

Optical Constants of Germanium in the Region 1 to 10 ev

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The reflectance, $|r(\lambda)|^2$, of single-crystal germanium was measured in the range 0.6 to 11.3 ev. The phase, $\theta(\lambda)$, was computed from these data using the Kramers-Kronig relation between the real and imaginary parts of the complex function $\ln r = \ln|r| + i\theta$. The optical constants, n and k , were then determined from the Fresnel reflectivity equation. The real part of the refractive index, n , has maxima of 5.5 at 2.07 ev and 4.2 at 3.2 ev. Above 6 ev, the index is very nearly 1. The extinction coefficient, k , shows maxima of 2.0 at 2.5 ev and 4.2 at 4.4 ev. Below 3.5 ev, the results are in good agreement with the recent measurements of Archer. Beyond this point, they depart from his extrapolated curve.

INTRODUCTION

DIRECT experimental data relating to optical transitions in single-crystal materials are difficult to obtain for quantum energies much above the threshold of intrinsic absorption. Absorption coefficients rise above 10^5 cm^{-1} and techniques for preparing thin crystalline samples for transmission measurements become extremely tedious. Resort is often made to studies of thin evaporated films. However, such specimens are frequently found to have properties differing from those of the bulk material.

Information may be obtained from measurements of reflectivity at non-normal incidence.^{1,2} Further, Robinson³ has set forth a technique for evaluating the optical constants, n and k , from normal incidence reflectance data on bulk material. It appears to be particularly convenient. His method, based on the work of Bode,⁴ is summarized by Jahoda⁵ who used this technique to determine the optical constants of BaO near the fundamental absorption edge.

In brief, the procedure is as follows. The Fresnel equation for the reflection of normal incidence radiation is

$$r = (n - ik - 1)/(n - ik + 1) = |r|e^{i\theta}, \quad (1)$$

where $n - ik$ is the complex index of refraction. The measured reflectance is $|r|^2$, the square of the amplitude of r . The phase θ , for any frequency ν_0 , is computed from these data using the Kramers-Kronig relation between the real and imaginary parts of the complex function $\ln r = \ln|r| + i\theta$. This relation, which may be written as⁴

$$\theta(\nu_0) = -\frac{1}{\pi} \int_0^\infty \frac{d \ln|r(\nu)|}{d\nu} \ln \left| \frac{\nu + \nu_0}{\nu - \nu_0} \right| d\nu, \quad (2)$$

can be integrated with the aid of tables^{4,6} or by computer

techniques.⁷ The Fresnel equation then relates $|r|$ and θ to n and k .

It is desirable to evaluate the integrand of Eq. (2) over as wide a frequency range as possible. Contributions to θ are small, however, in the regions remote from ν_0 and it is not necessary to know the entire reflectivity spectrum to arrive at meaningful values for θ . If the integral is computed for a value of ν_0 in a region of optical transparency ($k=0$) any unknown contribution may be accurately estimated.

This paper presents the optical constants for germanium in the spectral region 1 to 10 ev computed in a similar manner. The reflectivity was measured in the range 0.6 to 11.3 ev. This material was chosen for study primarily because of the bearing such measurements might have on the elucidation of the proposed models for the band structure of germanium.⁸ Secondly, germanium, with its small band gap,^{9,10} allows the Kramers-Kronig integral relation to be computed from experimental data obtainable with available optical apparatus over a wide frequency range.

An extensive review of previous evaluations of the optical constants of germanium is presented in a recent paper² and will not be repeated here. It clearly points out the distinct lack of agreement in this field and stresses the need for accurate measurements on carefully selected specimens. Values of n and k reported here agree with the work of Archer² who carefully evaluated the optical constants, in the spectral region 1 to 3.5 ev, from measurements of the ellipticity of reflected polarized light. The data are also consistent with direct measurements of optical absorption below¹⁰ 1.8 ev and index of refraction below 0.7 ev.¹¹

PROCEDURE

Measurements of reflectance, at nearly zero angle of incidence, were obtained in the region 0.6 to 11.5 ev

¹ R. Tousey, *J. Opt. Soc. Am.* **29**, 235 (1939); D. Avery, *Proc. Phys. Soc. (London)* **B65**, 425 (1952).

² R. J. Archer, *Phys. Rev.* **110**, 354 (1958).

³ T. S. Robinson, *Proc. Phys. Soc. (London)* **B65**, 910 (1952).

⁴ H. Bode, *Network Analysis and Feedback Amplifier Design* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1945).

⁵ F. C. Jahoda, *Phys. Rev.* **107**, 1261 (1957).

⁶ D. E. Thomas, *Bell System Tech. J.* **26**, 870 (1947).

⁷ Nelson, Schainblatt, and Hartman, *Bull. Am. Phys. Soc. Ser. II*, **3**, 272 (1958).

⁸ F. Herman, *Revs. Modern Phys.* **30**, 102 (1958); *Physica* **20**, 801 (1954).

⁹ G. Macfarlane and V. Roberts, *Phys. Rev.* **97**, 1714 (1955).

¹⁰ W. C. Dash and R. Newman, *Phys. Rev.* **99**, 1151 (1955).

¹¹ C. Salzberg and J. Villa, *J. Opt. Soc. Am.* **47**, 244 (1957); H. B. Briggs, *Phys. Rev.* **77**, 287 (1950).

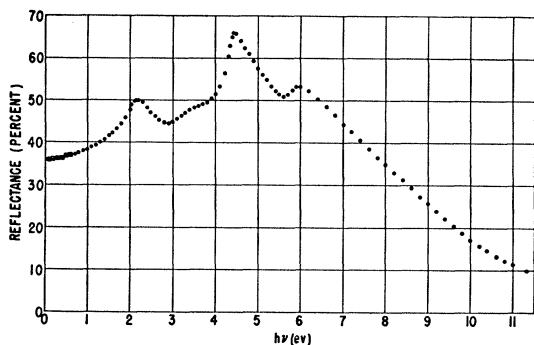


FIG. 1. Spectral dependence of the reflectance of Ge. Below 0.7 eV, these values are calculated from direct measurements of index of refraction (see reference 11).

using a Cary spectrophotometer (0.6 to 2 eV), a quartz prism monochromator (2 to 6.5 eV), and a vacuum grating monochromator¹² (5 to 11.3 eV). The last named instrument was kindly placed at our disposal by Johnson. Data for etched single-crystal germanium surfaces at 300°K are shown in Fig. 1. The uncertainty in the value of reflectance is estimated, from repeated measurements on different samples, to be less than 5% in the region 0.6 to 7 eV. Above 7 eV, the inaccuracy may be considerably larger.

Curves obtained on mechanically polished and on etched samples showed some variations, particularly in the region of high reflectance. The peak near 4.4 eV was much less pronounced and values of reflectance considerably lower when distorted layers produced by mechanical polishing were not removed by etching techniques.¹³ These effects were not studied in great detail in this work; however, it appears that useful information concerning surface damage might be obtained from more comprehensive measurements of reflectivity in regions of high optical absorption. The

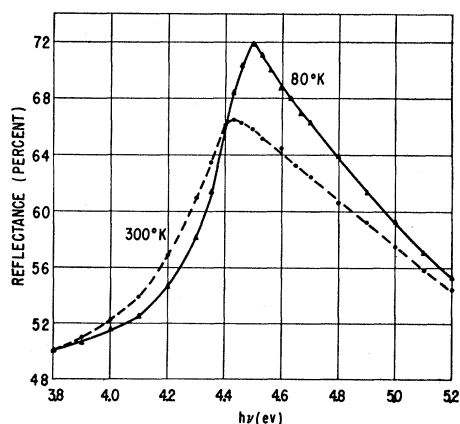


FIG. 2. Spectral dependence of the reflectance of Ge at 300°K and 80°K in the region of the peak near 4.5 eV.

¹² P. D. Johnson, *J. Opt. Soc. Am.* **42**, 278 (1952).

¹³ W. C. Dash, *J. Appl. Phys.* **29**, 228 (1958).

results obtained from etched surfaces are more significant for the purposes of the present investigation.

No corrections were made in these data for the presence of an oxide layer on the crystal surface.^{2,14} Values of reflectance measured immediately after etching and again at a later time were not significantly different.

For germanium surfaces, measurements of reflectivity appearing in the literature¹⁵ have been confined in general to the region below 4 eV. The values of Fig. 1 are in rough accord with these data although there are differences in some details.

Limited reflectance data were obtained at 80°K in a special vacuum tube.¹⁶ These data were confined to the region of pronounced structure near 4.5 eV and are shown in Fig. 2. The peak is slightly sharper and is shifted about 0.06 eV toward higher energy at the lower temperature.

RESULTS AND DISCUSSION

Values for n and k derived from the reflectance data of Fig. 1 are shown in Figs. 3 and 4. The Kramers-Kronig integral was evaluated beyond 11.3 eV, with two

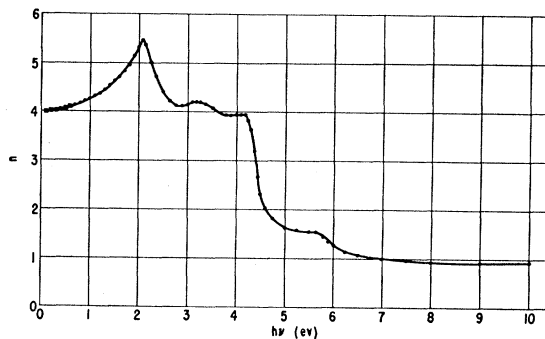


FIG. 3. Spectral dependence of the real part of the index of refraction of Ge. Below 0.7 eV, the values are taken from the literature (see reference 11).

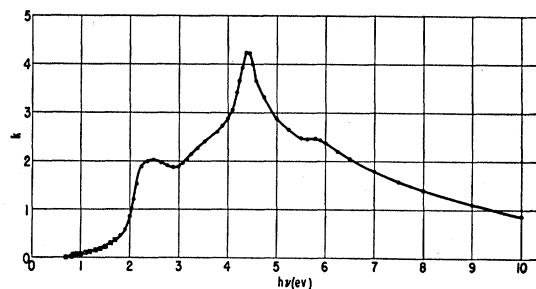


FIG. 4. Spectral dependence of the extinction coefficient (the imaginary part of the index of refraction) of Ge. The absorption data of Dash and Newman are plotted below 1.7 eV.

¹⁴ R. J. Archer, *J. Electrochem. Soc.* **104**, 619 (1957).

¹⁵ Vavilov, Gippius, and Gorshkov, *Tech. Phys. U.S.S.R.* **28**, 254 (1958) [translation: *Soviet Phys. Tech. Phys.* **3**, 230 (1958)]; S. Koc, *Czechoslov. J. Phys.* **7**, 91 (1957); W. Brattain and H. Briggs, *Phys. Rev.* **75**, 1705 (1949).

¹⁶ E. A. Taft and H. R. Philipp, *J. Phys. Chem. Solids* **3**, 1 (1957).

requirements being imposed. First, the absorption coefficient computed at 0.6 ev must be zero. Second, in the region 0.6 to 1.7 ev, it must agree with direct measurements of optical transmission of single crystals. Both conditions were satisfied by assuming the reflectivity to decrease logarithmically from its value of 10% at 11.3 ev to 1.7% at 30 ev. This extrapolation is somewhat arbitrary and its exact shape may influence the values of n and k especially at higher energies, say above 7 ev. In the present case, calculated values of n fall slightly below 1.0 above 8 ev, a possible indication of small errors in the measured reflectance beyond 7 ev or in the extrapolated portion. The results agree quite well with those of Archer in the range covered by his experiments. Values of n and k are slightly smaller in the region of 2–3 ev but show the same structural detail.

Above 3.5 ev, the results differ from the curve proposed by Archer on the basis of results in the literature. The second peak in the extinction coefficient occurs at slightly higher energy than he indicates and is sharper. In addition, the extinction coefficient drops off much more slowly above 5 ev. If the index above 6 ev is indeed near one, then his extrapolation would require the reflectance to be almost zero at 10 ev, a value considerably beyond the limit of error estimated in the data presented here.¹⁷

In addition optical constants have also been computed here by using slightly different values for the reflectance than those of Fig. 1. The general character of the results was not altered. If the reflectance has a maximum of 52% instead of 50% in the peak near 2.15 ev (a value just within the estimated experimental error) then n and k values are almost identical with those of Archer. However, in this situation, exact agreement with the absorption measurements of reference 10 was not possible.

A different perspective is given the values of Fig. 4 if they are plotted as absorption coefficient, $\alpha = 4\pi k/\lambda$. This plot is shown in Fig. 5 and more clearly indicates

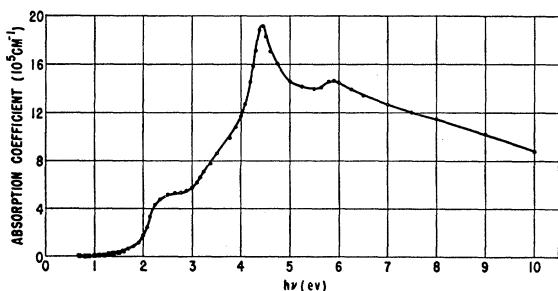


FIG. 5. Spectral dependence of the absorption coefficient ($\alpha = 4\pi k/\lambda$) of Ge.

¹⁷ This situation could be checked by direct measurements of optical transmission or, in a more complicated way, by measurements of the spectral distribution of the photoelectric yield. For measurements of the energy distribution of emitted photoelectrons in this spectral range see, W. C. Walker and G. L. Weissler, *Phys. Rev.* **97**, 1178 (1955).

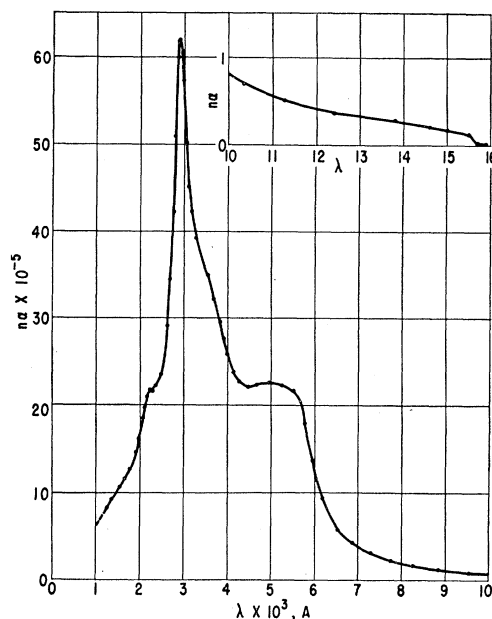


FIG. 6. $n\alpha$ as a function of wavelength for Ge.

the edge like appearance of the absorption near 2 ev and the sharpness of the absorption peak near 4.4 ev. The extent to which this curve gives the complete absorption spectrum of germanium can be determined by applying the Kramers-Kronig relation between the real and imaginary parts of the complex dielectric constant, in the form^{2,18}

$$\pi^2(\epsilon_0 - 1) = \int_0^\infty n\alpha d\lambda. \quad (3)$$

Here ϵ_0 is the dielectric constant which has the value 16 for germanium.^{11,19} The integrand of Eq. (3) is given by the curve of Fig. 6. Integrated graphically above 1000 Å it yields a value $\epsilon_0 = 15$ only 6% smaller than the accepted value. Optical absorption below 1000 Å will make this difference even less. This agreement is considered satisfactory in view of conceivable experimental errors in the reflectance measurements and extrapolation.

No attempt will be made here to describe the absorption spectrum in terms of proposed models of the band structure. The sharpness and strength of the peak near 4.4 ev should be useful in testing and refining band structure calculations.

These results show that sharp structure can occur in valence-conduction band optical absorption which pre-

¹⁸ J. H. Van Vleck, Massachusetts Institute of Technology Radiation Laboratory Report No. 735, 1945 (unpublished). T. S. Moss, *Proc. Phys. Soc. (London)* **B66**, 141 (1953).

¹⁹ W. C. Dunlap, Jr., and R. L. Watters, *Phys. Rev.* **92**, 1396 (1953).

sumably is not associated with exciton transitions.²⁰ Maxima occurring in the absorption spectra of the alkali halides,²¹ 1 eV or more beyond the valence-conduction band edge,¹⁶ have frequently been identified with exciton transitions. This interpretation may be valid, but until more information is available, detailed identi-

²⁰ E. O. Kane has suggested this conclusion. Exciton absorption has been observed just below the direct gap in germanium [Zwerdling, Roth, and Lax, *Phys. Rev.* **109**, 2207 (1958)]. One would not expect to find excitons with integrated absorption larger than that of the observed line since this transition is fully allowed having a finite cellular optical matrix element at the band edge and conserving crystal momentum.

²¹ R. Hilsch and R. Pohl, *Z. Physik* **59**, 812 (1930); E. Schneider and H. O'Bryan, *Phys. Rev.* **51**, 293 (1937); Hartman, Nelson, and Siegfried, *Phys. Rev.* **105**, 123 (1957).

fication of such structure should probably be considered tentative.²²

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We are indebted to Dr. R. S. McDonald for his assistance in obtaining infrared measurements. We are grateful to Dr. E. O. Kane and Dr. H. Ehrenreich for many stimulating conversations.

²² Relatively sharp structure has been observed in the absorption spectrum of K₃Sb [W. E. Spicer, *Phys. Rev.* **112**, 114 (1958)]. We have been able to correlate this detail with peaks in the energy distribution of emitted photoelectrons. The peak positions move linearly toward higher energy with increasing $h\nu$. This behavior is not associated with exciton processes, and we are led to ascribe this absorption to structure in the valence-conduction bands themselves. [See E. A. Taft and H. R. Philipp, *Bull. Am. Phys. Soc. Ser. II*, **4**, 45 (1959)].

Domain Structure of WO₃ Single Crystals*

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Transparent single crystals of WO₃, in the form of plates as large as 10 mm×10 mm, have been prepared by a sublimation method. The domain structure of these crystals was investigated from room temperature to 1350°C, and a new and peculiar domain structure was found between 740°C and 810°C. This domain structure is probably associated with the change in crystal structure from orthorhombic to tetragonal. Lattice parameters determined optically from measurements of the angle between extinction positions of two neighboring domains agreed well with those obtained by x-ray analysis. The shift in the absorption edge to the infrared at 740°C was observed to take place for light polarized in a direction perpendicular to the *c* axis, but not for light polarized parallel to the *c* axis.

I. INTRODUCTION

IN WO₃, there exists a strong possibility of the existence of ferroelectricity as in BaTiO₃, or of antiferroelectricity as in PbZrO₃, owing to its pseudo-cubic crystal structure, its several transition temperatures, its domain structure, and its high permittivity. A number of investigations¹⁻⁴ have been made to ascertain ferroelectricity or antiferroelectricity in WO₃, but no conclusive results have been obtained because of its high electrical conductivity and its volatility, which make measurements at high temperatures extremely difficult.

Recently, we have succeeded in getting large clear single crystals of WO₃, and have carried out a more thorough observation of their domain structure.

* This work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

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¹ B. T. Matthias and A. Wood, *Phys. Rev.* **84**, 1255 (1951).

² K. Hirakawa and T. Okada, *Mem. Fac. Sci. Kyusyu Univ. Ser. B* **1**, 1 (1951).

³ S. Sawada, *J. Phys. Soc. Japan* **12**, 1237 (1956).

⁴ S. Sawada, *J. Phys. Soc. Japan* **12**, 1246 (1956).

II. PREPARATION OF CRYSTALS

Crystals of WO₃ can be prepared by a sublimation method. Small crystals are found on the surface of powder put into a platinum or quartz crucible, when the temperature of the crucible is maintained at about 1350°C for a long time.^{5,6} Somewhat larger crystals are obtained when the vapor of WO₃ is condensed on a quartz disk maintained at an appropriate temperature.⁷ Crystals obtained by these conventional methods, however, have dimensions less than 2 mm and the size of the single domains is usually very small. With such small crystals much difficulty has been experienced in attempts to determine the anisotropy of the physical properties of WO₃.

We have succeeded in getting larger crystals by enclosing the powder in a platinum vessel as perfectly as possible. Since it is not easy to have a completely closed platinum vessel, a platinum crucible (diameter 7 cm,

⁵ R. Ueda and T. Ichinokawa, *J. Phys. Soc. Japan* **6**, 122 (1951).

⁶ S. Tanisaki, *J. Phys. Soc. Japan* **11**, 620 (1956).

⁷ R. Ando and S. Sawada, *Repts. Inst. Sci. and Technol., Univ. Tokyo* **4**, 223 (1950).