by carrier injection versus distance from the $p-n$ junction: $\lambda = 2.4\mu$, injection current = 100 ma.

so that

$$p_i = \frac{\sigma_i - \sigma_n}{e(\mu_p + \mu_n)}.$$

Here μ_n and μ_p are the mobilities of electrons and holes, respectively, and e is the electronic charge. Heating effects in the germanium sample containing the $p-n$ junction restricted the injection currents to values not greater than 1 ampere per cm^2 for which value the maximum calculated carrier density was 2×10^{15} per cm^3 .

Measurements have also been made on p -type and n -type samples in thermal equilibrium (hereinafter called normal to distinguish them from the injection experiments). Extinction coefficients for these samples were obtained by the conventional means of measuring the ratio of incident to transmitted light, and using a value for the reflectivity obtained from a separate experiment. The carrier densities were calculated from resistivity measurements using the drift mobilities measured at room temperature for lattice scattering⁷ and corrected for impurity scattering according to the Conwell-Weisskopf⁸ formula. This method was checked by using two p -type samples in which J. D. Struthers of these Laboratories had measured the impurity concentration by using radioactive gallium for the impurity. The temperature dependence of the absorption of the several p -type samples was measured by putting the sample in contact with a copper block, which was cooled by an appropriate refrigerant. Higher temperatures were obtained by passing heavy currents through the samples. Temperatures were measured with an iron-constantan thermocouple attached to the pressure contacts to the samples.

RESULTS

The relative modulation of light by injected carriers, $r = \alpha_i d$, is shown in Fig. 3 as a function of distance from

⁷ J. R. Haynes and W. Shockley, Phys. Rev. **81**, 835-843 (1951).
⁸ E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1330 (1952).

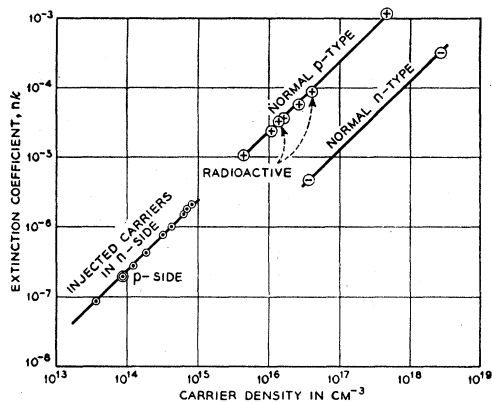


FIG. 4. The extinction coefficient due to injected carriers plotted vs carrier density at a wavelength of 2.5μ . To compare with this the extinction coefficient of several normal germanium samples are plotted vs their carrier densities. The heavy straight lines are drawn at 45° on the log-log plot indicating a direct proportionality. The carrier densities of the two samples indicated by arrows were determined by radioactive methods.

the p - n junction. To obtain these points the crystal was moved with respect to the illuminating slit. The resulting straight lines on this semilog plot indicate approximately an exponential dependence of α_i on distance. Because of the high current densities used in these experiments, the current is mainly carried by field drift rather than diffusion. Thus, the slopes of the two exponentials determine the distance the minority carriers drift in a lifetime. This distance is approximately 0.19 cm on both sides of the junction for the

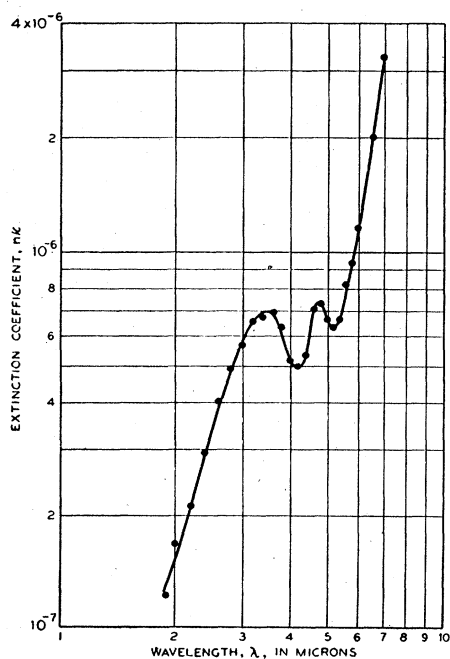


FIG. 5. The extinction coefficient for injected carriers plotted vs wavelength of the incident light (total carrier density $= 3 \times 10^{14}$ cm^{-3}). The absorption maxima at 3.4μ and 4.7μ previously observed in normal p -type germanium (see reference 3) are clearly evident here also.

current used in Fig. 3. In the experimental results to follow, the slit was maintained from 1.5 to 4 mm from the junctions.

The dependence of the absorption on carrier density as obtained by injection methods is compared with that obtained by conventional methods in Fig. 4. The circled points are values of the extinction coefficient ($\lambda\alpha_i/4\pi$) measured for injected carriers as a function of the added carrier density (p_i). Light of 2.5μ wavelength was used, with the light slit located on the n side of the junction. Essentially the same results were obtained by injection into the p side of the junction, as is indicated by the doubled-circle point. The circled crosses represent the values of the extinction coefficient at the same wavelength for normal p -type germanium (Ga-doped) as a function of hole density. Likewise the circled bars indicate the extinction coefficients for some n -type germanium (As-doped). The straight lines on this log-log plot are drawn at a 45° angle indicating that the extinction coefficient is proportional to the carrier concentration. This same proportionality was found using wavelengths of 3.4μ , 4.2μ , and 4.8μ . This proportionality can be expressed as a cross section by dividing the absorption coefficient by the carrier concentration. For the injected carriers at 2.5μ as determined from Fig. 4 is thus $1.2A^2$. For the p -type samples the cross section is $1.2A^2$ and for n -type samples it is $0.07A^2$. It can be observed that the cross section for injected carriers is very nearly the sum of the cross sections of the n - and p -type samples, as it should be if the absorption in both instances is by the free carriers.

Figure 5 shows the extinction coefficient as a function of wavelength for injection into the n -type side of the junction for a total injection carrier density (holes plus electrons) of 3×10^{14} cm^{-3} . The absorption maxima at 3.4μ and 4.7μ previously reported for normal p -type germanium³ are clearly present also in the absorption by injected carriers into n -type germanium.

Finally the absorption by normal p -type germanium for several different temperatures is plotted in Fig. 6.⁹ This absorption is plotted as a cross section, by subtracting from the observed absorption the absorption in a pure sample, which is presumably caused by lattice interactions, and dividing by the carrier density. Also, for convenience of theoretical interpretation the wavelength has been converted to photon energy. It is observed that the cross section of the 0.39 eV ($\lambda=3.2\mu$) absorption maximum increases, sharpens, and moves to lower energies as the temperature is decreased. The absorption of the 0.26 eV ($\lambda=4.7\mu$) maximum decreases until it practically disappears at low temperatures. The broad maximum at low photon energies (0.06 eV or 20μ) increases and sharpens as the temperature is lowered.

⁹ Reports of similar work have been made by Kaiser, Collins, and Fan, Bull. Am. Phys. Soc. 28, No. 2, 32 (1953).

DISCUSSION

The simplest way to explain the direct proportionality between the absorption and the concentration of the carriers is to assume that the extra absorption observed in the infrared is caused by the free carriers, whether they be introduced by ionization of chemical impurities or whether they are injected across junctions.

We have considered two other possibilities to explain the observed proportionality. First, the absorption might be associated with the normal ionized acceptor and donor impurities. This absorption would be proportional to the number of such impurities present and would thus explain the observed proportionalities in normal samples. However, the fact that injected carriers have the same absorption eliminates this as a possibility. In addition, experiments have been carried out with compensated samples in which the carrier density was not proportional to the impurities.³ In these the absorption was found to be proportional to the carrier concentration and not to the impurity concentration.

A second possibility is that the absorption is associated with impurities other than the impurities governing the electrical resistivity or with crystal imperfections. These are assumed to introduce an energy level into the forbidden band from which either electrons or holes can be excited by absorbing light. This possibility is suggested particularly by the absorption bands observed in *p*-type germanium. In order that this absorption be proportional to the carrier concentration we must assume that the carriers change the population of these levels. For instance, consider the absorption caused by ionizing a hole trapped on an impurity level (Fig. 7). In this case the absorption will be proportional to the number of empty impurity levels. If the Fermi level is above the impurity level, as shown in Fig. 7, the relative population of levels in the impurity level and in the valence band will be governed by a Boltzmann distribution. That is, the number of empty impurity levels in thermal equilibrium will be proportional to the number of free holes. This would thus explain the observed proportionality between absorption constant and free holes.

When carriers are introduced by injection, however, the holes are not in thermal equilibrium, and we would expect that the ratio of empty impurity levels to free holes would be considerably different. The fact that the cross section for injected carriers is the same as that for carriers in thermal equilibrium strongly suggests that the absorption is not caused by impurities or imperfections.

Moreover it should be pointed out that in order for the cross section to remain constant from sample to sample, the concentration of impurity levels must remain constant. Every sample tried had essentially the same cross section. This same cross section has also been measured on samples prepared in other laboratories

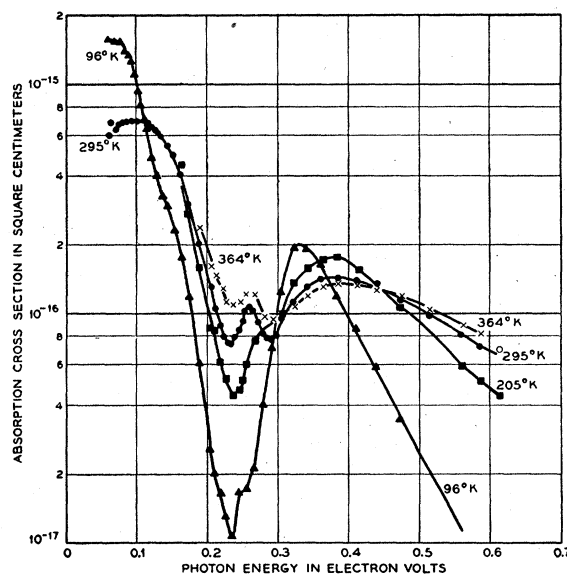


FIG. 6. The absorption cross section for free holes measured in normal *p*-type germanium plotted vs the energy of the incident light for four different temperatures. The lattice absorption at long wavelengths (energies less than 0.1 ev) has been subtracted from the normal absorption in order to get the cross section.

with different doping materials.¹⁰ It seems most unlikely that an uncontrolled impurity or imperfection would remain as constant under such a variety of situations.

Finally, it should be observed that in order for the absorption to be ascribed to empty energy levels in the forbidden band, the cross section for capture of photons by these empty levels is required to be extremely large. If the number of impurity levels is so small that it does not affect the resistivity in fairly pure samples where the concentration of donors and acceptors are lower than 10¹⁴ cm⁻³, the impurities must be present in concentrations smaller than this. At the same time the extinction coefficient for the heaviest concentration of

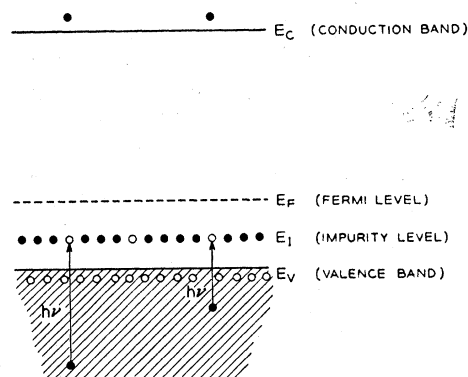


FIG. 7. An energy scheme for impurities or imperfections (E_I) which could explain how an impurity absorption could be proportional to the concentration of free holes as long as the Fermi level is above the impurity level. This is probably not the explanation of the observed absorption, however.

¹⁰ D. Cronmeyer (private communication).

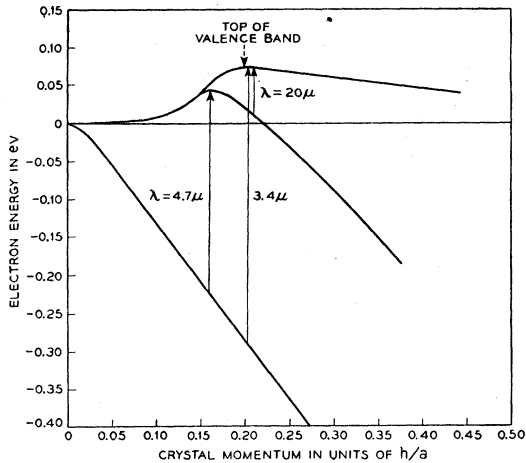


Fig. 8. A proposed energy scheme for the degenerate bands within the valence band plotted vs the crystal momentum of an electron along the direction in which the valence band has its maximum energy. The absorption maxima in *p*-type germanium are indicated by the arrows. This scheme is consistent with the observed dependence of the absorption cross section of free holes on wavelength and temperature. (Here h is Planck's constant and a is the edge length of the unit cube.)

holes (Fig. 4) is observed to reach values of 10^{-3} (corresponding to an absorption constant of 50 cm^{-1}). Even if all of the impurity levels were empty, this would require a cross section for capture of photons by empty impurity levels in excess of 5000 \AA^2 , an unreasonably large value.

Thus to summarize we do not believe the extra absorption beyond the fundamental absorption edge can be associated with the normal acceptors or donors because the cross section measured in normal samples is the same for (1) injected carriers and (2) compensated samples. We do not believe it is associated with impurities or imperfections because (1) the cross section is the same for injected carriers, (2) the concentration of such uncontrolled impurities is required to be the same for different samples and (3) too large a cross section is required. We feel that the most reasonable explanation of the extra absorption is that the free carriers themselves are absorbing the light by some mechanism other than that proposed by the simple Drude-Zener theory.

Bardeen has proposed a modification of the Drude-Zener theory¹¹ which predicts a higher absorption cross section. He points out that the optical modes of vibration may contribute to the scattering of the excited carriers whereas these modes have only a small influence on the scattering of the unexcited carriers. Thus the mean free time between collisions would be much smaller for the excited carriers than that estimated from the mobility of the thermal carriers, and a larger cross section for capture of a photon would be expected. This may explain the absorption observed in *n*-type germanium, where the dependence on wavelength is ap-

¹¹ J. Bardeen, Phys. Rev. **79**, p. 216 (1950).

proximately that predicted by the Drude-Zener theory.¹ In *p*-type germanium the appearance of absorption bands with an unpredicted temperature dependence suggests that an entirely new explanation needs to be found.

POSSIBLE EXPLANATION OF ABSORPTION BY FREE HOLES

A possible explanation of the absorption by free holes might be that the light induces transitions between the various branches of the degenerate bands.^{12,13} The feature of such degenerate bands which is essential for explaining the observed absorption is that there be two energy maxima, associated with different bands and/or directions, which are within approximately 0.03 eV of each other. One possible energy scheme is shown in Fig. 8. Here the electron energy of the three degenerate bands within the valence band is plotted against the crystal momentum in such a way as to be approximately consistent with the observations. The scale of the momentum axis was chosen so that the effective mass associated with the curvature at the top of the valence band be made equal to the free electron mass. The absorption bands arise because two of the bands are assumed to have maxima at values of momentum greater than zero. The holes will be concentrated within $\approx kT$ of the highest maximum, so that if the next highest maximum is within kT of the first, it will have an appreciable population. Transitions may thus occur from both maxima to the lower band, giving rise to the two absorption bands. The long wavelength (low-energy) absorption may be caused by transitions between the two upper bands. As the temperature is lowered, the lower-energy maximum will become depopulated and the associated absorption maximum will disappear. The other absorption band will increase and narrow. Finally, the long wavelength absorption will also tend to increase and its cutoff will shrink to lower photon energies. These effects are just what are observed.

There are, however, theoretical objections to the above explanation. Calculations¹³ which have been made of the energy band structure indicate that the valence band is of the order of 10 eV wide. The detail shown in Fig. 8 covers only 0.3 eV. This suggests that all of this detail occurs near the center of the Brillouin zone, ca , $P < h/20a$. Such detail does not seem to be within the framework of the theoretical calculations.¹³ In addition it requires a rather small effective mass (ca , $\frac{1}{10}$ of the free electron mass). These objections have not yet been resolved.

The authors are glad to acknowledge their indebtedness to J. R. Haynes, who suggested the techniques used in the measurement of absorption by injected carriers, to Conyers Herring for stimulating discussions, and to H. R. Moore who designed and built the detector amplifier system used in the measurements.

¹² W. Shockley, Phys. Rev. **78**, 173 (1950).

¹³ F. Hermann and J. Callaway, Phys. Rev. **89**, 518-19 (1953).