

If the effect of charge transfer is neglected, the theoretical mobility of He^{++} should be nearly equal to that of He^+ , since in doubling the charge, the mean free path between ion and atom is reduced to about half the value for the singly charged ion. On the other hand, the effect of total charge transfer

between He^{++} and He should be nearly absent. Therefore, it is suggested that Tyndall and Powell may actually have measured the mobility of He^{++} in their second experiment, inasmuch as their criterion was to select the fastest ion as the one which was to be measured.

PHYSICAL REVIEW

VOLUME 75, NUMBER 11

JUNE 1, 1949

The Optical Constants of Germanium in the Infra-Red and Visible

W. H. BRATTAIN AND H. B. BRIGGS

Bell Telephone Laboratories, Murray Hill, New Jersey

(Received February 14, 1949)

Thin films of germanium have been evaporated on glass, quartz, and calcium fluoride slides. The thickness of these films ranged from 4×10^{-6} to 1×10^{-4} cm. Transmission of infra-red light through the films exhibited the usual interference phenomena, showing alternate maxima and minima as the wave-length was varied. From these maxima and minima the index of refraction of the films was determined. This index was 4.3 for λ greater than 6×10^{-4} cm wave-length. It increased to 5.2 at 8.0×10^{-5} cm and then fell off rapidly to 2.3 at 4.0×10^{-5} cm. To determine the values of the index and extinction coefficients in the visible region where the absorption is large, a wedge of germanium was made. Trans-

mission was then determined as a function of film thickness for several wave-lengths. The values of the optical constants in this region were then obtained by comparing these results with the theoretical transmission equations. The extinction coefficient increased from 0.4 at $\lambda = 1 \times 10^{-4}$ cm to 2.8 at $\lambda = 4 \times 10^{-5}$ cm. The density of the films was determined by an interferometric method and was found to be the same as bulk germanium. The real and imaginary parts of the dielectric constant for germanium are calculated and compared with the known results for silicon. The absorption bands for both elements are shown to be consistent with the electron band structure deduced from their semiconducting properties.

I. EXPERIMENTAL RESULTS

A TYPICAL result for a germanium film on calcium fluoride is shown in Fig. 1. Here the transmission through the film is plotted as a function of the reciprocal of the wave-length λ in cm. The data were obtained with an infra-red spectrometer.¹ It is seen that seven orders of reinforcement were obtained before the absorption at shorter wave-lengths became too large. Another set of results on a thinner germanium film on glass is shown in Fig. 2. These results were obtained with a quartz spectrometer. Here both the transmission through the film at normal incidence, and the reflection from the film at 45° incidence are plotted against the wave-length λ in cm. Three orders of reinforcement are obtained and it is seen that the transmission maxima and minima correspond respectively to the reflection minima and maxima as they should. The well-known simple relations which govern the position of the maxima and minima are: The condition for transmission maxima

$$2nt = m\lambda, \quad (1)$$

where n is the index of refraction, t the thickness, m the order, and λ the wave-length; and the condition for transmission minimum

$$2nt = \frac{1}{2}(2m+1)\lambda. \quad (2)$$

It is therefore obvious that if one knows the thickness of the film and the order number m , one can calculate the index n for every value of λ for which either a maxima or minima occurs. Since the order number² must be an integer, choice of the wrong order number makes a large difference in n . It is therefore easy to assign the correct order numbers if data are available on films of several thicknesses.

If the films are uniform in thickness and the density of the films is known, one can determine the thickness by weighing the films. The slides on which films of germanium were deposited were weighed before and after deposition of the film, and the area of the film was determined in each case. The uniformity in thickness of a film was determined by choosing a particular wave-length and measuring the transmission through different parts of the film. Since λ is fixed, n should be the same for all parts of the film, and therefore, if the thickness varies, the order m in Eq. (1) must vary. The percentage variation in the thickness of the film can be determined from the change in order:

$$\Delta t/t = \Delta m/m, \quad (3)$$

where t is the thickness and m the order for a particular spot on the film, and Δt is the change in thickness for a given change Δm in order as the position on the film is changed. By making such measurements on a single film for two different wave-lengths, the interpretation could be made

¹ We are indebted to P. P. Debye of these laboratories for use of the spectrometer to make these measurements.

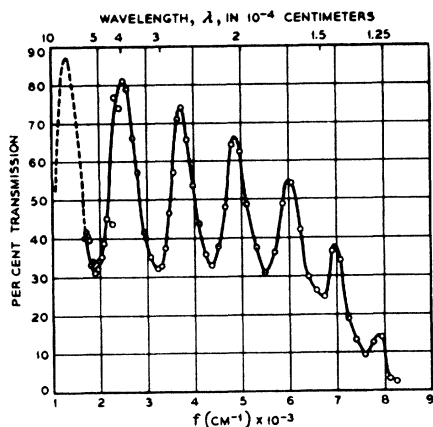


FIG. 1. Percent transmission *vs.* the reciprocal of the wavelength for a germanium film, 9.0×10^{-6} cm thick on a fluorite slide.

unambiguous. As might be expected for films evaporated from finite sources, considerable variation in thickness was found over the area of the films, of the order of 20 percent on some of the first films. It was found possible, however, by using four properly spaced sources, to make films with less than 5 percent variation in one direction across the film, and less than 10 percent in a direction normal to that. Then, with the spectrometer slit parallel to the direction of least variation, accurate measurements could be taken over an area of the film that was quite uniform in thickness, and moreover, the actual thickness of this area could be determined if the weight, density, and percentage variation in thickness along the film were known. Thus, the index could be determined for this film for various wave-lengths, and then using wave-lengths in this same region, one could in turn determine the correct effective thickness for all the other less uniform films.

The density of a typical film was measured in the following manner. A film of germanium was evaporated on a glass slide² so arranged that a small section in the center of the slide was left bare. The area of the glass covered with germanium was measured carefully. The slide was weighed both before and after evaporation to determine the weight of the germanium. An additional film of germanium was then evaporated over the whole surface of the slide just to make the reflection from all parts of the surface uniform. Another blank glass slide was then placed on top of the first slide while both slides were immersed in water. The combination was then examined in sodium light. The shift in the fringes could be observed between the region where the first germanium film was on the glass and where only the second germanium film

² The four-source method was used here to give a film of uniform thickness.

was on the glass, thus enabling one to determine the thickness of the first germanium film, and from its area and weight, the density. The area covered by the first film was 9.7 cm^2 .³ The fringe shift was 4.25 fringes of sodium light ($\lambda = 5.9 \times 10^{-5} \text{ cm}$) in water (the medium between the two glass slides) giving a thickness of $9.4 \times 10^{-5} \text{ cm}$. The weight of the film was $4.83 \times 10^{-3} \text{ gram}$. This gives 5.3 for the density of the film, agreeing with the bulk density of germanium. All films were therefore assumed to have the bulk density.

In order to determine both the index n and the extinction coefficient k for these films in the region of wave-length 3.5×10^{-5} to $7 \times 10^{-5} \text{ cm}$, where the absorption is so large that interference maxima and minima are not easily seen, a germanium wedge was evaporated on a glass slide using a two-source arrangement to assure that the thickness was uniform to at least 5 percent across the wedge. The variation in thickness with distance along the wedge was determined by getting the change in order with distance for several wave-lengths in the range 8.0×10^{-5} to $2.0 \times 10^{-4} \text{ cm}$. The relation between thickness and distance that was found is shown in Fig. 3. The transmission *vs.* thickness was then determined for each of four wave-lengths 3.65×10^{-5} , 4.36×10^{-5} , 5.02×10^{-5} , and $6.8 \times 10^{-5} \text{ cm}$. These results are shown in Fig. 4. The solid curves represent the experimental results; at least 20 points were taken for each curve. The circles are from theoretical calculations and will be discussed later. The results for the shorter wave-lengths approximate the simple case where the transmission is just an exponential function of the thickness, and the logarithm of the transmission *vs.* the thickness should give a curve which is a straight line with a slope which determines the value of the extinction coefficient k . Deviations from such a linear relation are, however, apparent for the 3 longer wave-

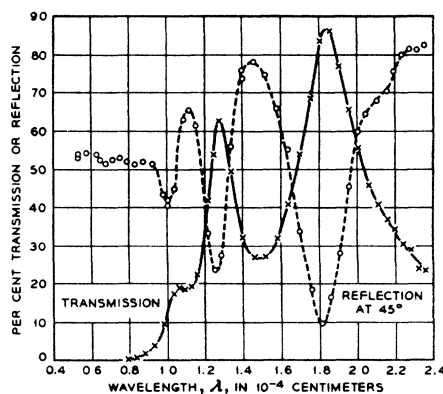


FIG. 2. Reflection and transmission *vs.* wave-length for a germanium film, $3.9 \times 10^{-5} \text{ cm}$ thick on glass.

³ This method was suggested by W. Shockley of these Laboratories.

lengths, and for the case of $\lambda = 6.8 \times 10^{-5}$ cm these deviations are very pronounced. As will be seen in the next section, the index n and the extinction coefficient k can be determined from these curves.

Before closing this section, a few more of the experimental details should be mentioned. The germanium was evaporated from tantalum boats. Care was taken to load the boats uniformly. In each case more germanium was put in the boats than was used in depositing the film. The germanium was of the high purity type used for making point contact rectifiers.⁴ The slides were heat treated to approximately 400°C before depositing the germanium, and each germanium film was heat treated to approximately the same temperature after deposition. Both of these operations were performed in vacuum. The pressure during deposition was less than 10^{-5} mm of Hg. The weight of the germanium films was of the order of milligrams. The weighing was done on a balance good to 0.05 milligram. Slides were generally heat treated in vacuum and then weighed before deposition to eliminate weight

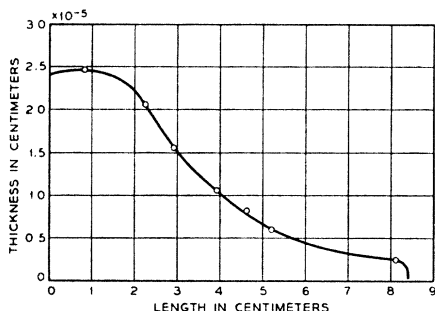


FIG. 3. Thickness contour of germanium wedge on glass.

loss due to removal of adsorbed films. As another check on the variation of index with density of film, one slide was made in which the germanium was deposited when the slide was at a temperature of 150°C . Transmission measurements were then made on the film. After this it was put back in vacuum and heat treated to 400°C and taken out and measured again. The results of this test are shown in Fig. 5. They correspond to a shift in index of about 3 percent probably due to an increase in density on heat treatment. This result indicates that there was no large density change due to heat treatment.

II. THEORY

Starting from Drude's equation for transmission of light in various media, Barnes and Czerny⁵ have

⁴ H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, Inc., New York, 1948).

⁵ R. B. Barnes and M. Czerny, *Phys. Rev.* **38**, 338 (1931). See also T. C. Fry, *J. Opt. Soc. Am.* **22**, 307 (1932); and A. W. Crook, *J. Opt. Soc. Am.* **38**, 954 (1948).

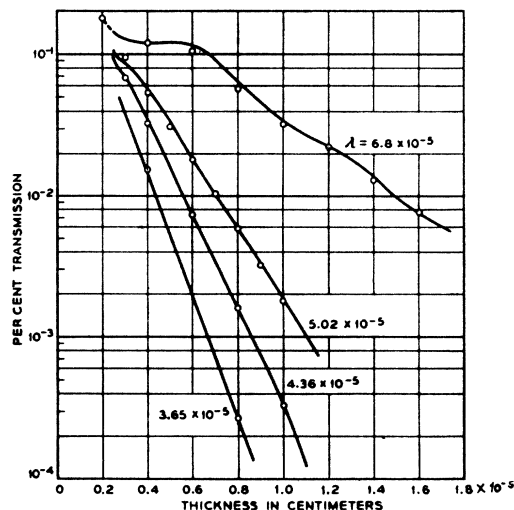


FIG. 4. Transmission vs. thickness for several wave-lengths obtained for germanium wedge.

worked out the equations for reflection at normal incidence from a film of index n , extinction coefficient k , and thickness t immersed in a medium of index n_1 . Our case is more complicated. We have first air, then the film, and then the glass, quartz, or fluorite as the case may be, and then air again. It was decided that the approximation would be sufficiently good if the last interface between the slide and the air were neglected. The problem then involves air of index $n_1=1$, the film, of index n , extinction coefficient k , and thickness t ; and the slide of index n_2 . Working out the correct boundary conditions for this case, one gets the two equations for reflection and transmission at normal incidence.

$$\frac{E_R}{E_T} = \frac{(1-a)(1+b)e^{-ip} + (1+a)(1-b)e^{+ip}}{(1+a)(1+b)e^{-ip} + (1-a)(1-b)e^{+ip}} \quad (4)$$

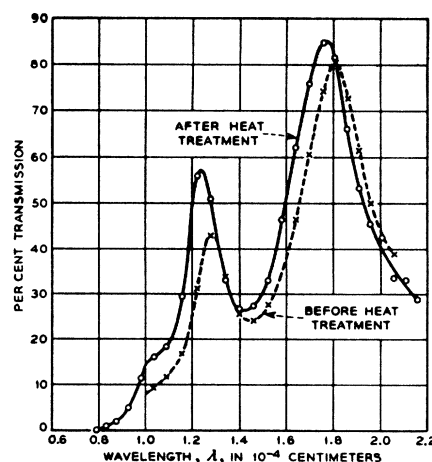


FIG. 5. Dependence of transmission on heat treatment of a germanium film, 3.7×10^{-5} cm thick on glass.

and

$$\frac{E_T}{E_I} = \frac{4e^{ip_2}}{(1+a)(1+b)e^{-ip} + (1-a)(1-b)e^{+ip}}, \quad (5)$$

where

$$a = (n - ik)/n_1, \quad b = n_2/(n - ik), \\ p = (2\pi t/\lambda)(n - ik), \quad p_2 = (2\pi t/\lambda)n_2;$$

t is the thickness, λ the wave-length in a medium of index 1, and E_I , E_T , and E_R are the incident, transmitted, and reflected amplitudes, respectively. Multiplying by the complex conjugate in each case, one obtains (R) the fraction of the power reflected, and (T) the fraction transmitted as follows.

$$R = \frac{|E_R|^2}{|E_I|^2} = \frac{r_1^2 [(\epsilon^x - (\rho_1/r_1)\epsilon^{-x})^2 + 4(\rho_1/r_1) \sin^2(y + \frac{1}{2}(\varphi_1 - \theta_1))] }{r^2 [(\epsilon^x - (\rho/r)\epsilon^{-x})^2 + 4(\rho/r) \sin^2(y + \frac{1}{2}(\varphi - \theta))]}, \quad (6)$$

$$T = \frac{n_2}{n_1} \frac{|E_T|^2}{|E_I|^2} = \frac{16n_1n_2(n^2 + k^2)}{r^2 [(\epsilon^x - (\rho/r)\epsilon^{-x})^2 + 4(\rho/r) \sin^2(y + \frac{1}{2}(\varphi - \theta))]}, \quad (7)$$

where

$$r^2 = [(n_1 + n)^2 + k^2][(n_2 + n)^2 + k^2], \\ \rho^2 = [(n_1 - n)^2 + k^2][(n_2 - n)^2 + k^2], \\ r_1^2 = [(n_1 - n)^2 + k^2][(n_2 + n)^2 + k^2], \\ \rho_1^2 = [(n_1 + n)^2 + k^2][(n_2 - n)^2 + k^2], \\ \tan \varphi = [-k(2n + n_1 + n_2)] / [(n_1 + n)(n_2 + n) - k^2], \\ \tan \theta = [-k(2n - n_1 - n_2)] / [(n_1 - n)(n_2 - n) - k^2], \\ \tan \varphi_1 = [-k(2n - n_1 + n_2)] / [(n - n_1)(n + n_2) - k^2], \\ \tan \theta_1 = [-k(2n + n_1 - n_2)] / [(n + n_1)(n - n_2) - k^2], \\ x = (2\pi kt/\lambda) \quad \text{and} \quad y = (2\pi nt/\lambda).$$

In Eq. (7) the nominal result has been multiplied by n_2 , and divided by n_1 , to compensate for the fact that the ratio of the transmitted power to incident power is not equal to the square of the absolute magnitude of the ratio of the amplitudes, when the amplitudes are measured in media of different index of refraction.

When k is small or zero, Eqs. (6) and (7) become much simpler. The phase angles become zero, and from Eq. (7) one can verify at a glance that T will be a maximum when $\sin^2 y$ is zero and a minimum

when $\sin^2 y = 1$, giving Eqs. (1) and (2), respectively. Also when k is large so that the ϵ^{-x} and the $\sin^2 y$ terms in the denominator of (7) can be neglected in comparison with ϵ^x , one gets the well-known transmission formula,

$$T = A \exp(4\pi kt/\lambda), \quad (8)$$

where

$$A = [16n_1n_2(n^2 + k^2)]/r^2.$$

For all cases in between these two limits, it is necessary to use the complete equation. It is fairly obvious that when this is necessary, it is easier to keep the wave-length fixed and vary the film thickness t , and look for one n and one k that will fit the data, than it is to work with a fixed thickness t and vary the wave-length which means finding a different value of n and k for each wave-length. This is the reason that the wedge described in Section I was made. The circles shown in Fig. 4 are calculated from Eq. (7) using the values for n and k that were found to give the best fit in each case. For example, consider the results for $\lambda = 6.8 \times 10^{-5}$ in Fig. 4. After several trials the values $k = 1.3$ and $n = 5.15$ were found to be approximately right. Substituting these values into Eq. (7) one gets the specific equation for this case,

$$T = 0.375 / [(\epsilon^x - 4\epsilon^{-x})^2 + 1.6 \sin^2(y + 0.135)], \quad (9)$$

where $x = 1.2 \times 10^5 t$ and $y = 4.76 \times 10^6 t$. The fit that can be obtained is quite sensitive to the values of n and k used. A ten percent change in either n or k would make the fit very poor. It should also be mentioned that it would be quite impossible to fit these data if account had not been taken of the fact that the index of the slide was different from that of the air.

III. SUMMARY AND CONCLUSIONS

Using the experimental data from all the germanium films that were measured and Eqs. (1) and (2), or when necessary Eq. (7), values of n and k were determined as a function of wave-length λ . These results are shown in Fig. 6. The open

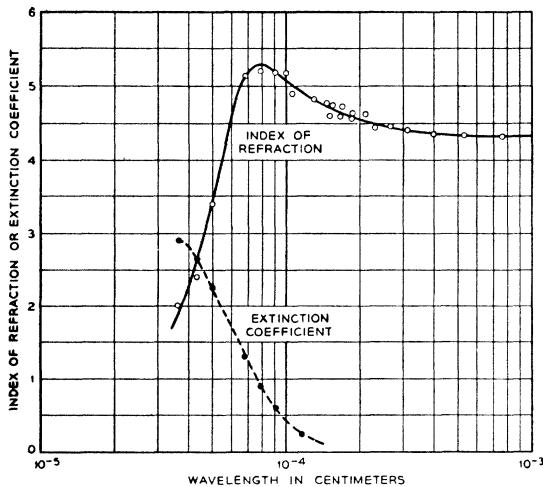


FIG. 6. Index of refraction and extinction coefficient vs. wave-length, for germanium, experimental points with smooth curves drawn through them.

circles are the separate determinations of n and likewise the solid points are the values of k . The solid lines are simply smooth curves drawn through the experimental points. The only other data on the optical constants n and k for germanium were taken by O'Bryan.⁶ His values of n range from 2.85 at $\lambda=4.046\times 10^{-5}$ to 3.42 at $\lambda=5.78\times 10^{-5}$, and the respective values of k are 1.67 and 1.35. The values of n are the same order as ours in the range we covered, but they do not vary as rapidly with wave-length, and his values of k are considerably smaller than ours. We do not know how to explain these differences. His method involved measurements of reflection at other than normal incidence, whereas our results in this region involve the actual transmission through the germanium film at normal incidence.

Having values for n and k at all wave-lengths such as shown in Fig. 6, it should be possible to calculate from Eq. (7) the actual shapes of the transmission *vs.* wave-length curves for any of the germanium films we measured. This was done for one film which was found to be quite uniform in thickness. In this case, the transmission through the germanium film and its glass backing was compared with the transmission through a blank glass slide to eliminate, as nearly as possible, the effect of the glass air interface that has been neglected in Eq. (7). The results are shown in Fig. 7. The experimental points are shown with a smooth curve through them, and for comparison, the points calculated from Eq. (7) are shown as circles. The agreement is good and it can be said that the values of the optical constants n and k obtained for these films explain the intensity relations as well as the position of the maxima and minima.

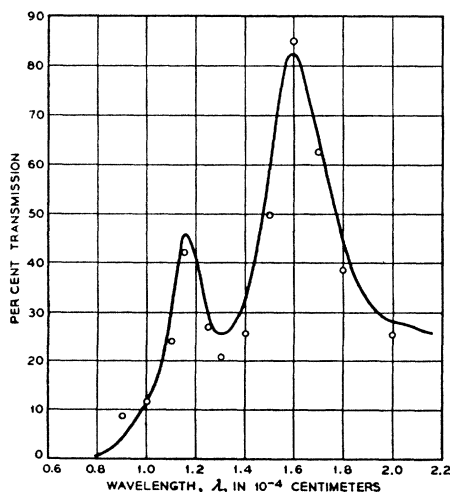


FIG. 7. Comparison of calculated (circles) and experimental results (smooth curve) for transmission through a germanium film, 3.4×10^{-5} cm thick on glass.

⁶ H. M. O'Bryan, J. Opt. Soc. Am. 26, 122 (1936).

TABLE I. Reflecting power of germanium.

Wave-length	R calculated	R for thick film	R for bulk surface
10^{-3}	0.39		
5×10^{-4}	0.39		
2×10^{-4}	0.42		0.40
1.5×10^{-4}	0.43		0.41
1.0×10^{-4}	0.47	0.46	0.42
9×10^{-5}	0.48	0.48	0.46
8×10^{-5}	0.48	0.51	0.48
7×10^{-5}	0.48	0.53	0.52
6×10^{-5}	0.46	0.54	0.56
5×10^{-5}	0.45		0.48
4.5×10^{-5}	0.47		0.54
4.0×10^{-5}	0.52		

As another check on the values we have obtained for n and k , the reflection coefficient for a thick germanium film was calculated for these values. These results were compared with experimentally determined values of reflection coefficient obtained for near normal incidence on a polished sample of bulk germanium and a thick germanium film. It is difficult to obtain good data on reflection coefficients. The experimental data were taken by comparing the reflection from germanium with that from an evaporated aluminum film. No correction was made for reflection loss at the aluminum surface. The data are given in Table I. The agreement is not perfect but does indicate that the reflection from bulk germanium is approximately the same as that from the germanium film, and that these results are of the same order as calculated.

All these results indicate that the values of n and k obtained are characteristic of these germanium films, and there is no reason to think that they are not also characteristic of bulk germanium.

The results that have been obtained are a typical example of how the optical constants n and k vary in the region of a well defined absorption band. The absorption band in this case is due to the excitation of electrons from the filled band in germanium to the empty conduction band by absorption of the incident radiation.

From the values of n and k one can calculate the real and imaginary parts of the dielectric constant n^2-k^2 and $2nk$, respectively. The real part n^2-k^2 is shown in Fig. 8, and the imaginary part $2nk$ is shown in Fig. 9. It is interesting to compare these results for germanium with another similar case. The optical constants for silicon have been measured by several observers,⁷ and the real and imaginary parts of its dielectric constant are also shown in Figs. 8 and 9, respectively. It is seen that the curves are quite similar in shape. The main differences are in magnitude and in the wave-length at which the absorption occurs. Silicon and ger-

⁷ E. O. Hulburt, Astrophys. J. 42, 222 (1915); G. Pfestorf, Ann. d. Physik 81, 906 (1926).

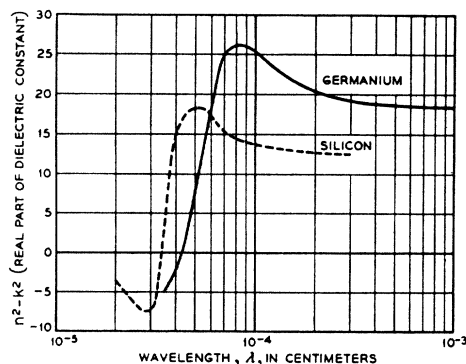


FIG. 8. The real part of the dielectric constant for silicon and germanium vs. wave-length.

manium both have the diamond lattice structure, the atoms in each case being held together by covalent bonds (filled band). The absorption occurs when a quantum of light has sufficient energy to remove an electron from one of these bonds. This minimum energy can be estimated from the wavelength at which absorption sets in. From Fig. 9 these wave-lengths are approximately $\lambda = 1.0 \times 10^{-4}$ cm for silicon, and $\lambda = 1.6 \times 10^{-4}$ cm for germanium, corresponding to energies of 1.2 and 0.77 equivalent electron volts, respectively. These values are to be compared with the values determined from the intrinsic electrical conductivity of silicon and germanium (thermal excitation of electrons from the covalent bonds to the conduction band), namely 1.1 and 0.76 electron volts.⁴ The asymptotic value of the dielectric constant at long wave-lengths, 12.5 for silicon and 18.5 for germanium, are important in the theory of the impurity conductivity in these semiconductors.⁴

Mention should be made of the fact that the real and imaginary parts of the dielectric constant are not independent. If either part is known for all wave-lengths, the other part is also determined for all wave-lengths.⁸ While the data here are not quite

⁸ H. W. Bode, *Network Analysis and Feedback Amplifier Design* (D. Van Nostrand Company, Inc., 1945), Chapter XIV.

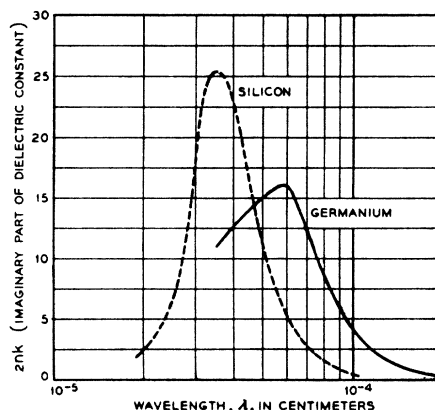


FIG. 9. The imaginary part of the dielectric constant for silicon and germanium vs. wave-length.

that inclusive, the relation is such that an approximate check can be made for internal consistency of the data in Figs. 8 and 9. It was found that the data for silicon were quite consistent, but for germanium there was evidence of a considerable inconsistency. The indications were that, for λ less than 10^{-4} cm, either the experimental values of k are too small or the rate of change of n with wave-length is too large, and that the discrepancy could not be resolved without extending the wave-length range to smaller wave-lengths and taking more data. Since there is little likelihood that we will be able to do this in the near future, it was thought best to published the data we now have. There is little question about the essential correctness of the results for λ greater than 1×10^{-4} cm, and it is not impossible that a peculiar behavior in the absorption in germanium at still shorter wave-lengths would explain the present inconsistency.

The authors wish to thank F. S. Goucher for his interest and help in connection with the experimental work, and R. H. Dietzold of these Laboratories who helped in resolving the mathematical difficulties involved in the theory.