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Effect of Pressure on the Infrared Absorption of Semiconductors*†

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Measurements have been made of the effect of hydrostatic pressure upon the intrinsic infrared absorption of germanium, silicon, and tellurium in the pressure range 1–2000 atmospheres. In germanium the variation with pressure of the lowest lying conduction band minimum, (111), is found to be $(7.3\pm1.5)\times10^{-6}$ ev/atmos. It is suggested that the variation with pressure of the next highest conduction band edge, (000), has a value of $(11\pm3)\times10^{-6}$ ev/atmos. The shift of the infrared absorption edge with pressure in silicon is small and is toward smaller energy, amounting to about -2×10^{-6} ev/atmos between 1 and 2020 atmospheres. The sign and magnitude of the pressure coefficient in this material are in agreement with the results of Warschauer, Paul, and Brooks. For tellurium both $E_{g\perp}$, the energy gap corresponding to light polarized perpendicular to the *c*-axis of the crystal, and $E_{g\parallel}$, the energy gap for polarization parallel to the *c*-axis, decrease as the pressure is increased. It appears that $E_{g\perp}$ decreases more rapidly with pressure than $E_{g\parallel}$. The mean pressure coefficient of $E_{g\perp}$ is $-(2.2\pm0.4)\times10^{-5}$ ev/atmos. For $E_{g\parallel}$ the mean pressure coefficient is $-(1.8\pm0.3)\times10^{-5}$ ev/atmos. The measured pressure coefficients are used to calculate the thermal dilation term in the equation for the change of the energy gap with temperature for each material. The electron-lattice interaction term appearing in this equation is then deduced. In silicon these two terms are of opposite sign with the electron-lattice term dominant. In germanium the electron-lattice interaction effect accounts for 75% of the effect of temperature on the energy gap. For tellurium the two effects are almost equal in magnitude but of opposite sign.

1. INTRODUCTION

RECENTLY the techniques[1] of high pressure have been applied to a variety of solid-state problems. In semiconductors most of the work has been directed towards deducing the variation with pressure of the forbidden energy gap,[2–8] density of states effective masses,[7–9] and mobilities.[7,9,10] The experimental procedure has been to measure the pressure-induced changes in the conductivity, Hall coefficient, and magnetoresistance of the various semiconductors. In this paper we shall present measurements of the pressure variation of the intrinsic infrared absorption of germanium, silicon, and tellurium. Experiments of this type were first reported in 1954, and almost simultaneously, by the groups working at Purdue University,[11] Harvard University, and the University of Pennsylvania.[12]

In some cases it is not possible to study an energy gap change with pressure by purely electrical experiments. Thermal excitation promotes electrons to the lowest lying edge in the conduction band. Therefore, if a material possesses another conduction-band edge somewhat higher in energy, it cannot be studied under ordinary circumstances[13] by electrical measurements. On the other hand, optical excitation of carriers, provided transitions of electrons to these states are allowed, offers a method of investigating these higher lying bands. This is the case in germanium for the (000) conduction-band minimum and in tellurium for $E_{g\parallel}$, the energy gap corresponding to radiation polarized parallel to the *c* axis of the crystal.

Another aspect to these experiments was furnished by the evidence[14] that in polar semiconductors and in CdS the temperature variation of the energy gap, $(\partial E_g/\partial T)_P$, cannot be accounted for solely in terms of a thermal expansion of the lattice. It is necessary to include a term which represents the explicit temperature dependence of the energy gap arising from the electron-lattice interactions.[15,16] Thus, a change in temperature effects the energy gap by altering the lattice constant and further introduces a perturbation in that the excited electrons interact with phonons and produce a shift in the electronic energy levels. We have measured the pressure coefficient of the energy gap, $(\partial E_g/\partial P)_T$. This variation with pressure of the energy gap can be

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[1] P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, Ltd., London, 1946).

[2] P. H. Miller, Jr., and J. Taylor, Phys. Rev. **76**, 179 (1949); J. Taylor, Phys. Rev. **80**, 919 (1950).

[3] Hall, Bardeen, and Pearson, Phys. Rev. **84**, 129 (1951).

[4] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).

[5] W. Paul and G. L. Pearson, Phys. Rev. **98**, 1755 (1955).

[6] R. W. Keyes, Phys. Rev. **99**, 490 (1955).

[7] Benedek, Paul, and Brooks, Phys. Rev. **100**, 1129 (1955).

[8] J. Taylor, Phys. Rev. **100**, 1593 (1956); Bull. Am. Phys. Soc. Ser. II, **1**, 111 (1956).

[9] D. Long, Phys. Rev. **99**, 388 (1955); **101**, 1256 (1956).

[10] A. C. Smith, Bull. Am. Phys. Soc. Ser. II, **3**, 14 (1958).

[11] Fan, Shepherd, and Spitzer, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley and Sons, Inc., New York, 1956), p. 184.

[12] See discussion following paper of reference 11.

[13] The work of Paul and Brooks[4] and of F. Herman, Phys. Rev. **95**, 847 (1954), suggests that in germanium the (100) conduction-band minumum may lie lower in energy than the (111) minimum at sufficiently high pressures and should therefore be susceptible to electrical measurements.

[14] R. Seiwert, Ann. Physik **6**, 241 (1949); A. Radkowsky, Phys. Rev. **73**, 749 (1949).

[15] H. Y. Fan, Phys. Rev. **78**, 808 (1950); Phys. Rev. **82**, 900 (1951).

[16] T. Muto and S. Oyama, Progr. Theoret. Phys. (Kyoto) **5**, 833 (1950).

used to obtain the contribution of thermal dilation to the temperature coefficient of the energy gap, $(\partial E_g/\partial T)_P$. Using the known value for $(\partial E_g/\partial T)_P$ and the measured value of $(\partial E_g/\partial P)_T$ the electron-lattice interaction term can be deduced experimentally.

2. EXPERIMENTAL

A. Apparatus

The pressure vessel consisted of a steel cylinder with provision to accommodate a $1\frac{1}{2}$-inch diameter ram at its top, synthetic sapphire windows and a manganin wire pressure gauge. Pressure on the ram was generated by a commerically available hydraulic pump (Blackhawk, Model P76), capable of producing a maximum pressure of 670 atmospheres. Pressure multiplication was achieved by having the ram act upon a $\frac{1}{2}$-inch diameter piston.

In the initial phases of this work a conventional-type piston intensifier[1] with *T*-head and packing utilizing the unsupported area principle was used. With this piston, pressures approaching 5000 atmospheres were attainable, the limit being set by the hydraulic pump. However, the $\frac{1}{2}$-inch diameter bore which accommodates the piston expands with use, making necessary the inconvenience of regrinding the bore, piston, and piston head. It was found that a simpler piston head could be used satisfactorily up to about 2500 atmospheres. This was a solid stainless steel cylinder with three O-rings fitted in annular grooves spaced $\frac{1}{8}$ apart along its length. The piston, too, was made of stainless steel. This was convenient inasmuch as the piston and the head can be machined rather quickly, they need not be hardened and the bore does not have to be reground. Nevertheless, this reduced pressure range was still sufficient for these experiments.

The direction of the optical beam was transverse to the $\frac{1}{2}$-inch bore of the pressure vessel. A sample holder consisting of a brass cylinder was made to fit snugly in the transverse hole which the light beam traversed. One end of this cylindrical sample holder had a base with two holes of identical aperture in it. One of these holes was covered by the sample under investigation, the other serving as a reference for the intensity transmitted by the sample. The pressure vessel was mounted securely on a sliding baseboard which provided for translational motion in a direction perpendicular to the light beam. In this fashion the light could be made to fall on the sample or on the reference hole. This apparatus thereby furnished a simple, accurate method for performing sample in—sample out transmission measurements with the sample mounted within the pressure vessel.

The pressure gauge was a 300-ohm manganin wire coil which was calibrated by determining its resistance at 2068 atmospheres, the pressure of transition of water from ice I to ice III at $-23°$C.[17]

The hydrostatic fluid to be used in an experiment of this type must satisfy rather stringent requirements: (1) it must be transparent in the near infrared, (2) it must be chemically inert to rubber, steel, sapphire, and the sample under investigation, and (3) it must transmit pressures hydrostatically up to several thousand atmospheres. The fluids used in these experiments were Freon-113, (CCl_3F_3), produced by duPont and one of the 200 series of silicone oils manufactured by Dow Corning. The silicone oil chosen had a viscosity of 20 centistokes and could be used over the pressure range realized with the pressure bomb. The undesirable feature of Freon-113 is that it freezes at roughly 1200 atmospheres, thereby setting an upper limit to the hydrostatic pressure attainable with it. The high-pressure seals at the sapphire windows and at the pressure gauge plug were provided by neoprene O-rings.

The optical apparatus which was assembled for the tellurium experiments consisted of a Beckman monochromator equipped with a rock salt prism, Nernst glower, and Perkin-Elmer radiation thermocouple detector. Because of the order in which the experiments were performed, this system was also used for the germanium work. For silicon a Beckman DU monochromator using a tungsten bulb as source and a dry-ice-cooled PbS cell (Eastman Kodak) as a detector was used.

B. Sample Preparation

All the samples used in these experiments were ground and polished by the author. The samples were mounted following the method of Dash and Newman.[18] The sample was ground using various grits of carborundum until the desired thickness was obtained. Germanium and silicon were polished on pitch laps using successively grade *A* and grade *B* Linde alumina. The mechanical properties of tellurium create several problems because of its softness and brittleness. It was mandatory, therefore, to use nothing coarser than No. 400 grit and to proceed with the grinding very slowly. Also a 50% beeswax—50% resin lap was used for the first stage of polishing. The final polishing was done on a canvas cloth drawn taut over an optical flat. By using these techniques, optically flat tellurium samples of 0.025-cm thickness could be prepared. Each sample was checked for flatness by placing an optical flat in contact with its surface and observing the shape of the fringes produced by a sodium vapor lamp. The thickness of the sample was determined with a 0.1 mil per division micrometer caliper. For further experimental details the author's thesis[19] should be consulted.

3. MEASUREMENT PROCEDURE

For each material studied the entire range of absorption coefficients was determined from transmittance

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[17] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **47**, 441 (1912).

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

[19] L. J. Neuringer, Ph.D. thesis, University of Pennsylvania, 1957 (unpublished).

measurements on a single specimen. Taking into account multiple reflections, the expression for the absorption coefficient, $\mu(E)$, is

$$\mu(E)=\frac{1}{d}\left[\ln R_0(E)+\cosh^{-1}\left(\frac{[1-R_0(E)]^2}{2R_0T(E)}\right)\right], \qquad (1)$$

where $T(E)$ is the measured transmittance, $R_0(E)$ is the reflection coefficient at a single sample-air interface, d is the specimen thickness, and E is the incident photon energy. The values to be substituted for $R_0(E)$ in the case of germanium and silicon were derived from Briggs'[20] measurements of the index of refraction by minimum deviation. For tellurium, $R_0(E)$ was computed from Hartig's[21] dispersion curves for both directions of polarization of the incident radiation. Because of the method of averaging used in deriving the equation for the absorption coefficient, its magnitude at the extremely low values may be in error by a few percent[22] but this does not alter the general results to any appreciable degree.

In order to determine the pressure variation of the absorption coefficient three basic experiments must be performed, since the sample is surrounded by the hydrostatic fluid whose index of refraction in the infrared is unknown. In Experiment 1 the transmittance of the sample is measured in its mounted position within the pressure vessel with the sapphire windows and their retaining plugs in place in the *absence* of any hydrostatic fluid. From these data the absorption coefficient is calculated from Eq. (1). This represents the atmospheric pressure data. Experiment 2 is the same as Experiment 1 except now the hydrostatic fluid has been added. Equation (1) for the absorption coefficient is solved for $R(E)$, the reflection coefficient of a single sample-fluid interface at atmospheric pressure. This quantity is then determined by substituting the measured transmittances of Experiment 2 and the absorption coefficients derived from Experiment 1. Experiment 3 is the high-pressure experiment and it is assumed that $R(E)$ is independent of pressure. The absorption coefficients calculated from Experiment 3 represent the high-pressure data.

Other effects which may arise at the elevated pressures are changes in the geometry of the vessel and changes of index of refraction of the fluid. The former might increase the optical path through the fluid by introducing more of it, but this would cancel out, as would any possible defocussing effects, because of the symmetry and the method of performing the measurements. To the author's knowledge there is no experimental data on the variation of the index of refraction with pressure of nonpolar liquids at infrared frequencies. The only information of this sort available are some measurements of Danforth[23] in the range 1–12 000 atmospheres of the pressure variation of the dielectric constant of several fluids, among them carbon disulfide. At a frequency of 3000 $\sec^{-1}$ and at 30°C he found an increase of 8% in the dielectric constant for 1000 atmospheres. At 2.0 microns this corresponds to a decrease of $R(E)$ by less than 1% for 1000 atmospheres, assuming that the refractive index of the sample does not change. This is insignificant as soon as the sample starts absorbing even to a slight degree. Furthermore, the transmittance of the fluid at the elevated pressure relative to atmospheric pressure was very nearly unity, so that certainly no striking effects are noticeable. Nevertheless, it would be very desirable, and in fact necessary, to know exactly what the pressure variation of the refractive index of the fluid and sample are, in order to place the optical experiments on more accurate ground.

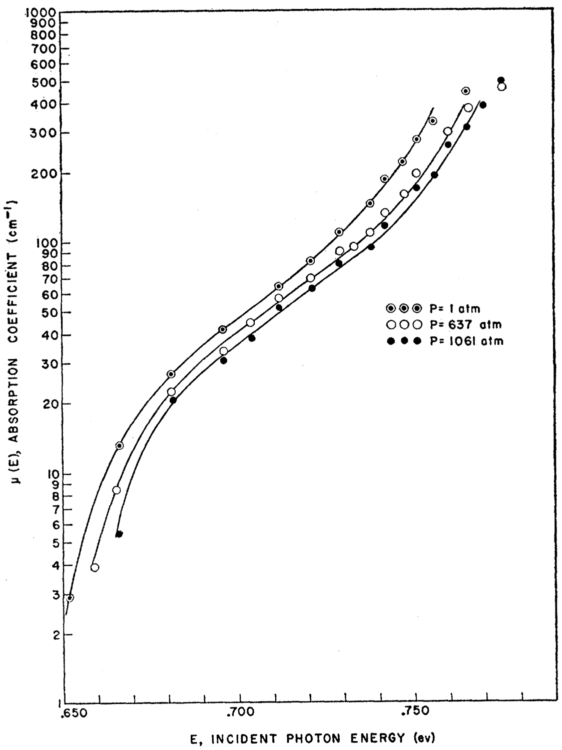

FIG. 1. Effect of pressure on the optical absorption of germanium.

4. RESULTS

A. Pressure Experiments

(*i*) *Germanium*

The sample used was a *p*-type single crystal with a resistivity of approximately 35 ohm-cm and was provided by the Philco Corporation. It had a thickness of 0.0127 cm and parallel faces. Its surfaces were flat to better than one wavelength of sodium light. Freon-113 was used as the hydrostatic fluid to a maximum pressure which was well below its freezing point. In Fig. 1 the absorption coefficient is plotted semi-

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[20] H. B. Briggs, Phys. Rev. **77**, 287 (1950).

[21] P. A. Hartig and J. J. Loferski, J. Opt. Soc. Am. **44**, 17 (1954).

[22] F. Stern (private communication).

[23] W. E. Danforth, Jr., Phys. Rev. **31**, 1224 (1931).

logarithmically against incident photon energy at atmospheric pressure and at pressures of 637 and 1061 atmospheres. It is seen that increasing the pressure causes the curves to shift to larger photon energies. This shift does not appear to be constant over the entire range of absorption coefficient. Above 100 cm^{-1} the shift is somewhat larger. This is in agreement with the data of Fan, Shepherd, and Spitzer[11] although they do not discuss this portion of the absorption edge in their paper.

(*ii*) *Silicon*

The motivation for the pressure experiment on silicon arose from the divergent results obtained by two groups of investigators. Warschauer, Paul, and Brooks[24] found a value of about -2×10^{-6} ev/atmos for the shift of the absorption edge, whereas Fan, Shepherd, and Spitzer[11] measured $+5\times10^{-6}$ ev/atmos which is not only different in magnitude but opposite in sign. The latter result is surprising in view of the resistivity measurements as a function of pressure Performed by Taylor[25] and by Paul and Pearson[5] which indicate that the energy gap *decreases* at a rate of -1.5×10^{-6} ev/atmos.

In our experiments the sample was a *p*-type single crystal with a resistivity of about 50 ohm-cm furnished by the Philco Corporation. It had a thickness of 0.021 cm. Silicone oil was the hydrostatic fluid used in this experiment. The lowest pressure at which a systematic shift over the entire wavelength range of the absorption edge was observed was at 2020 atmospheres. The shift in silicon has been remeasured by Paul and Warschauer[26] using a grating monochromator and the value so deduced is -1.3×10^{-6} ev/atmos. Our results are shown in Fig. 2, where transmittance is plotted against incident photon energy at atmospheric pressure and at 2020 atmospheres. The transmittance at the latter pressure is taken with the fluid at 2020 atmospheres as reference, indicating that the observed displacement of the curves is a property of the silicon and not the fluid. This experiment was repeated on many separate occasions and each time the sample was removed from the pressure vessel and the vessel itself taken out of the optical beam before repeating the experiment. Furthermore, a lead sulfide cell was used as the detector making it possible to close the slit to 0.035 mm. According to the manufacturer's claims the monochromator should have a resolution of 0.008 ev at this slit setting. Because the shift is so small we have purposely refrained from applying all the corrections previously described which are required to convert the data to absorption coefficient. It is seen from Fig. 2 that the high-pressure curve has moved to smaller photon energies indicating that the energy gap *decreases* as the pressure is increased.

(*iii*) *Tellurium*

Tellurium crystallizes in an unusual hexagonal structure,[27] the atoms being arranged in spiral chains which are oriented along the *c* axis of a hexagon. The adjacent chains are held together weakly as manifested by the ease with which single crystals cleave along a direction parallel to the *c* axis. The anisotropic character of its crystal structure further betrays itself in the magnitudes and signs of the thermal expansion coefficients and compressibilities. Thus, heating or exerting pressure on tellurium causes it to expand in a direction parallel to the *c* axis and contract in the plane of the *a* axis.

Tellurium and selenium are the only elemental anisotropic semiconductors whose properties have been studied experimentally.[9,28] Recently, they have received considerable attention from a theoretical point of view.[29]

The samples used in these experiments were grown in this laboratory by D. Long and were *p* type. Their resistivity measured parallel to the *c* axis was 0.3 ohm-cm. The sample used for the pressure experiment on $E_{g\parallel}$ was 0.035 cm thick and that used for $E_{g\perp}$ was

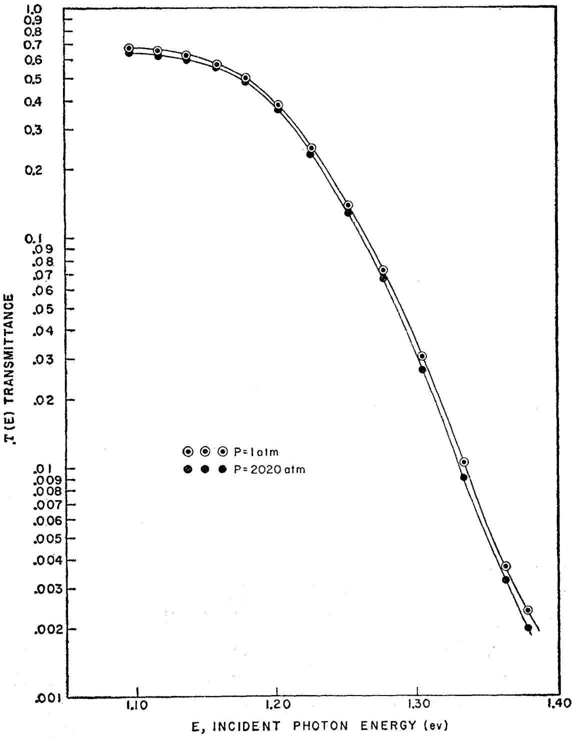

FIG. 2. Effect of pressure on the transmittance of silicon.

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[24] Warschauer, Paul, and Brooks, Phys. Rev. **98**, 1193 (1955).

[25] J. Taylor (unpublished).

[26] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 102 (1958).

[27] A. von Hippel, J. Chem. Phys. **16**, 372 (1948).

[28] V. E. Botton, Science **115**, 570 (1952); J. J. Loferski, Phys. Rev. **93**, 707 (1954); A. Nussbaum, Phys. Rev. **94**, 337 (1954); R. S. Caldwell and H. Y. Fan, Phys. Rev. **94**, 1427 (1954); L. J. Neuringer, Phys. Rev. **98**, 1193 (1955).

[29] H. B. Callen, J. Chem. Phys. **22**, 518 (1954); J. R. Reitz, Phys. Rev. **105**, 1233 (1957); R. Asendorf, Bull. Am. Phys. Soc. Ser. II, **2**, 147 (1957).

0.031 cm thick. For the former Freon-113 was used as the hydrostatic fluid, and for the latter, silicone oil. The incident radiation was polarized by means of five unsupported films of amorphous selenium about 50 microns thick mounted so that the radiation to be polarized was incident on the films at Brewster's angle. This construction is described by Elliot *et al.*[30] The *c* axis of the sapphire windows was not perpendicular to the face, thereby introducing a rotation of the plane of polarization of the incident radiation upon passage through the window. For this reason it was first necessary to determine the proper orientation of the windows relative to the sample and polarizer. For radiation polarized parallel to the *c* axis of the crystal, the results are shown in Fig. 3 at 1 and 1095 atmospheres. The results for radiation polarized perpendicular to the *c* axis are given in Fig. 4 at atmospheric pressure and at pressures of 425 and 778 atmospheres. It is seen that the energy gaps for both directions of polarization decrease as the pressure is increased.

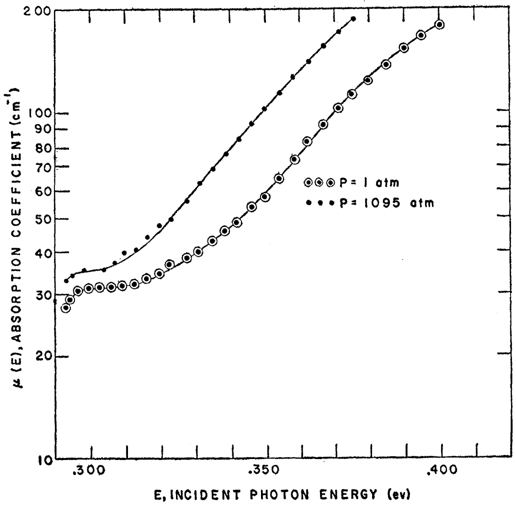

FIG. 3. Effect of pressure on the optical absorption of tellurium for radiation polarized parallel to crystalline *c* axis.

B. Temperature Experiments

Using a metal cryostat equipped with rock salt windows, the dependence of the absorption edge upon temperature was investigated. This was measured between 90°K and 400°K in silicon and in tellurium for both directions of polarization of the radiation. In both materials it was observed that as one proceeds towards low temperatures the absorption edge moves towards larger energy, the energy gap increases as the temperature decreases. The mean temperature coefficient of the energy gap which was deduced is listed in Column 4 of Table I.

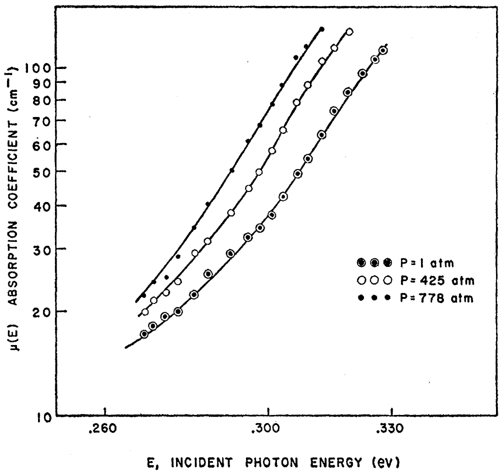

FIG. 4. Effect of pressure on the optical absorption of tellurium for radiation polarized perpendicular to crystalline *c* axis.

5. DISCUSSION

A. Pressure Coefficient

An expression relating the linear absorption coefficient, $\mu(E)$, to the energy gap, effective masses, and other parameters of a given material has been derived by Bardeen, Blatt, and Hall.[31] They have split up the problem of absorption near the edge into two separate processes—direct and indirect electronic transitions from the valence band to the conduction band. The first of these is characterized by the selection rule that the wave vector of the electron remains unchanged and corresponds to a transition from E_v to E_{c0}, the (000) conduction-band minimum, in Fig. 5.

Bardeen *et al.*[31] have shown that it is possible to have a phonon-aided optical transition such that the electronic energy difference is $E_v - E_c$, the phonon supplying the extra momentum required to scatter an electron from a point near $\mathbf{k}=0$ to the (111) conduction-band minimum.

Near the threshold the absorption coefficient for direct electronic transitions, $E_v \rightarrow E_{c0}$, varies as $(\hbar\omega - \hbar\omega_t)^{\frac{1}{2}}$ where $\hbar\omega$ is the incident photon energy and $\hbar\omega_t$ is the threshold absorption energy corresponding to the separation between the (000) conduction-band minimum and the top of the valence band. Examining Fig. 1, we observe that while our data do not extend very much above 100 cm^{-1} the displacement of the curves is greater for $\mu > 100$ cm^{-1}. Strictly, the threshold for the μ^2 dependence upon E, characteristic of direct transitions, does not start until $\mu \approx 10^4$ cm^{-1} in germanium, as is evidenced by the work of Dash and Newman.[18] Their data indicate that below $\mu \approx 10^4$ cm^{-1} there is a very sharp and rapid decrease in absorption coefficient, so that the horizontal displacement with

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[30] Elliot, Ambrose, and Temple, J. Opt. Soc. Am. **38**, 212 (1948).

[31] Bardeen, Blatt, and Hall, *Proceedings of the Conference on Photoconductivity, Atlantic City, 1954*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley and Sons, Inc., New York, 1956), p. 146.

TABLE I. Experimental results of the optical pressure coefficients for germanium, silicon, and tellurium.

Material	Conduction-band minimum	Pressure coeff. of energy gap $(\partial E_g/\partial P)_T$ (ev/atmos)	Temperature coeff. of energy gap $(\partial E_g/\partial T)_P$ (ev/deg)	Thermal expansion coeff. α $(\text{deg})^{-1}$	Isothermal compressibility κ_T $(\text{atmos})^{-1}$	Dilation term $-(\alpha/\kappa_T)(\partial E_g/\partial P)_T$ (ev/deg)	Electron-lattice interaction term $(\partial E_g/\partial T)_V$ (ev/deg)
Germanium	(111)	$(7.3\pm1.5)\times10^{-6}$ $(8\pm1)\times10^{-6}$[a] 4.0×10^{-6}[b]	-4.4×10^{-4}	17.76×10^{-6}[f]	1.24×10^{-6}[h]	-1×10^{-4}	-3.4×10^{-4}
	(000)	$(11\pm3)\times10^{-6}$ 13×10^{-6}[c] 10×10^{-6}[b]	$\sim-4\times10^{-4}$[e]			$\sim-1.6\times10^{-4}$	$\sim-2.4\times10^{-4}$
Silicon	(100)	-2×10^{-6} 5×10^{-6}[a] -1.3×10^{-6}[d]	-4.5×10^{-4}	12.45×10^{-6}[f]	0.98×10^{-6}[h]	0.3×10^{-4}	-4.8×10^{-4}
Tellurium	$E_{g\parallel}$	$-(1.8\pm0.3)\times10^{-5}$	-4×10^{-5}	-1.6×10^{-6}[g]	-4.14×10^{-7}[g]	7×10^{-5}	-11×10^{-5}
	$E_{g\perp}$	$-(2.2\pm0.4)\times10^{-5}$	-4×10^{-5}	27.2×10^{-6}[g]	2.75×10^{-6}[g]	2×10^{-6}	-4.2×10^{-5}

[a] See reference 11.
[b] See reference 32.
[c] Deduced from data in reference 11.
[d] See reference 26.
[e] See reference 18.
[f] M. E. Straumanis and E. J. Aka, J. Appl. Phys. **23**, 330 (1952).
[g] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **60**, 305 (1925).
[h] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **77**, 187 (1949).

temperature of their curves in the range of μ just above 100 cm^{-1} is not drastically different from the shift at the direct transition threshold. We would like to speculate that pressure data might follow the same pattern. In the absence of published pressure data for the true μ^2 region we shall assume that the shift of the curves in Fig. 1 for $\mu > 100$ cm^{-1} is characteristic of the (000) conduction-band minimum in germanium. The scatter of the data points is somewhat large and at the highest absorption the curves tend to bend over and flatten out. This is probably due to the fact that at these wavelengths $1/\mu$ is very much smaller than the specimen thickness and long-wavelength light of spurious origin is being transmitted. At these low pressures we tend to think that the apparent nonlinearity in the shift is likewise spurious. Nevertheless, we would like to suggest that the (000) conduction-band minimum moves relative to the valence band at a rate of about $+(11\pm3)\times10^{-6}$ ev/atmos in germanium. This is in good agreement with the value obtained from the data of Fan *et al.*[11] and the value deduced indirectly by Paul and Warschauer[32] from the change in shape of their absorption curves.

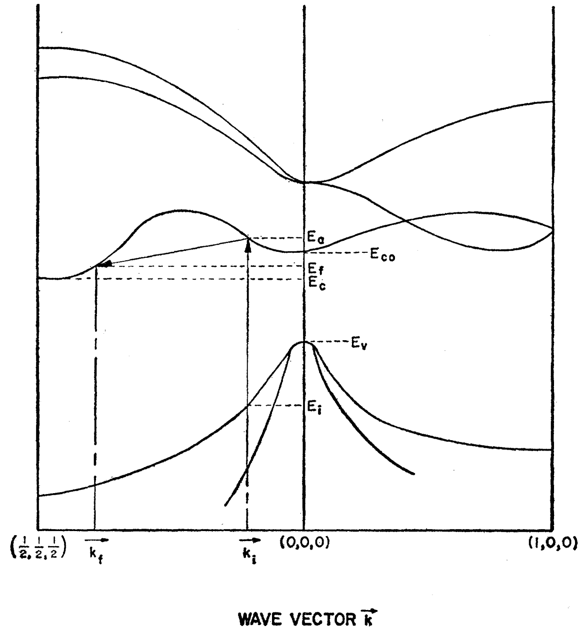

FIG. 5. Energy band contour of germanium along (111) and (100) axes in **k** space, showing possible optical transition.

With respect to the pressure variation of $E_c - E_v$, the situation is not as clear cut. The equation for the absorption coefficient near the threshold for indirect transitions derived by Bardeen, Blatt, and Hall,[31] assuming that the transition at $\mathbf{k}=0$ is allowed, is

$$\mu(E)=\frac{AM_s^2(2N_s+1)(m_cm_v)^{\frac{3}{2}}(\hbar\omega\pm\hbar\omega_s-E_g)^2(E_{c0}-E_v)}{\hbar\omega(E_{c0}-E_c)^2}, \tag{2}$$

where A is a constant assumed not to vary with pressure, N_s is the number of phonons excited, m_v and m_c are the density of states effective masses of the valence band and conduction band, respectively, M_s is the matrix element for the interaction of electrons with phonons of wave vector **s**, $\hbar\omega$ is the incident photon energy and $\hbar\omega_s$ is the phonon energy. The plus sign associated with $\hbar\omega_s$ is to be used for phonon destruction and the minus sign for phonon creation. The thermal energy gap corresponds to $E_g = E_c - E_v$. In germanium the energy band structure is such that $(E_{c0}-E_c) < (E_c - E_v) < (E_{c0}-E_v)$ at atmospheric pressure and room temperature with $(E_c-E_v)=0.65$ ev and $(E_{c0}-E_v)=0.80$ ev. If the transition at $\mathbf{k}=0$ is not allowed then the absorption coefficient is given by

$$\mu(E)=\frac{BM_s^2(2N_s+1)m_v(m_cm_v)^{\frac{3}{2}}(\hbar\omega\pm\hbar\omega_s-E_g)^3}{\hbar\omega(E_{c0}-E_c)^2}, \tag{3}$$

where B is a constant assumed to have negligible pressure variation.

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[32] W. Paul and D. M. Warschauer, J. Phys. Chem. Solids **5**, 89 (1958).

Paul and Warschauer[32] have measured the shift of the absorption edge of germanium as a function of pressure up to 7000 atmospheres for $1<\mu<70$ cm^{-1}. They observed a change of shape of the absorption edge with pressure and, therefore, in order to correlate the pressure variation of $\mu(E)$ in a unique way with a change in (E_c-E_v) they extrapolated to $\mu=0$ on both a $\mu^{\frac{1}{3}}$ and a $\mu^{\frac{1}{2}}$ *versus* $\hbar\omega$ plot. It is interesting that while a law of the form of Eq. (3) yielded a better straight line than Eq. (2), the pressure coefficient of the energy gap determined from either law, using extrapolation to $\mu=0$, was about the same amounting to $+4\times10^{-6}$ ev/atmos. This is to be compared to $+5\times10^{-6}$ ev/atmos found from the resistivity data of Paul and Brooks.[4] Paul and Warschauer[30] conclude that on the basis of pressure coefficient alone one cannot choose between a $\mu^{\frac{1}{2}}$ or $\mu^{\frac{1}{3}}$ law.

We have attempted to fit our data to Eqs. (2) and (3) and find that neither give very straight lines over the range $1<\mu<50$ cm^{-1}, although the $\mu^{\frac{1}{2}}$ dependence is the better of the two. By careful extrapolation to $\mu=0$ on a plot of $(\mu\hbar\omega)^{\frac{1}{2}}$ *versus* $\hbar\omega$ we find the mean value of the pressure coefficient of (E_c-E_v), the (111) conduction-band minimum, to be $+(7.3\pm1.5)\times10^{-6}$ ev/atmos. Fan *et al.*[11] likewise find no shape change to 1000 atmospheres. They deduce a value of 7.5×10^{-6} ev/atmos from the horizontal shift necessary to superimpose the curves of a $(\mu\hbar\omega)$ *versus* $\hbar\omega$ plot (a procedure valid if there is no shape change).

Our data do not cover as extensive a pressure range as that of Paul and Warschauer. Further we do not observe the shape change of the absorption edge which must be present and which arises from the pressure dependence of $(E_{c0}-E_c)$ and $(E_{c0}-E_v)$. The reason for this may be seen from the following considerations. At any pressure, P, and near the threshold of absorption, we may write from Eq. (2)

$$(\hbar\omega\mu)^{\frac{1}{2}}{}_P\sim\frac{(\hbar\omega-E_g{}^P)(E_{c0}-E_v)^{\frac{1}{2}}}{(E_{c0}-E_c)}(1+\Delta), \tag{4}$$

where Δ corrects for the pressure variation of $(E_{c0}-E_v)$ and $(E_{c0}-E_c)$ and is given to first order by

$$\Delta=\delta(E_{c0}-E_v)/2(E_{c0}-E_v)-\delta(E_{c0}-E_c)/(E_{c0}-E_c), \tag{4a}$$

with

$$\delta(E_{c0}-E_v)=\frac{\partial}{\partial P}(E_{c0}-E_v)\delta P,$$

$$\delta(E_{c0}-E_c)=\frac{\partial}{\partial P}(E_{c0}-E_c)\delta P.$$

For $\delta P=1000$ atmospheres, $(\partial/\partial P)(E_{c0}-E_v)=11\times10^{-6}$ ev/atmos, and $(\partial/\partial P)(E_{c0}-E_c)\approx6\times10^{-6}$ ev/atmos, we obtain $\Delta\cong-0.3$. This implies that to observe a change in slope at 1000 atmospheres would necessitate the experimental accuracy in μ to be much less than 6%, which is difficult to attain in these experiments at present. An estimate similar to this for a law of the form of Eq. (3) indicates a somewhat less stringent limit on the accuracy required of the absorption data. It is therefore felt that had we been able to proceed to higher pressures, a shape change would have been detected. However, it does not necessarily follow that a pressure coefficient deduced from such data after the manner of Paul and Warschauer would agree with theirs. The change of shape of the absorption edge with pressure only serves to decrease the *slopes* of $\mu^{\frac{1}{2}}$ or $\mu^{\frac{1}{3}}$ *versus* $\hbar\omega$ lines, leaving the intercepts, from which the energy gap variation is ascertained, unchanged. Consequently, the discrepancy between our results as well as Fan *et al.*[11] and those of Paul and Warschauer need not be due to the lack of higher pressure data and presumably would persist even if our experiment had been extended in pressure. It is interesting to note that while our result for the pressure coefficient of (E_c-E_v) is roughly 40% gereater than the resistivity data,[4] that of Paul and Warschauer is smaller than the resistivity data by about 20% for both a $\mu^{\frac{1}{3}}$ and $\mu^{\frac{1}{2}}$ dependence. If it is difficult to think of a physical mechanism which will yield a pressure coefficient, deduced as above for an optical energy gap, larger than a thermal one, the degree of difficulty is no less in explaining why it should be smaller. We feel, therefore, that because proceeding to higher pressures would not alter our result, our value is equally valid as that of Paul and Warschauer and can be taken to be an energy gap change.

In deducing the pressure coefficient by extrapolating to $\mu=0$, it has been tactitly assumed that $\hbar\omega_s$ has negligible pressure variation. It is possible to obtain an order-of-magnitude estimate of its pressure dependence by examining the variation of θ_D, the Debye temperature. For this purpose we use the Grüneisen relation connecting the Grüneisen constant γ, to the molar specific heat at constant volume, C_v, the isothermal compressibility, κ_T, the volume coefficient of thermal expansion, α, and the molar volume, V_m:

$$\gamma=\alpha V_m/\kappa_T C_v=-d(\ln\theta_D)/d(\ln V). \tag{5}$$

Substituting the appropriate values into (5), we find $d\omega_s/\omega_s=d\theta_D/\theta_D=0.1\%$ for a pressure of 1000 atmospheres. Now $dE_g/E_g=1\%$ for 1000 atmospheres, so that we may neglect the effect of a variation of phonon energy with pressure over the range in which our experiments were performed.

The negligible variation of θ_D with pressure gives us some measure of confidence in the assumption that N_s, the number of phonons excited, remains essentially constant with pressure, if in the expression for N_s we substitute $\hbar\omega_s=k\theta_D$.

The other terms in (2) which may effect the shape of the absorption edge are $(m_cm_v)^{\frac{3}{2}}$ and $M_s{}^2$. Information about the quantity $(m_cm_v)^{\frac{3}{2}}$ can be obtained from the experiments of Smith[9] and of Benedek, Paul, and

Brooks.[7] The work of Benedek, Paul, and Brooks indicates that the shape parameter $K=m_l/m_t$ decreases by roughly 2% for 1000 atmospheres, where m_l is the longitudinal effective mass and m_t the transverse effective mass of the conduction electrons. By assuming that the elastic constants are pressure independent, they have concluded that m_l decreases while m_t increases. If we assume as a crude first approximation that the percentage changes of m_l and m_t with pressure are the same, then $m_c^{3/2} \sim (m_l m_t^2)^{1/2}$ increases by roughly 0.5% for 1000 atmospheres. Smith has deduced that the effective mass of the high mass holes increases by 0.2% in 1000 atmospheres. The change in the effective mass of the low-mass holes was found to amount to 1.6% in 1000 atmospheres. Thus $(m_c m_v)^{3/2}$ is not expected to exhibit a very strong pressure dependence in this experiment. It is not clear at present how one should estimate the pressure dependence of M_s^2. The values of the pressure coefficient of the (111) minimum and (000) minimum are given in column 3 of Table I. It is seen that increasing the pressure causes the (000) minumum-valence band separation to increase more rapidly than the (111) minimum-valence band separation.

Examining Fig. 2 we notice that to 2000 atmospheres the absorption edge of silicon does not exhibit a shape change. Because of the smallness of the pressure effect we have not converted the transmittance data to a μ *versus* $\hbar\omega$ plot. This lack of shape change is in agreement with the work of Paul and Warschauer[26] carried out to 8000 atmospheres and using a grating as the dispersing element. In the absence of a shape change, the pressure coefficient for silicon was arrived at by a horizontal shift of the higher pressure curve of Fig. 2. Our result, in agreement with that of Paul and Warschauer, indicates that the pressure coefficient in silicon is small and negative.

Since there is no theory giving the explicit dependence of $\mu(E)$ upon the basic crystal parameters of tellurium and because the curves appear parallel to within the fairly large experimental error, we have deduced the pressure coefficient of $E_{g\parallel}$ and $E_{g\perp}$ from the data of Fig. 3 and Fig. 4 by shifting the curves horizontally. As may be seen by referring to Table I, the pressure coefficients of both energy gaps are one order of magnitude larger than for silicon and about twice as large as for germanium. Further, it appears that $E_{g\perp}$ decreases more rapidly with pressure than $E_{g\parallel}$. This latter aspect is interesting in the light of the band structure proposed by Reitz.[29]

In calculating the energy bands of tellurium, Reitz first considered the crystal structure with 90° bond angles in the chain, thereby obtaining three p bands each of which was triply degenerate. This degeneracy is removed and further splitting of the p bands is produced when the crystal is stretched out along the c axis to the proper bond angle. The resultant energy band scheme is shown in Fig. 6, where there are three separated groups of p bands. The lower and middle group of p bands are filled; the upper p group and d bands are empty. The optical transitions of electrons correspond to transitions between the middle p group and one of the conduction bands whose edges occur at $k_z=\pi/c$. The symbols next to the arrows indicate whether the transitions correspond to radiation polarized parallel ($\parallel$) or perpendicular ($\perp$) to the crystalline c axis. It is seen that the energy gap at $k_z=\pi/c$ is smaller for radiation polarized perpendicular to the c axis, in agreement with experiment.

The compressibility of tellurium is such that it expands along the c axis and contracts perpendicular to this axis. Increasing the pressure thus causes an increase in the bond angles between adjacent bonds in each chain, thereby producing a decrease in the energy gap. Assuming that the transitions are $p \rightarrow p$, we find with the aid of Table I in Reitz's paper, that the change in $E_{g\perp}$ is given by

$$\Delta E_{g\perp} = -2\Delta w(\sigma - 2\pi + \pi^2/\sigma), \tag{6}$$

where Δw is a measure of the change of bond angle and σ and π are the values of certain energy integrals. For $E_{g\parallel}$ we obtain

$$\Delta E_{g\parallel} = -2\Delta w(\sigma + \pi - 2\pi^2/\sigma). \tag{7}$$

From the theoretical considerations of Reitz, π is a negative quantity and is smaller in magnitude than σ. It can then be shown that $\Delta E_{g\perp} > \Delta E g_{\parallel}$, which is in

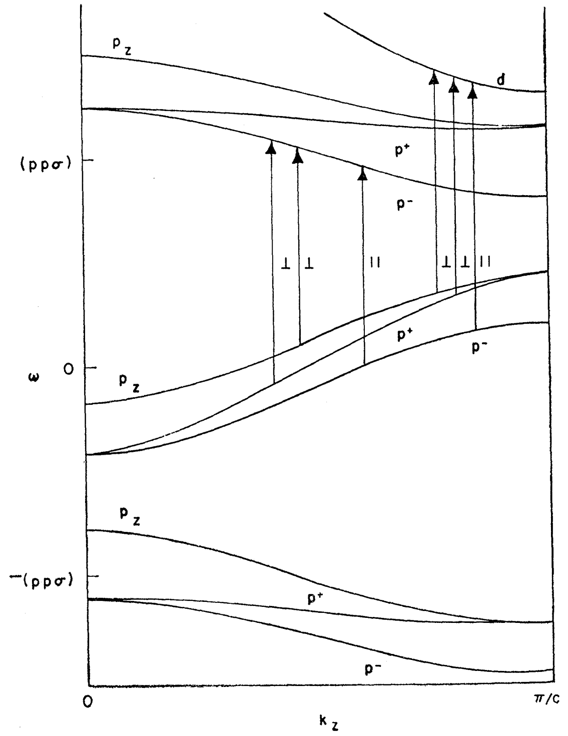

FIG. 6. Energy band contour of tellurium along the z axis in **k** space, showing possible optical transitions.

qualitative agreement with our experimental result. Further, if indeed the dominant effect of pressure upon the energy gap arises from a change in bond angle, then (6) and (7), together with the experimental values of $\Delta E g_{\perp}/\Delta P$ and $\Delta E_{g\parallel}/\Delta P$, could be used to ascertain σ and π. This would necessitate a calculation of Δw. In the absence of knowledge of Δw, the ratio σ/π can be determined. Proceeding in this fashion, we find $\sigma/\pi \cong 16$. It might actually be that σ/π is not really this great because our value for $\partial E_{g\perp}/\partial P$ is an average value of the shifts between 1 and 425 atmospheres and between 425 and 778 atmospheres, the shift exhibiting a nonlinearity. A larger value of $\Delta E_{g\perp}/\Delta E_{g\parallel}$ would in fact produce a smaller value of σ/π. Reitz in his paper takes $\sigma/\pi = 3$ in part of his discussion. It would appear that more data at several pressures would be helpful in the case of tellurium in arriving at a more accurate value of $\Delta E_{g\perp}/\Delta E_{g\parallel}$ and of σ/π.

B. Relation to Temperature Dependence of E_g

The energy gap of a semiconductor is found to change with temperature. This cannot be accounted for solely by the dilation of the lattice and it has been necessary, in order to explain this discrepancy, to assume an explicit temperature dependence of the energy gap which comes about from the interaction between electrons and lattice vibrations. It can easily be shown that the temperature coefficient of the energy gap, $(\partial E_g/\partial T)_P$, may be written as

$$(\partial E_g/\partial T)_P = (\partial E_g/\partial T)_V - (\alpha/\kappa_T)(\partial E_g/\partial P)_T, \qquad (8)$$

where α is the volume coefficient of thermal expansion and κ_T is the isothermal compressibility. The first term of (8) gives the direct dependence of the energy gap upon the temperature (electron-lattice interaction effect) and the second term represents the thermal dilation effect. Each of these are listed in Table I for germanium, silicon, and tellurium. The temperature coefficient of the (000) minimum was taken to be $\sim -4\times 10^{-4}$ ev/deg as seems to be indicated by the data of Dash and Newman.[18]

6. SUMMARY

A technique for measuring the change with hydrostatic pressure of the intrinsic optical absorption of semiconductors has been developed. By allowing almost simultaneous comparison of sample transmission with that of the hydrostatic fluid at any pressure and wavelength, several of the usual sources of error associated with this type of measurement are eliminated. To improve the accuracy, the pressure dependence of the index of refraction of the sample[33] and of the hydrostatic fluid must be known. Further, measurements should be made on a family of samples of varying thickness, the data of each specimen spanning a portion of the absorption edge. By working in the low-transmission range of each sample, say $0.01 < T(E) < 0.1$, and by overlapping the data of successive specimens, the errors arising when $1/\mu \gg d$ and $1/\mu \ll d$ will be minimized.

The pressure coefficient of the energy gap has been determined from the shift of the absorption edge with pressure in tellurium, silicon, and germanium. In tellurium $E_{g\perp} > E_{g\parallel}$ and therefore $E_{g\perp}$ can be studied only by optical means. The motion of $E_{g\perp}$ with pressure has been observed. The results for tellurium are consistent with the energy-band calculations of Reitz, although it would be profitable to extend the range of the data both in absorption coefficient and in pressure. The ratio of the pressure coefficients of $E_{g\perp}$ and $E g_{\parallel}$ in tellurium have been used to determine experimentally the ratio of certain energy integrals occurring in Reitz's calculations. For silicon, our results are in agreement with those of Paul and Warschauer, the pressure coefficient of the energy gap is small and negative. In germanium we deduce a pressure variation of the (111) conduction-band minimum which is in qualitative agreement with the resistivity data. It is suggested that the (000) minimum moves about twice as rapidly with pressure as the (111) minimum although the evidence for this is not completely unequivocal. A suggested experiment, therefore, is the study with pressure of the absorption coefficient in germanium for $\mu(E) \gg 100$ cm^{-1} in order to gain precise information on the motion of the (000) band edge.

From the measured pressure coefficient the explicit dependence of the energy gap upon temperature has been determined, apart from the dilation effect.

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[33] The work of Cardona, Paul, and Brooks, International Conference on Semiconductors, Rochester, New York, 1958 (to be published), indicates that this effect is very small in germanium and is practically zero in silicon.