CONCLUSIONS

The fundamental equation for the free energy is given by (5), from which a general equation for other ferroelectrics expressing the equilibrium slope of the threshold field with respect to temperature can be derived.

ACKNOWLEDGMENTS

Pressure Dependence of the Resistivity of Germanium

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(Received January 26, 1954)

The effect of hydrostatic pressure on the resistivity of a sample of 35 ohm-cm germanium has been investigated up to 30 000 kg/cm² pressure at temperatures between 25°C and 76°C, and up to 7000 kg/cm² pressure at temperatures down to −195°C. The results indicate an increase in the total energy gap to 15 000 kg/cm² at a rate in agreement with earlier experimental determinations at lower pressures. A rapid rise in resistivity above 15 000 kg/cm² that seems to apply to n-type germanium crystals of any purity has also been investigated. Explanations based on the deionization of impurities and on a decrease in electron mobility are discussed.

THE effect of hydrostatic pressure on the electrical properties of germanium has been investigated experimentally by measurements of p-n junction resistance,[1] the resistivity of impure samples,[2] and the resistivity of high-purity material at elevated temperatures.[3,4] It has also been estimated theoretically by a deformation potential method.[5] Both experiment and theory indicated a uniform increase of resistivity with pressure in the intrinsic conduction range, corresponding to a widening of the energy gap between valence and conduction bands. Bridgman's results also showed interesting behavior at pressures above 15 000 kg/cm² where the resistivity of n-type samples of a wide range of purity increased rapidly with increasing pressure. In the present work new measurements are reported at elevated temperature which extend the effective pressure range for intrinsic conduction. New measurements are also reported for temperatures down to liquid nitrogen. An attempt is made to correlate the new and the older measurements and to clarify the behavior above 15 000 kg/cm².

APPARATUS AND METHOD

The pressure apparatus used in the present set of experiments is that developed by Bridgman. The first,

which allowed resistivity determinations up to 30 000 kg/cm², has been sufficiently described already in the literature,[6] so that only a general discussion of it, and of any features peculiar to this experiment, need be set down here. The chamber in which the high pressure is generated is slightly coned on its external surface. As the main moving piston produces high hydrostatic pressure in a central cylindrical hole, this cone is simultaneously thrust into coned receiving sleeves by a second piston; the external support of the chamber compensates the effect of the internal pressure and allows its prolonged operation at pressures higher than a single unsupported cylinder can stand.

The pressure, which was produced in liquid isopentane, was measured by a manganin wire gauge previously calibrated by Bridgman at 30°C and 75°C; sufficient data were therefore available for a determination of the pressure at any of the temperatures of the present set of experiments.

The sample, a germanium single crystal of 35 ohm-cm room temperature resistivity, had been previously investigated by Bridgman,[3] and was originally supplied by Bell Telephone Laboratories through the interest of Dr. W. Shockley. The crystal dimensions were 3 cm×3 mm², and the contacts to it were soldered with pure tin. The resistance was measured by a potentiometric method for both increasing and decreasing pressure; care was taken that temperature equilibrium had been reestablished after each alteration of pressure. No hysteresis was found, and no variation of resistivity

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[1] Hall, Bardeen, and Pearson, Phys. Rev. **84**, 129 (1951).
[2] P. Miller and J. Taylor, Phys. Rev. **76**, 179 (1949).
[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **79**, 139 (1951); **82**, 71 (1953).
[4] W. Paul, Phys. Rev. **90**, 336 (1953).
[5] W. Shockley and J. Bardeen, Phys. Rev. **77**, 407 (1950); **80**, 72 (1950).
[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **72**, 157 (1938).

with time when both temperature and pressure were constant. The resistivities to be quoted were derived from the measured resistances at high pressure and the dimensions at atmospheric pressure and room temperature. The error involved in disregarding any changes in dimensions of the crystals with pressure and temperature is usually small.[7] Readings of resistivity were usually made at 5000 kg/cm² intervals up to 30 000 kg/cm², and on reducing pressure at 27 500 kg/cm² and at 5000 kg/cm² intervals thereafter. An initial pressure of about 100 kg/cm² was applied before the temperature was raised above 25 °C in the high-temperature experiments, to prevent boiling of the isopentane.

For runs at elevated temperatures, the apparatus was immersed in a symmetrically-heated, continuously stirred oil bath to a point above the top of the carboloy piston transmitting pressure to the central cavity. A mercury regulator switched the heating current to a very low value when the temperature rose too high. The variation of temperature in the bath was less than 0.02°C, and doubtless the regulation at the sample was better than this because of the very large mass of metal shielding it from the oil. As indicated above, it is necessary to wait for the heat of compression to be dissipated after each increase of pressure; ten minutes was generally found to be sufficient time for all the pressures and pressure increments of these experiments.

The second pressure apparatus[8] yielded pressures up to 7000 kg/cm² with temperatures from −80°C to 350°C using commercial nitrogen as transmitting gas; its use for this purpose has been described by Bridgman.[3] Below −80°C, commercially produced helium was used as transmitting fluid, necessitating some changes in technique: for example, a pressure of some 4–5000 kg/cm² was applied at −80°C before the temperature was further lowered, in order to flow the lead washers that formed part of the sealing mechanism for the pressure chamber. Without this device the washers become stiff at zero pressure at the temperature of boiling nitrogen, and will not seal effectively.

The experiments here described were all carried out at temperatures below room temperature so that cryostats with ice, CO₂, and nitrogen coolants could conveniently be used. The pressure is produced in a cavity some 2 in. long by ¼ in. diameter in a cylindrical tube 4 in. long by 1 in. diameter. This is connected to an upper cylinder, in which the main pressure producing piston moves, by a slim tube 12 in. long by ¼ in. diameter pierced by a $\frac{1}{32}$ in. hole. Before the main piston is operated the cavity is filled to a pressure of 2000 kg/cm² by two precompressors. The thermostatting bath liquid covers the bottom cylinder and most of the connecting tube; the upper cylinder is at room temperature. A pressure increase therefore produces a

rise in temperature of the germanium by virtue of the compression, and also by the addition of warmer gas to the cold lower chamber. It was found in practice that the resistivity reading settled very quickly—within minutes—to its final value, so that any temperature variation would seem to be unimportant here. It must be noted, however, that in this temperature range the germanium was relatively insensitive to temperature change; a more careful consideration of these variations might be necessary for a semiconductor with a high temperature coefficient at the temperature of the experiment. The thermoelectric emf's present were small in comparison with the applied ones, and were conveniently eliminated by suitable switching.

The connections to the crystal were made by Teflon covered copper wires threaded through the slim connecting tube and out by way of insulated plugs in the upper cylinder. The manganin gauge was also located in the upper cylinder. Both pressure and resistivity were determined as in the experiments to 30 000 kg/cm². Again no hysteresis or time variation in the readings was found. Except at −195°C, readings were usually taken at 1000 kg/cm² intervals from 0 to 7000 kg/cm² and from 6500 kg/cm² down to zero pressure.

THEORY

It can be shown that the resistivity of an intrinsic semiconductor is given by

$$\rho = [1/e(\mu_e + \mu_p)](1/2A) \exp(E_g/2kT), \qquad (1)$$

where μ_e and μ_p are the electron and hole mobilities, respectively, e the electronic charge, E_g the energy gap between the valence and conduction bands, k Boltzmann's constant, T the absolute temperature, and A given by

$$A = (2\pi kT/h^2)^{\frac{3}{2}} (m_e m_p)^{\frac{3}{4}},$$

where m_e and m_p are the effective masses for electrons and holes, respectively. The assumption is made that the energy vs crystal momentum curves for both bands are nonmultiple; multiplicity of branches would result in a more complicated expression for A, and an alteration in the estimated values of m_e and m_p.

When donor or acceptor impurities contribute to the conductivity, the expression for ρ is altered; in the case of a single donor level, the resistivity is given by

$$\rho = 1/e(n\mu_e + p\mu_p), \qquad (2)$$

where n and p, the number densities of electrons and holes, are given by

$$n = n_0/2 + [(n_0/2)^2 + n_i^2]^{\frac{1}{2}},$$
$$p = -n_0/2 + [(n_0/2)^2 + n_i^2]^{\frac{1}{2}}, \qquad (3)$$
and
$$n_i^2 = 4A^2 \exp[-E_g/kT], \qquad (4)$$

where n_0 is the number density of ionized donors.

E_g, the minimum energy gap between valence and conduction bands, we assume dependent on both tem-

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[7] However, in two of the low-temperature experiments the corrections are not inconsiderable. These will be indicated later in the text.

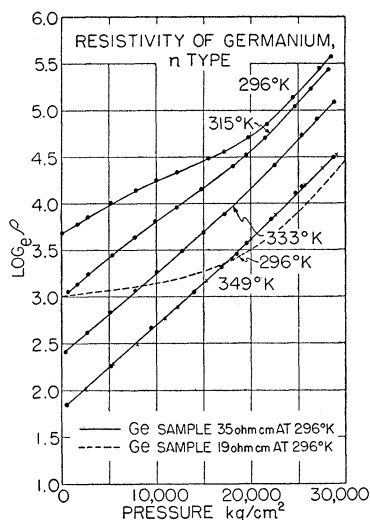[8] P. W. Bridgman, Proc. Am. Acad. Arts. Sci. **67**, 305 (1932).

Fig. 1. Resistivity of high-purity germanium vs pressure, at several temperatures, (with two runs at 349°K). Also shown is the resistivity vs pressure curve for a less pure sample at room temperature.

perature T and pressure P

$$E_g{}^{P,T}=E_g{}^{0,0}+\int_0^P\left(\frac{\partial E_g}{\partial P}\right)_T dP+\int_0^T\left(\frac{\partial E_g}{\partial T}\right)_P dT. \quad (5)$$

Under certain conditions of low temperature and/or high pressure we shall see that the contribution of the intrinsically derived carriers (n_i) will become negligible compared to that of the impurity derived carriers. For a single donor level of depth below the conduction band,

$$\epsilon^{P,T}=\epsilon^{0,0}+\int_0^P\left(\frac{\partial \epsilon}{\partial P}\right)_T dP+\int_0^T\left(\frac{\partial \epsilon}{\partial T}\right)_P dT, \quad (6)$$

the value of p tends to zero and n to the solution of

$$n^2+A_e n\ \exp(\epsilon/kT)-n_0 A_e \exp(\epsilon/kT)=0, \quad (7)$$

where

$$A_e=(2\pi m_e kT/h^2)^{\frac{3}{2}}.$$

RESULTS

Figure 1 shows the resistivity—pressure relation at several temperatures, Fig. 2 the corresponding resistivity—temperature curves at several pressures. Figure 3 shows the results to 7000 kg/cm² at low temperatures. $\text{Log}_e R$ is plotted here: the conversion to $\text{log}_e \rho$ involves a correction of some 10 percent of the total change under pressure at $-80°C$, and 20 percent at $-195°C$, due to the change in dimensions of the sample. This change is insignificant at the other temperatures.

Figure 2 shows that at 76°C the sample is intrinsic over the entire pressure range; in this case the log resistivity vs pressure relation is almost linear. Figure 3, and room temperature experiments by Bridgman on less pure samples,[3] suggest that up to about 15 000 kg/cm² the carrier mobility is substantially independent

of pressure. If we assume that both the mobilities and effective masses are independent of pressure, we can deduce from Eqs. (1) and (5) that in the pressure range to 15 000 kg/cm²,

$$(\partial E_g/\partial P)_T=5.5\times10^{-12}\text{ ev dyne}^{-1}\text{ cm}^{-2}\text{ at }76°C. \quad (8)$$

This compares reasonably well with previously determined values: for example, Bridgman found 5.6×10^{-12} and Miller and Taylor, 5.2×10^{-12}. It also agrees with the value deduced by Shockley and Bardeen from the hole and electron mobilities by the deformation potential method,[5] although in view of the probable complexity of the energy band structure, it seems likely that this last agreement is coincidental.

As the temperature is reduced from 76°C, the curve of log resistivity vs pressure tends to become S shaped, approaching a plateau below 15 000 kg/cm², and then bending upwards back towards parallelism with the 76°C curve above 15 000 kg/cm². This effect is barely visible at 42°C, but becomes quite definite at room temperature. Above 15 000 kg/cm² the curves, which are fairly parallel, have a slope about equal to that found by Bridgman in this pressure range for less pure samples (see the 19 ohm-cm sample in Fig. 1). Although this slope is very close to the slope of the intrinsic curve, a consideration of the resistivity-temperature relation shows that at the low temperatures and high pressures the sample is not intrinsic. Bridgman's results for less pure samples[3] support the view that in the pressure range above the bend the conduction is by impurity-derived electrons.

DISCUSSION

The data appear to warrant the conclusion that the increase of E_g with pressure extends to at least 15 000
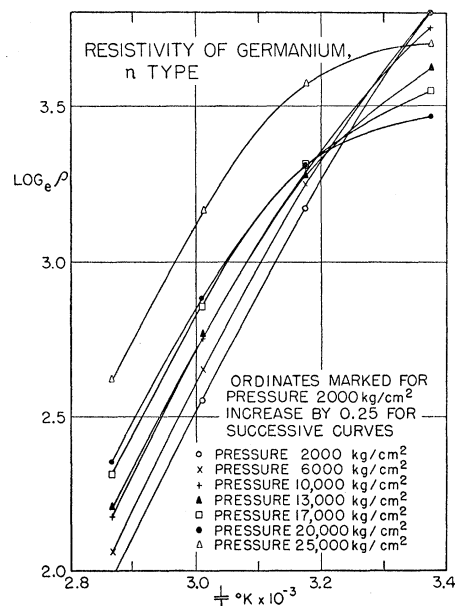

Fig. 2. Resistivity of high-purity germanium vs temperature, at several pressures.

kg/cm^2, and our value for $(\partial E_g/\partial p)_T$ agrees with those previously determined. The unexplained element in the situation is the increase of resistivity above 15 000 kg/cm^2, even for impure samples, and in view of this any interpretation of the intrinsic curve above 15 000 kg/cm^2 in terms of energy gap variation is not necessarily justified. It is to these aspects of the situation that attention will now be directed. We examine several alternative hypotheses.

(a) First let us suppose that the total energy gap is changing at the rate quoted above throughout the entire pressure range, that the impurity activation energy is constant, and that the carrier mobilities are unaffected by pressure.

The curves of Fig. 3, in conjunction with Bridgman's earlier results,[3] support the assumption that the mobility is independent of pressure up to about 15 000 kg/cm^2 for electrons[9] while Bridgman's experiments on relatively impure p-type samples[3] indicate that to a first approximation the hole mobility may be considered independent of pressure up to 30 000 kg/cm^2. If we attempt to ascribe the entire resistivity variation in Figs. 1 and 2 to changes in carrier concentration, resulting from change in energy gap, then Eqs. (2), (3), (4), and (5) apply.

n_0, the number of electronic carriers at low temperatures, is determined from the resistivity values of Fig. 3, assuming an electron mobility of 3600 cm^2/volt sec at 300°K and a $T^{-\frac{3}{2}}$ law of variation with temperature: its value is 2×10^{13} cm^{-3}. The determination of $n_i{}^2$ involves some uncertainty. In practice $E_g{}^{0,0}$ and $\beta = (\partial E_g/\partial T)_{P=0}$ can be found from the slope and intercept on the $1/T$ axis of curves of $\log_e n_i{}^2$ vs $1/T$ at zero pressure. In germanium such a curve follows
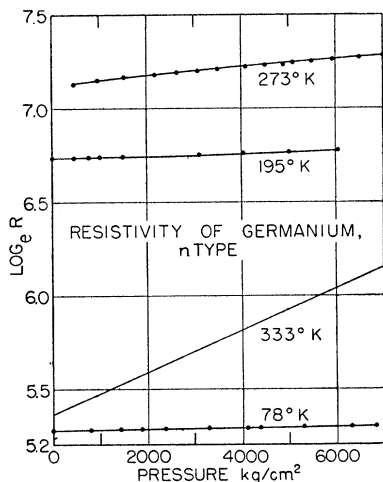
FIG. 3. Resistance of high-purity germanium vs pressure, at low temperature. Also shown for comparison is a resistance vs pressure curve at high temperature.

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[9] The indications are that there is a slight increase in hole mobility and a slight decrease in electron mobility, in this pressure range, but the evidence is not conclusive.
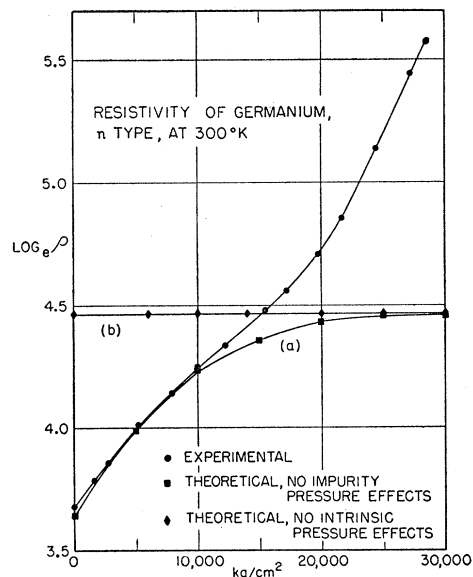
FIG. 4. Resistivity of high-purity germanium vs pressure, at room temperature, along with theoretical curves for two hypothetical cases quoted in the text.

the rule[10]

$$n_i{}^2 = 9.3\times10^{31}T^3$$
$$\times\exp(-0.75/kT)\ \text{cm}^{-3}\ \text{at temperature}\ T,\quad(9)$$

where $E_g{}^{0,0}=0.75$ ev, and $4A^2\exp(\beta/K)=9.3\times10^{31}$. Comparison of (4) and (9) give $E_g{}^{0,0}$ and β (β is assumed independent of T) if A is assumed. The value for β thus depends on the assumed band structure, and on the assumed effective masses. The value for β normally assumed, -0.0001, is a good round figure, but is not exactly consistent with $E_g{}^{0,0}=0.75$ ev and with an A deduced assuming $m_e=m_p=m$ the free electron mass.

When the pressure is varied at a temperature T, (9) becomes

$$n_i{}^2 = 9.3\times10^{31}T^3\exp[(-E_g{}^{0,0}-\alpha P)/kT],\quad(10)$$

where $\alpha=(\partial E_g/\partial P)_T$ and P is the pressure. Throughout the following discussion we shall use Eq. (10) where a value of $n_i{}^2$ at pressure P and temperature T is required.

n and p are thus determined from (3) and (10), and thence ρ, at any pressure. Figure 4 (a) represents the expected room temperature behavior of $\log_e\rho$ with pressure. Although it describes the actual low-pressure behavior well, and the flattening predicted around 15 000 kg/cm^2 is obtained, it is clearly inadequate at the higher pressures.

(b) The analysis above indicates that above 15 000 kg/cm^2 conduction should be largely by impurity-derived electrons. Thus the high-pressure resistivity behavior must be ascribed to a change of impurity activation energy with pressure or a pressure variation of electron mobility or a combination of the two. Let

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[10] E. M. Conwell, Proc. Inst. Radio Engrs. **40**, 1327 (1952).
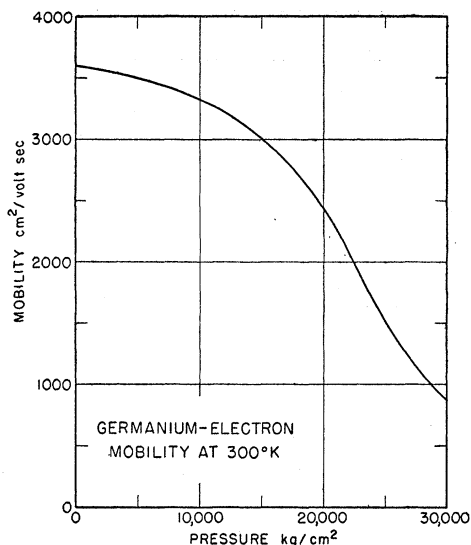
FIG. 5. Variation of mobility of electrons in germanium with pressure, deduced from conductivity of a relatively impure n-type sample.

us first examine the possibility of a change of activation energy with pressure. It is necessary to suppose that the activation energy changes with pressure at the same rate as the total energy gap; we assume that in Eq. (6), $\epsilon^{0,T}=0.01$ ev. Then, ignoring any contribution from the intrinsically derived electrons, n is given by (7). The resultant variation of $\log_e \rho$ with pressure, given by (2), is that of Fig. 4 (b). There is but 2 percent deionization by 40 000 kg/cm² at room temperature, and the sharp rise in resistivity due to rapid deionization does not set in until we are beyond attainable hydrostatic pressures. Also, the effect of deionization would appear at lower pressures the lower the temperature. The curves in Fig. 3 which should show the rapid rise in resistivity, indicate only a very slow uniform increase.

(c) We have concluded that the hole mobility is substantially constant to 30 000 kg/cm², and the electron mobility to 15 000 kg/cm². However, it is not possible to infer anything about the electron mobility above 15 000 kg/cm². Let us, then, examine the supposition that the behavior of n-type Ge above 15 000 kg/cm² is due entirely to a decrease of electron mobility with pressure. At 76°C, the rate of increase of resistivity above 15 000 kg/cm² would then be due both to the decreasing carrier density and to the decreasing mobility of the electronic carriers, and should be somewhat greater than the rate due to energy gap change alone. In fact, there is a slight increase of slope in the 76°C curve around 15 000 kg/cm², but still the slope of the curve above 15 000 kg/cm² at this temperature is little different from that at room temperature in impure n-type germanium samples.

We can derive the supposed change of electron mobility with pressure from 0–30 000 kg/cm², assuming

constant carrier density, from Bridgman's results for impure n-type samples, avoiding the complication of intrinsic carrier depopulation in the 35-ohm-cm sample. This is shown in Fig. 5. For this derivation we used the curve of $\log_e \rho$ vs pressure for a 4-ohm cm sample [see second reference under (2)]. If we then suppose that the total energy gap increases at the quoted rate, that the impurity activation energy is constant, and that the mobilities of electrons and holes are as indicated, (corrected for $T^{-\frac{3}{2}}$ and $T^{-2.3}$ law of variation[11] with temperature for electrons and holes, respectively, and with $\mu_e^{P,T}/\mu_e^{0,T}$ assumed independent of temperature) we can derive the curve of Fig. 6 for $\log_e \rho$ vs pressure at 76°C. Clearly, although there *is* a slight increase in slope of the experimental curve above 15 000 kg/cm² the fit of the theoretical curve is not very good. In order to account for the nearly constant slope of the intrinsic curve it would be necessary to suppose that in the same region where the mobility change begins there is a reduction in the rate of increase in band gap with pressure. Such a change is, in fact, not too unlikely if it is assumed, as seems probable, that the change in mobility is associated with a change of the point in k space at which the minimum energy in the conduction band comes.

(d) An explanation based on the presence of a large number of p-n junctions in the material is excluded by the absence of any resistance change with pressure at very low temperatures, and by the fact that the rapid resistance increase above 15 000 kg/cm² at and above room temperature also occurs in very impure samples.
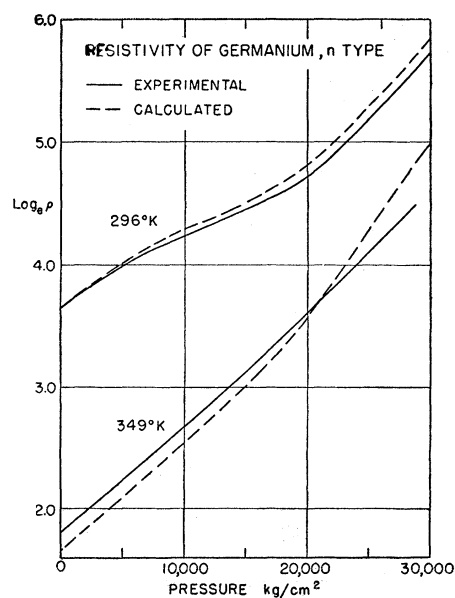

FIG. 6. Resistivity of high-purity germanium vs pressure, along with theoretical curves based on a decrease in electron mobility at high pressures.

[11] M. B. Prince, Phys. Rev. **91**, 208 (1953).

Bridgman[12] found a sharp maximum in the resistivity-pressure relation for n-type germanium in experiments out to 100 000 kg/cm² pressure, but the interpretation of this result may be complicated by the nonhydrostatic nature of the pressure.

The suppositions of (c) can be used somewhat differently. From (2) and (3), $[(n_0/2)^2+n_i^2]^{\frac{1}{2}}=1/(\mu_e+\mu_p)$ $\times[(1/\rho e)-(n_0/2)(\mu_e-\mu_p)]$. Hence, with the assumptions of (c), and using the experimentally determined values of ρ vs P at 76°C, we can find n_i^2 vs P and hence E_g from (4). Figure 7 shows E_g vs P determined in this way. We note that in the linear range the rate of change of E_g with P is nearly 10 percent less than when constant carrier mobility was assumed. It is suggested that the flattening in the E_g vs P curve at high pressures is not an unreasonable additional hypothesis on which to base a full explanation of the experimental facts.

The small differences between the slopes of the experimental curves above 15 000 kg/cm² at the various temperatures measured are not implausible. Although it is not obvious from the general expression for the slope of $\log_e\rho$ vs P, derived from Eq. (2), how the slope will change with temperature, some idea of the change can be obtained from the two cases (a) where the conduction above, say 20 000 kg/cm², is by impurity derived electrons. This corresponds to our sample at room temperature; (b) where the conduction above, say 20 000 kg/cm², is mostly by intrinsic electrons and holes. This corresponds to our sample at 76°C. In (a) $\rho=1/en_0\mu_e$, and

$$\frac{d\log_e\rho}{\partial P}=-\frac{1}{\mu_e}\frac{\partial\mu_e}{\partial P}.$$

This expression is nearly temperature independent. For (b) $\rho=1/[en_i(\mu_e+\mu_p)]$, and

$$(d/dP)\log_e\rho=(1/2kT)(\partial E_g/\partial P)_T$$
$$-\{1/(\mu_e+\mu_P)\}\{\partial\mu_e/\partial P\}.$$

The first term in this expression decreases as the temperature is raised. The second term is also temperature dependent because of the $T^{-2.3}$ law for holes as opposed to a $T^{-1.5}$ law for electrons; since $d\mu_e/dP$ is negative, this term tends to increase $d\log_e\rho/dP$ as the temperature is raised. The net effect can be greater or smaller than the slope given by (a). In fact the slope of the 76°C curve above 15 000 kg/cm² is smaller than that of the room temperature case, while the slopes for the 42°C and 60°C experiments are greater than both.

CONCLUSION

The energy gap between conduction and valence bands in germanium increases with hydrostatic pres-

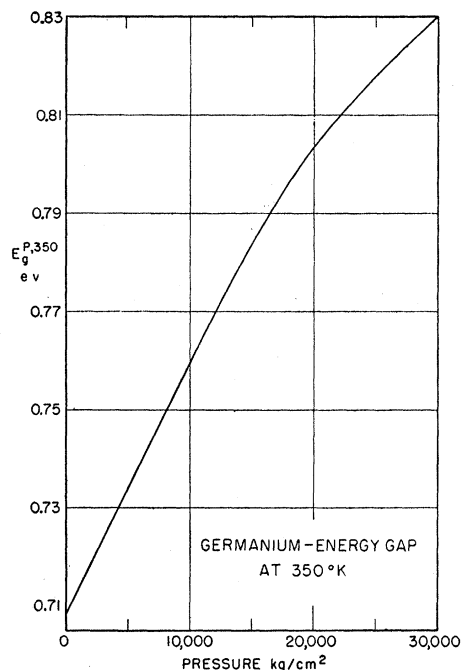[12] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 221 (1952).

FIG. 7. Variation of energy gap in germanium, deduced from resistivity data, and assuming the decrease in electron mobility with pressure indicated in Fig. 5.

sure up to at least 15 000 kg/cm² at a rate in agreement with earlier determinations at lower pressures. A rapid increase of resistivity with pressure above 15 000 kg/cm² found in n-type germanium, but not in p type, cannot be explained by a change in impurity activation energy, and is not wholly consistent with a change in mobility, unless the additional assumption is made that the rate of increase of energy gap decreases at the same pressure at which the reduction of electron mobility sets in. Any theoretical explanations must also ultimately be consistent with the possibility of a maximum in the resistivity at 50 000 kg/cm² found by Bridgman, and with the relative insensitivity of the resistivity to pressure at low temperatures.

Experiments to determine the Hall constant and the drift mobility under pressure are planned, in addition to experiments to examine the pressure shift of the optical absorption edge.

ACKNOWLEDGMENTS