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OPTICAL PROPERTIES OF SEMICONDUCTORS UNDER HYDROSTATIC PRESSURE—I. GERMANIUM*

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Abstract—The room-temperature absorption spectrum of high-purity single-crystal germanium has been measured between absorption coefficients of 1 and 100 at hydrostatic pressures up to 7000 kg/cm². The results have been interpreted to give a pressure coefficient for the optical energy gap in satisfactory agreement with the more precise value determined from measurement of the intrinsic resistivity as a function of pressure.

INTRODUCTION

MEASUREMENTS of the variation of the electrical resistivity of germanium with pressure[1] can be interpreted to show that, up to pressures of 10,000 kg/cm², the thermal energy gap between the valence and conduction bands of this element increases uniformly with pressure at a rate of approximately 5×10^{-12} eV/dyne cm⁻². Consideration of the band structure of germanium, as established by the theoretical calculations[2] of HERMAN and his co-workers, and by the cyclotron resonance experiments† shows that this increase is due to an increase in the separation of a conduction band minimum in the (111) direction in the Brillouin zone, and a valence-band maximum in the (000) position.‡ (See Fig. 1). Complicated behavior involving the electrons in the (100) conduction band minimum is suggested by the data at pressures greater than 10,000 kg/cm².[1] We shall not elaborate on this here, since the work to be reported is at pressures up to but not exceeding 10,000 kg/cm². No calculation of the effect of pressure on the band edges predicting the sign and size of the change to be expected has been reported to date. It might be expected that the change
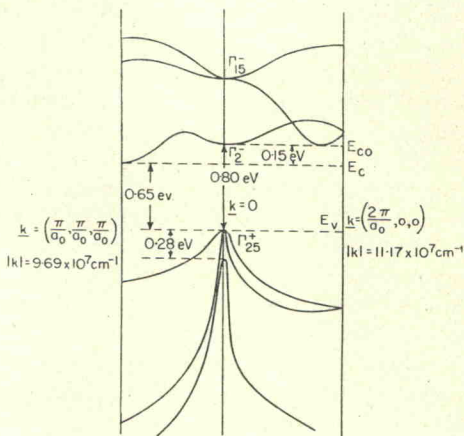

FIG. 1. Band structure of germanium.

in gap with pressure would be related to the electron and hole mobilities through a deformation potential theory.[3] An approximate attempt to derive such relations for germanium and silicon has been made by BROOKS[10] and the correlation found was fair. However, the complexity of the

band edge structure and of the full mobility theory have, up to the present, prevented a really quantitative correlation being arrived at between theory and experiment. At the moment we can but try to fit the results of the measurement of resistivity and other parameters into one consistent pattern.* For this, the measurement of the effect of pressure on the infrared absorption spectrum is of considerable interest. This has been briefly reported before.[5]

Similar measurements on silicon and on alloys of silicon and germanium of varying composition will be reported in Parts II and III of this series.

METHOD

It is necessary to discuss the experimental apparatus and technique in order to understand the nature and magnitude of the errors in the measurements to be presented.

A hardened-steel pressure vessel having two sapphire windows on an axis transverse to the central bore was used to subject the sample to hydrostatic pressure during optical-transmission measurements. An optically-polished plane-parallel slab of 30 Ω cm n-type germanium, 0·030 in. thick, was mounted in a mask-and-holder arrangement parallel to the window surfaces and approximately 1 mm from the nearer surface. The holder used brass shim "fingers" to hold the sample in place gently; this design was used to minimize the possibility of non-hydrostatic stresses on the germanium due to the difference in compressibility between holder and sample. At the end of the experiment, a check was made that the sample was in the same position as at the start; it was, and the assumption was made that it had not shifted its position reversibly during the experiment. The sapphire windows were sealed by the POULTER technique.[6] High pressure was produced by a press kindly provided by Professor BRIDGMAN.[7] The pressure was measured with a manganin gauge calibrated against the freezing-point of mercury. A Perkin–Elmer monochromator with a glass prism provided chopped monochromatic radiation which was directed through the vessel and sample by an auxiliary optical system. The

transmitted energy was detected by a cooled lead sulfide cell whose response was amplified and recorded by a 13 cycle Perkin–Elmer system. Carbon disulfide was used as the hydraulic fluid† in which the sample was immersed, because it was found to be the only common liquid meeting the requirements of transparency in the 1·5–2·5 micron infrared region and remaining liquid at room temperature up to 10,000 kg/cm².

The possible sources of error in the transmission measurements are:

(1) Source-intensity change with time.
(2) Source-spectral-dependence change with time.
(3) Detector-gain change with time.
(4) Detector-spectral-sensitivity change with time.
(5) Refractive-index changes with pressure:
    (a) Sample reflection correction.
    (b) Effect of sample-index change on beam geometry.
    (c) Change of index of refraction of fluid.
(6) Window distortion with pressure.
(7) Changes at reference wavelength (when used).
(8) Spectrometer resolution.

If a sample holder were available to move the sample in and out of the radiation beam during measurements at any given pressure, suitable and obvious procedures would allow for removal or minimization of error sources 1, 2, 3, 4, 6 and 7. Such a mechanism is now being built for use in this experiment, but it was not used in the present measurements. Another method of measuring the transmission was used for these data. A reference wavelength near the minimum of free carrier absorption was carefully chosen. Experimental runs of I (transmission with sample in vessel) were made at each pressure of interest, with the response always referred to the response at the reference wavelength. The sample was then removed and identical runs made of I_0 (vessel and fluid

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* For Hall-effect and magnetoresistance measurements, see BENEDEK et al.;[4] for optical data, see WARSCHAUER et al.[5]

† There are very few liquids which show no selective absorption whatsoever between 1 and 2 microns. Of the common liquids, carbon tetrachloride and freon freeze at pressures below 4000 kg/cm². Carbon disulfide remains both liquid and transparent, but its toxicity and low flash point demand extra precautions. The density of CS_2 in the experimental area was kept as low as possible. Also, because of the possibility of a fast pressure leak or even of rapid vaporization of the CS_2 in a pressure explosion, and of its ignition by the hot tungsten bulb of the optical apparatus, the room was carefully ventilated, and fire-hazard precautions followed.

transmission), again referred to the reference wavelength. It can be shown that I/I_0 is then a measure of the relative transmission of the sample within the errors mentioned above. Errors 1, 2, 3 and 4 have been demonstrated by separate experiment to be small when appropriate experimental precautions are taken. Error 6 is partially corrected, although a spectral effect arising from the birefringence of the sapphire may exist. In considering error 8, we note that the spectral slit width used in the experiments was 9×10^{-3} microns. It can be shown, as will be discussed in more detail in a subsequent paper on silicon, that neither the shape nor the movement of the absorption edge is affected by large changes in resolution, at least up to the value mentioned here. Errors 5(b) and 5(c) remain uncorrected only if there is a strong spectral-dependence of the fluid or sample refractive-index variation. Error source 5(a) is treated as follows:

It is unlikely that the change of index of refraction of germanium with pressure is large and has a strong spectral-dependence. The change of the refractive index with pressure, calculated from a translation of the refractive index versus frequency curve of BRATTAIN and BRIGGS[8] along the frequency axis by the amount of the energy gap change with pressure, is of the order of 1 per cent in 8000 kg/cm². Considering this to be small, the procedure outlined above yields a satisfactory measure of the relative transmission both at any given pressure and also at all pressures relative to one another. *Experiments* on the change of transmission at the reference wavelength with pressure indicate that both the reference wavelength transmission and that of wavelengths nearer the edge increase by the same amount, approximately 4 per cent from 1 to 8000 kg/cm². It is as yet undetermined whether this change occurs because of fluid or sample changes of refractive index. However, since these changes are very slow functions of wavelength, the relative transmissions are not affected. In the data to be presented, these relative transmissions have been normalized to absolute transmission, in order to allow computation of absorption coefficients needed by theory.

In practice, the reference wavelength chosen was 2·26 microns. It was determined that this wavelength, although very close to the absorption edge, gave I/I_0 results negligibly different from the experimentally less-accessible, longer reference wavelengths. The values of I, including those at 2·26 microns, were measured at convenient pressure intervals. The sample was then removed and the values of I_0 measured, with a determination at the reference wavelength included. Relative transmission was obtained from the ratio of I to I_0. Curves of n and k for germanium were then prepared from the literature[8] with a reasonable averaging of the data. The formula quoted by BRATTAIN and BRIGGS[8] for transmission was modified for our particular sample arrangement, and the absolute transmission at the reference wavelength computed. The relative transmissions at this wavelength were then normalized to the computed value. The formula was then used, in conjunction with the n and k curves, to determine the absorption coefficient; the small correction for reflection at the sample faces is automatically taken into account.

Absorption coefficient curves were determined several times, with slightly different assumptions. An exact calculation was made, using a suitable extrapolation of the data of BRIGGS,[8] in accord with the curve of refractive index versus wavelength of BRATTAIN and BRIGGS.[8] Subsequent calculations, using constant indices of 4·1 and 4·2, showed no significant difference from the first calculation, when applied to the atmospheric pressure data. The high-pressure curves of absorption coefficient were therefore computed using a constant
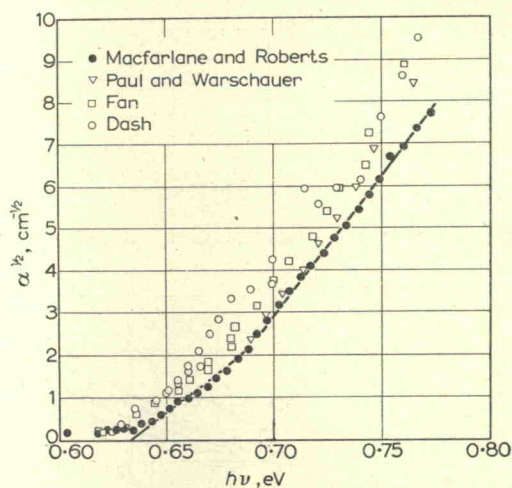

FIG. 2. Comparison of the germanium room-temperature low-absorption coefficients versus photon energy with the work of other investigators.

refractive index for germanium of 4·2. Fig. 2 compares our values of absorption coefficient at atmospheric pressure with those of other workers.

EXPERIMENTAL RESULTS

Fig. 3 shows the change in the absolute transmission as a function of wave-number, for several pressures between zero and 7000 kg/cm². The
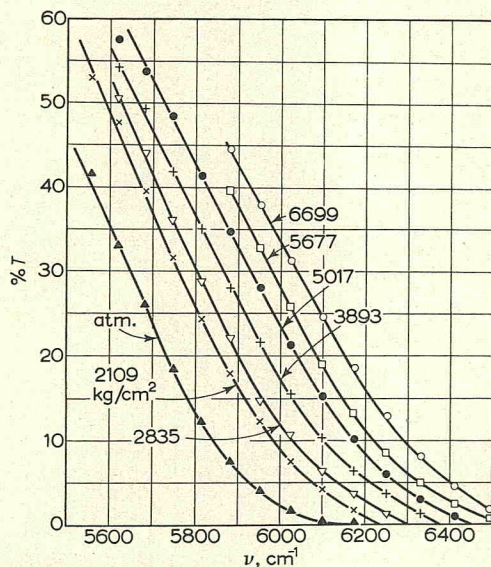

FIG. 3. Room-temperature transmissivity of a germanium sample versus wave-number at several pressures.

results clearly demonstrate a movement of the transmission edge toward higher wave number. The procedure outlined above is then applied to obtain Fig. 4, which shows the variation of absorption constant with the energy of the incident photon, for the chosen pressures.

Fig. 4 shows that there is a definite tendency for the shape of the curve of absorption coefficient α to change with pressure. This shape change will be more evident in later figures and will be interpreted in the next section.

Since some indication of the change in energy gap with pressure might be given by the horizontal shift of the absorption curves, Fig. 5 shows a set of isoabsorption curves. Pressure is plotted against photon energy, with α as a parameter. Apart from a slight scatter of the points, which is probably due to experimental error, the isoabsorption curves are straight lines. The slope of the isoabsorption lines varies from approximately 9×10^{-12} eV/dyne cm^{-2} to about 6×10^{-12} eV/dyne cm^{-2} at $\alpha = 3$.

It is to be noted that the interpretation of the low values of α is not obscured by the presence of appreciable free-carrier absorption, since this is considerably smaller at the frequencies of the measurement than the α values quoted.

Since the slope as $\alpha \to 0$ will correctly give the variation of the energy gap with pressure (apart from a possible correction for phonon energy changes discussed later), this variation must be
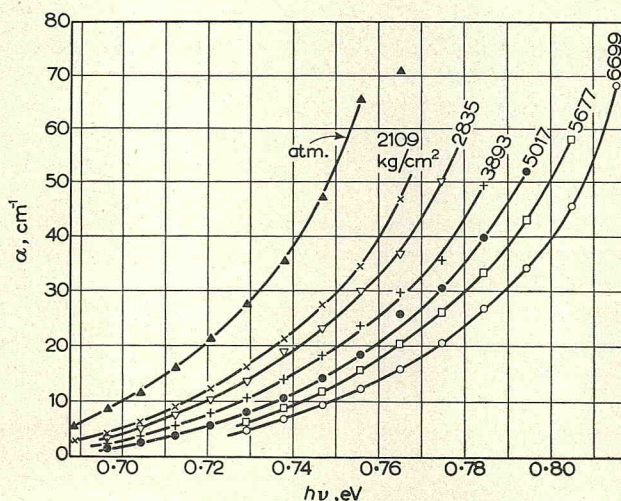

FIG. 4. Room-temperature absorption coefficient for germanium versus photon energy at several pressures.
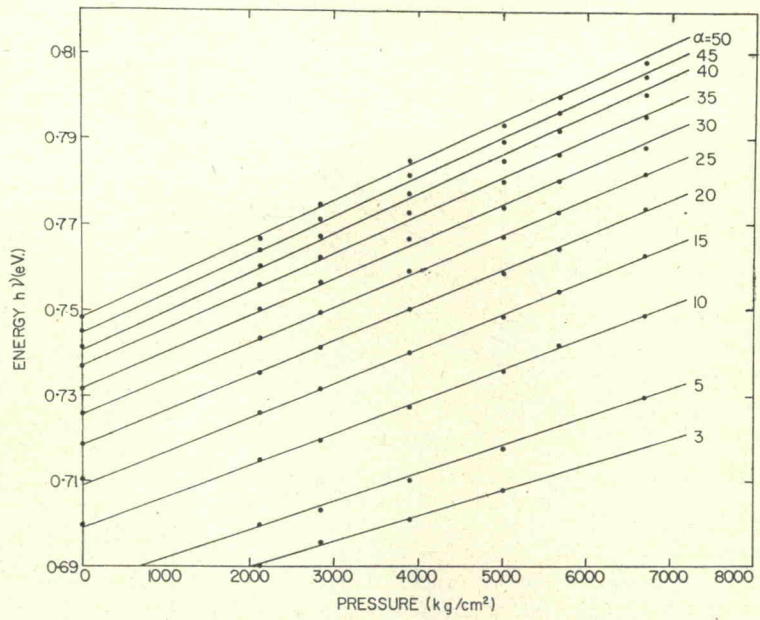
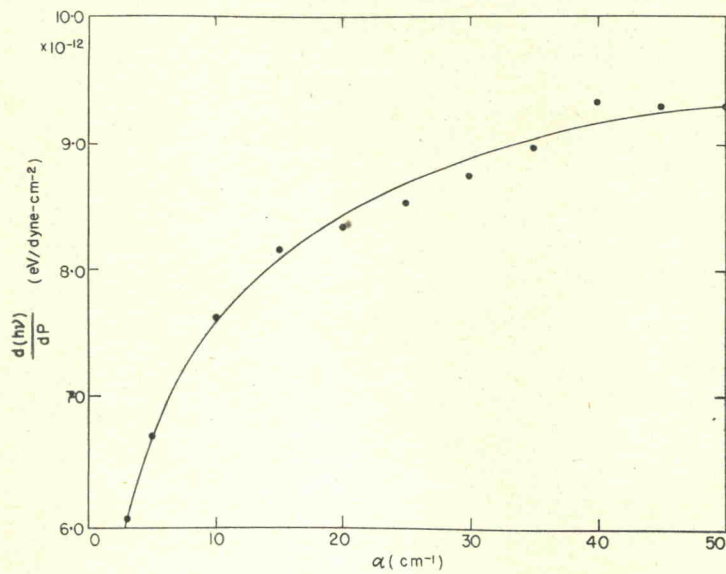FIG. 5. Isoabsorption curves for germanium at room-temperature.

FIG. 6. Variation with absorption coefficient of the slope of the
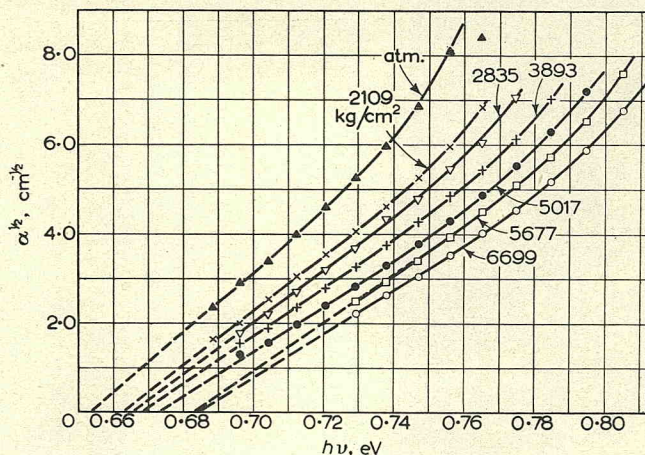isoabsorption lines shown in Fig. 5.

FIG. 7. Square root of absorption coefficient of germanium versus photon energy at several pressures.

less than 6×10^{-12} eV/dyne cm^{-2}. A more exact value requires a more reliable method of extrapolation than Fig. 6 would afford.

From the theoretical considerations of the next section, it appears that either $\alpha^{\frac{1}{2}}$ or $\alpha^{\frac{1}{3}}$ varies directly as $h\nu$ at low values of α. (Strictly speaking, $(\alpha\nu)^{\frac{1}{2}}$ or $(\alpha\nu)^{\frac{1}{3}}$ varies as $h\nu$, but for a limited range of ν our approximation will make little difference.) In Figs. 7 and 8 this is tested. From these figures alone it would appear that the $\alpha^{\frac{1}{3}}$ versus $h\nu$ curve is the better straight line. However, the apparent

deduction from this must be qualified; this will be discussed in the following section.

The straight-line fits to the data in Figs. 7 and 8 have been extrapolated, and the $\alpha = 0$ intercepts on the $h\nu$-axis plotted against pressure in Figs. 9 and 10. The results were checked by the method of least squares. It is clear from Figs. 7–10 that the intercepts show a fair amount of scatter, although there is no recognizable curvature. Nevertheless, the limits of the energy-gap change from Fig. 9 are approximately 3·9 and 4·7
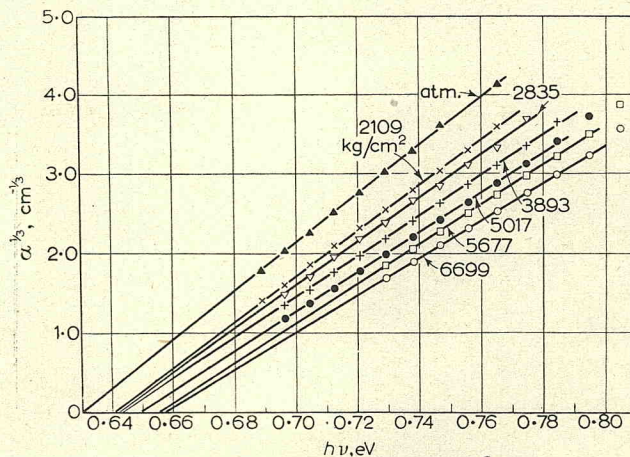

FIG. 8. Cube root of the absorption coefficient versus photon energy at several pressures.
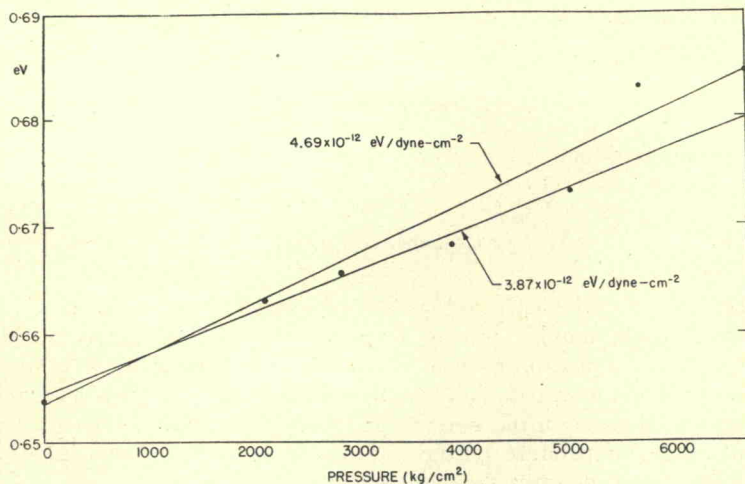
FIG. 9. Intercepts at $\alpha = 0$ from the $\alpha^{\frac{1}{2}}$ versus $h\nu$ curve of Fig. 7 plotted versus pressure.

eV/dyne cm^{-2}, and the change from Fig. 10 (where the line is straighter) is $4\cdot0 \times 10^{-12}$ eV/dyne cm^{-2}. This result is close to the value of $5\cdot0 \times 10^{-12}$ eV/dyne cm^{-2} found by PAUL and BROOKS.[1]

DISCUSSION

The general form of the absorption spectrum of germanium can be discussed in terms of the band-structure diagram of Fig. 1. The degeneracy of the valence band maxima E_v at the center of the Brillouin zone does not concern us. The conduction-band minimum at the center, E_{co}, is 0·80 eV above E_v.[9] The lowest conduction-band mini-

mum E_c is in the (111) direction in the Brillouin zone, about 0·65 eV above E_v[10] at 294°K. There is also a conduction-band minimum in the (100) direction about 0·15 eV above E_c, which becomes important in germanium–silicon alloys,[11] and is supposed to become the lowest minimum in germanium at high pressures.[1,12]

The main absorption corresponds to electrons making the $E_v \rightarrow E_{co}$ transition; at lower frequencies, absorption takes place by the $E_v \rightarrow E_c$ transition, the momentum probably being conserved by the absorption or emission of phonons. We observe the second process in our experiments.
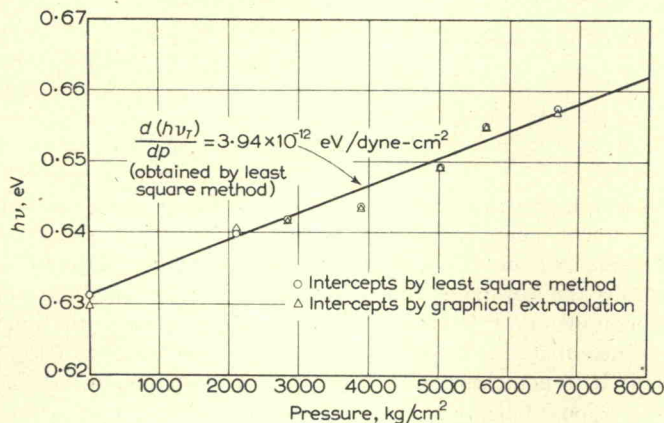

FIG. 10. Intercepts at $\alpha = 0$ from the $\alpha^{\frac{1}{2}}$ versus $h\nu$ curves of Fig. 8 plotted versus pressure.

BARDEEN *et al.*[13] obtain for this indirect or forbidden absorption the expression

$$\alpha = \frac{NM_s^2(2N_s+1)e^2(m_v m_c)^{3/2}f_{ia}(\Delta E)^2\langle(E_a-E_i)\rangle_{av}}{4\pi^2 ncm\hbar^6\nu\langle(E_a-E_f)^2\rangle_{av}} \tag{1}$$

when the $E_v{\rightarrow}E_{co}$ transition is allowed parity-wise, and

$$\alpha = \frac{NM_s^2(2N_s+1)e^2m_v(m_v m_c)^{3/2}(\Delta E)^3}{12\pi^2 ncm_T^2\hbar^6\nu\langle(E_a-E_f)^2\rangle_{av}} \tag{2}$$

when the $E_v{\rightarrow}E_{co}$ transition is forbidden.

In these expressions N is the number of conduction-band minima, M_s is a matrix element describing the electron-phonon interaction, N_s the number of the appropriate phonons in the Bose–Einstein distribution at the temperature of the crystal, m_v the valence band density-of-states effective mass, m_c the same mass for a conduction-band minimum, f_{ia} an oscillator strength for vertical transitions, n the refractive index, m the free electron mass, and ν the frequency of the incident radiation. m_T is an effective mass defined by BARDEEN *et al.*[13] as a convenience in describing parity-disallowed transitions. ΔE equals $h\nu-E_g$, where E_g is the forbidden-energy gap between E_c and E_v in Fig. 1. E_i is the initial state of the electron in the valence band, E_a the intermediate state in the conduction band, and E_f the final state. For the energy-band structure of Fig. 1,

$$\langle(E_a-E_i)\rangle_{av} \sim E_{co}-E_v$$

and

$$\langle(E_a-E_f)^2\rangle_{av} \sim (E_{co}-E_c)^2.$$

MACFARLANE and ROBERTS[14] have used a modified form of (1),

$$\alpha = A\left\{\frac{(h\nu-E_g+k\theta)^2}{e^{\theta/T}-1}+\frac{(h\nu-E_g-k\theta)^2}{1-e^{-\theta/T}}\right\}, \tag{3}$$

in fitting experimental results on germanium and silicon. They include the phonon energies $k\theta$ in their expression whereas BARDEEN *et al.*[13] ignore them. Coefficient A includes the constants and energy numerator and denominator of BARDEEN *et al.* Evidently it is assumed that the $E_v{\rightarrow}E_{co}$ transition is parity-allowed. It is not clear, from evidence on the indirect transitions alone, that this is so.[15] Plots of $\ln\alpha$ versus $\ln(\nu-\nu_t)$ where ν_t is the threshold frequency for absorption, might

be expected to resolve this point. Such plots involve an initial choice of ν_t, which is subject to critical errors, especially since it is complicated by phonon absorption. FAN *et al.*[15] have tried this, and found $n=2\cdot5$ in $\alpha\sim(\nu-\nu_t)^n$. Since the index is very sensitive to this choice, the deduced index is not too reliable.

It is clear that E_g can be obtained from equations (1) and (2) by plotting $\alpha^{\frac{1}{2}}$ or $\alpha^{\frac{1}{3}}$ against $h\nu$, and finding the intercept on the $h\nu$-axis at $\alpha=0$. If equation (3) is adhered to, the deduction is not as straightforward. When $E_g+k\theta > h\nu > E_g-k\theta$, absorption of radiation can take place only by the simultaneous absorption of a phonon of momentum sufficient to carry the electron from the center of the Brillouin zone to the position of the conduction-band minima. Then only the first term of equation (3) is operative, and the $\alpha=0$ intercept occurs when $h\nu=E_g-k\theta$. Since $k\theta$ is undetermined, this gives only an approximate value of E_g. When $h\nu > E_g+k\theta$, both terms in equation (3) are operative, and are of the same order of magnitude at room temperature. θ and A may be found from fitting complete absorption curves over a range of temperatures in a consistent fashion, assuming they are not functions of temperature. This is not really allowable, especially in the case of A, but there is no clear correction to apply. With θ known, E_g is determined.

MACFARLANE and ROBERTS[14] plot a curve of $\alpha^{\frac{1}{2}}$ versus $h\nu$ for $h\nu > E_g+k\theta$ and obtain a straight line. An analysis of this situation shows that the intercept of this line on the $h\nu$-axis at $\alpha=0$ is not simply E_g, but contains a second term in $k\theta$ and kT. The exact value of the intercept depends on how the straight line is fitted to the data. According to MACFARLANE and ROBERTS, $\theta=260°$K, which they deduced corresponds to the existence of eight minima in the conduction band about two-thirds of the way along the (111) axes to the

Brillouin zone boundary. Other evidence favors the location of the minima at the zone boundary.

If we assume that θ does not change with pressure* (which is not warranted *a priori*), and if we assume that we fit straight lines consistently to $\alpha^{\frac{1}{2}}$ versus $h\nu$ data, then the change with pressure of the $h\nu$ intercept at $\alpha = 0$ gives the pressure shift of the energy gap. If the correct law is not a law with squared terms on the right-hand side, but cubed terms, similar considerations apply.

It is straightforward to show that any one curve of $\alpha^{\frac{1}{2}}$ or $\alpha^{\frac{1}{3}}$ versus $h\nu$ where $h\nu > E_g + k\theta$ can be fitted equally well for $\theta = 260°$ or $\theta = $ (say) 360°, by changing the coefficient A slightly. We know of no good way of estimating A independently. BARDEEN et al.[13] tried to do this from the experimental value of the mobility, but this is a questionable procedure, since other phonons are involved. Certainly A is not known well enough to allow a distinction to be made between $\theta = 260°$ and $\theta = 360°$ on the basis of one experimental curve.

If data involving low values of α are available, information may be obtained, as indicated above, from extrapolation to $\alpha = 0$ and also by demanding a consistent fit of the slopes above and below the "knee" of MACFARLANE and ROBERTS' data.[14] However, we tend to think that the experimental accuracy demanded in this region is considerable and that the possible sources of error in the pressure measurements would preclude the obtaining of useful information. Reflection corrections are of prime importance in this region, and the variation in refractive index of both germanium and CS_2 with pressure is unknown. It also appears that interpretation of *reliable* α versus $h\nu$ curves may be troublesome. For example, in the measurements of MACFARLANE and ROBERTS, one curve of which is included in Fig. 2, the fit of the line in the region $0 < \alpha < 1$ is not particularly good.

Our data scan only a small range of α (1–100 cm⁻¹), at one temperature, where phonon emission and absorption take place simultaneously. It was not possible to measure higher values of α with the sample we used; at high values of α, however,

direct transition absorption is taking over, and the deductions made concern other inter-extrema transitions. Fig. 2 shows our data for α versus $h\nu$ at atmospheric pressure, plotted with those of other investigators. The general form of the curves is the same, but it is quite clear that quantitative information derived from the shape would not be consistent. Although our data are in reasonable agreement with those of the other investigators, we have not pressed for a determination of the absolute value of E_g (or $k\theta$), nor have we attempted to use the published values of A or θ in our interpretation, since we do not consider these sufficiently reliable at present. Instead, we have concentrated on the pressure coefficient of E_g and on changes in the coefficient A of equation (3). Fortunately, conclusions of value about these coefficients can be reached while uncertainty about the exact functional dependence of α still remains.

The isoabsorption curves of Fig. 5 and their slopes, as plotted in Fig. 6, indicate a shift of the absorption edge with pressure combined with a change in the shape of the edge. The value of the isoabsorption line slope at high values of α, about $8-9 \times 10^{-12}$ eV/dyne cm⁻², has been reported by us in a preliminary publication,[5] and is the value quoted for the change of the optical energy gap with pressure found by FAN et al.[15] and by NEURINGER.[16] The latter two investigations were carried out at pressures up to 1000 kg/cm⁻², and no change in the shape of the edge was mentioned, possibly because any change could not be positively identified in the small pressure range. We believe that the high value thus obtained is not to be interpreted as the gap change, and that from Fig. 6 alone this coefficient is less than 6×10^{-12} eV/dyne cm⁻². Since the pressure coefficient of the energy gap from measurements of the change of the intrinsic resistance is found to be about $5 \cdot 0 \times 10^{-12}$ eV/dyne cm⁻², the lower values are more plausible still.

Bearing in mind that the theoretical law for the absorption coefficient is not substantiated because there are uncertainties in the size of the phonons involved and in the application of $\alpha^{\frac{1}{2}}$ and $\alpha^{\frac{1}{3}}$ curves, and that possible changes of $k\theta$ with pressure must be ignored, we examine Figs. 7 and 8. It appears that the $\alpha^{\frac{1}{3}}$ versus $h\nu$ curve is the better straight line. We do not believe, however, that this warrants the conclusion that the appropriate law for α

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* We have estimated the change in Θ from the compressibility of germanium and data on the change in ultrasonic wave velocity with pressure given us by Dr. MARTIN BAILYN of Northwestern University. The change is about an increase of 3 per cent in 10,000 kg/cm² and is considered small enough to neglect here.

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contains cubed terms such as $(h\nu - E_g \pm k\theta)^3$. In the first place, very small changes in α, in the form of additive corrections due to errors in normalization, can alter the fit of the points to a straight line very considerably. This is true even though our absolute values for α are close to those of other investigators. In the second place, the assumption of a single interacting phonon for momentum conservation, and of one set of selection rules for vertical transitions, to explain absorption coefficients ranging over approximately 0.1 eV in photon energies, is probably an oversimplification. Nevertheless, if the laws have approximate validity, the pressure coeffi-

lines are found for n ranging from, say, $n = 1.5$ to $n = 3.5$. However, having obtained a set of corresponding n and ν_t for each pressure, ν_t can be plotted against pressure for any chosen n. The results show that the pressure coefficient, which is not too sensitive to the choice of n between 2 and 3, is about the same as that determined from the $\alpha^{\frac{1}{2}}$ or $\alpha^{\frac{1}{3}}$ curve intercepts. This method of determination is not a sensitive one, and is not recommended. We quote it only to illustrate that all these methods of analyzing the results give pressure coefficients near 5×10^{-12} eV/dyne cm^{-2}, in agreement with the electrical value.
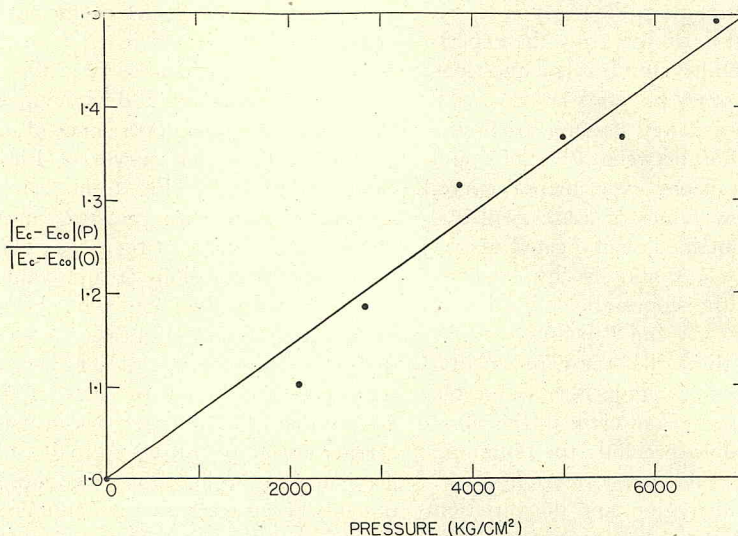

FIG. 11. Variation of the energy gap $(E_c - E_{co})$ with pressure.

cient of the energy gap as deduced from the $h\nu$ intercepts at $\alpha = 0$ has equal validity. The intercepts, as seen from Fig. 7 and 8, give a value for the gap change of 4×10^{-12} eV/dyne cm^{-2} which is in not unsatisfactory agreement with the electrical value. Interestingly enough, roughly the same value is obtained from either law.

A slightly different method of finding the energy-gap change has been tried by us. Suppose the law $\alpha = B(\nu - \nu_t)^n$ holds, with n assumed unknown. First, we can plot $\ln \alpha$ versus $\ln(\nu - \nu_t)$ with ν_t as parameter, at each pressure. The resultant curves are nearly straight lines whose slopes give values for n. It is not in practice easy to say what n should be from these graphs, since equally good straight

The method of interpretation above would indicate that the coefficient A of equation (3), which is given by the expressions of equation (1) or (2), is changing with pressure. This is clearly reasonable from an examination of the parameters in the coefficient.

The phonon matrix element M_S^2 may be changing with pressure, but we have no way of predicting its behavior. The phonon density N_S may change because of a change of the vibrational spectrum of germanium, or because of an alteration in the position of the (111) minimum, but again we have no way of predicting the effect. The effective masses can also change, but this change we know to be small from pressure experiments on the

mobility of electrons and holes. Any change in refractive index near the edge has not been investigated experimentally yet. However, all the above changes, if they occur, are expected to be smaller than the changes in the values of $E_{co}-E_c$ and $E_{co}-E_v$. The change of E_c-E_v is given by the gap change deduced from electrical-resistivity measurements, or less certainly by the interpretation of the optical results presented above. The change in $E_{co}-E_v$ can be found approximately from the experimental work of FAN et al.[15] or of NEURINGER,[16] which would give

$$d(E_{co}-E_v)/dp = 1 \cdot 2 \times 10^{-11} \text{ eV/dyne-cm}^{-2}.$$

This would make $d(E_{co}-E_c)/dp \approx 7\text{–}8 \times 10^{-12}$ eV/dyne cm^{-2}. We can now show that the present work gives indirect confirmation of this picture.

If we can assume a law of the form of equation (2), then we can write

$$\alpha = A(P)(h\nu - h\nu_t)^3 \qquad (4)$$

so that the slopes of curves of $\alpha^{\frac{1}{3}}$ versus $h\nu$ at several pressures give the variation of $A(P)^{\frac{1}{3}}$ with P. If we then assume $A(P) \propto 1/(E_{co}-E_c)^2$, we can find the variation of $E_{co}-E_c$ with P. This is presented in Fig. 11. There is considerable scatter to the points; however, the change is nearly 50 per cent in $E_{co}-E_c$ (atmospheric pressure) in 7000 kg/cm^2. Since the atmospheric pressure separation of E_{co} and E_c is about 0·15 eV, the pressure coefficient of $E_{co}-E_c$ is then approximately 1×10^{-11} eV/dyne cm^{-2}. Considering the assumptions involved, this is satisfactory agreement.

If we assume instead of equation (4) a law of the form

$$\alpha = A(P)(h\nu - h\nu_t)^2, \qquad (5)$$

where $A(P) \propto (E_{co}-E_v)/(E_{co}-E_c)^2$, we can again find $d(E_{co}-E_c)/dp$ by using the slopes of $\alpha^{\frac{1}{2}}$ versus $h\nu$ curves. As we saw, our data do not fit equation (5) very well. However, we do obtain order-of-magnitude agreement with 1×10^{-11} eV/dyne cm^{-2}.

CONCLUSIONS

Despite the fact that our determination of the absorption coefficients at atmospheric pressure is less direct than is usual because the sample has to be inside a pressure vessel, our curve of absorption coefficient versus photon energy is very similar to that published by other workers. It is apparent, however, that all the published curves of absorption coefficient are in qualitative but not quantitative agreement. The deduced energy gap will be approximately the same for each of these curves, but the phonon energy involved in the indirect transition process will not. In view of the importance attached to the deduction of the location of the conduction-band minima in establishing correct statistics for the carrier distributions, and in setting up a mobility theory for the germanium conduction band, it seems that the absorption curve found by MACFARLANE and ROBERTS[14] should be verified. This should be done preferably with high-purity single-crystal material to avoid the possibility of indirect transitions induced by imperfections and to reduce the free-carrier absorption background. MACFARLANE and ROBERTS' crystals were polycrystalline.

It may be difficult to obtain precise information from a *correct* absorption coefficient curve by the method used by MACFARLANE and ROBERTS. The theory assumes a single interacting acoustical phonon, whereas it is clear that beyond the foot of the absorption edge, lower-energy acoustical phonons can participate. It is not clear why transverse acoustical phonons and optical phonons are excluded at room temperature.

The law assumed by MACFARLANE and ROBERTS gives $E_g - k\theta$ as an intercept on the $h\nu$ axis at $\alpha = 0$ when the lower points on an experimental curve are extrapolated. These points are subject to considerable experimental error and, moreover, sometimes do not give a good straight line on which to perform the extrapolation. As is evident from an examination of Fig. 2, E_g cannot be assumed from electrical data in order to determine $k\theta$, since the value of E_g found from such data depends on a decision regarding four or eight minima in the conduction band. If eight minima are assumed, the thermal-energy gap is close to 0·673 eV. This would make the value of $k\theta$, required from MACFARLANE and ROBERTS' curves, about 0·040 eV, which is appreciably higher than the present estimate of $k\theta$ (Debye) = 360°K. If four minima are assumed, the thermal-energy gap is about 0·655 eV, making $k\theta = 0·022$ eV, or $\theta \approx 260$°K. This is smaller than $k\theta$ (Debye). It is not impossible that $\theta = 260$°K represents a fair average value for the energy of the interacting phonon, but that a better

knowledge of the vibrational spectrum for germanium will show that this phonon energy is consistent with the existence of minima at the Brillouin-zone boundary. The higher absorption coefficients (above the knee in MACFARLANE and ROBERTS' curve) cannot be extrapolated to give an intercept at $\alpha = 0$ independent of $k\theta$ and kT. An attempted fit of the absorption curve, above and below the "knee" may yield all the unknown parameters, but with doubtful correctness. If absorption curves at different temperatures are used, as by MACFARLANE and ROBERTS, then either the individual temperature curves must be analyzed separately or together. If done separately, the above remarks apply to each. If considered together, there is a net simplification only if: (1) $k\theta$ is assumed independent of temperature, which is probably reasonable; (2) the coefficients in equation (3) are assumed independent of temperature, which is not strictly correct. The coefficient A may depend on temperature through N_s, n, m, $E_{co} - E_c$, and $E_{co} - E_v$.

Because of the uncertainties in the exact expression for the absorption coefficient, the lack of quantitative agreement in the published absorption coefficient results, and the difficulty of a really reliable deduction of E_g and $k\theta$ from the experimental curves, we concentrated on finding the pressure coefficients of the different energy gaps independent of the gaps themselves.

From the change of the slope of the isoabsorption plots alone, we deduce that the variation of the energy gap $E_c - E_v$ with pressure is less than 6×10^{-12} eV/dyne cm^{-2}, which in itself can be compared with the pressure coefficient found from measurements of the intrinsic resistivity of $5 \cdot 0 \times 10^{-12}$ eV/dyne cm^{-2}. This agreement is not found by other workers. FAN et al.,[15] for example, find 8×10^{-12} eV/dyne cm^{-2} for this gap change. Since this agrees with the slope of our isoabsorption curves at high absorption coefficient and the range of pressure in FAN's experiment was so small (900 kg/cm^2) that a change in shape of the absorption edge might not be identifiable, we believe FAN's result and ours can be easily reconciled. NEURINGER[16] has recently reported a change of 8×10^{-12} eV/dyne cm^{-2}, at pressures, up to 1000 kg/cm^2, but he also finds no shape change, possibly for the same reason that FAN found none. He deduces, on the basis of the same type of analysis as

we perform, that this value represents the true energy-gap coefficient. It is hard to see what physical mechanism would give a pressure coefficient for an optical energy gap different from that for a thermal one. On this basis alone, a lower value is more plausible.

A more exact deduction of the energy gaps can be made by applying the correct theory for the absorption coefficient. We have tried to show above the difficulties inherent in this procedure at the moment. Nevertheless, we have analyzed our data after the fashion dictated by equations (1)–(3), in the hope that useful qualitative information can be found, from the general pattern of the deductions. In doing this, we realize that we add several dubious assumptions to those already made. We have to assume pressure independence of θ. Furthermore, if equation (3) is followed, various straight lines can be fitted to $\alpha^{\frac{1}{2}}$ versus $h\nu$ or $\alpha^{\frac{1}{3}}$ versus $h\nu$ curves, depending on the part of the curve being fitted, and these will give different intercepts on the $h\nu$-axis at $\alpha = 0$. We know, since the shape of the absorption curve is changing with pressure, that we are probably fitting different parts of the curve at different pressures, and that the intercepts will not be the same combination of E_g, θ, and T. This is accepted as contributing to the spread of the points in Figs. 9 and 10, for example. For the energy gap $E_c - E_v$, the pressure coefficient is about 4×10^{-12} eV/dyne cm^{-2}; this is in fair agreement with the thermal value. It is probable that the pressure coefficients of the optical and thermal energy gaps will be brought into exact agreement by the application of more correct expressions for the absorption coefficient. In this connection we note that the coefficient found by PAUL and BROOKS[1] may be reduced if the electron mobility pressure coefficient is temperature-dependent.

Still more assumptions have to be made when the pressure coefficients of $E_{co} - E_c$ and $E_{co} - E_v$ are deduced. However, the order-of-magnitude agreement with direct measurements of the shift of the absorption edge for direct transitions is to be noted.

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