Effects of Pressure on the Electrical Properties of Semiconductors*†

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Measurements have been made of the effects of hydrostatic pressures between one and 2000 atmospheres on the electrical properties of several different semiconductors. The materials studied are germanium, indium antimonide, indium arsenide, gallium antimonide, tellurium, and magnesium stannide. It has been found that the temperature at which the Hall coefficient of *p*-type Ge reverses sign shifts to a higher value under the application of a pressure of 2000 atmospheres, and that the magnitude of the shift is in good agreement with the shift predicted by the known increase of the energy gap from one to 2000 atmospheres. The transverse magnetoresistance of InSb is found to decrease slightly with increasing pressure in accordance with the known decrease of electron mobility. Conductivity and Hall coefficient *vs* pressure measurements on extrinsic *n*-type samples of InAs and GaSb show that the electron mobility in InAs decreases by about 7 percent from one to 2000 atmospheres and that there is no such mobility change in GaSb. Conductivity and Hall coefficient *vs* pressure measurements on Te indicate that the energy gap is smaller by 0.032 ev at 2000 atmospheres than its value of about 0.336 ev at atmospheric pressure, and that the hole and electron mobilities increase with increasing pressure. A consistent scheme of interpretation of the results of the various pressure experiments on tellurium is proposed. Conductivity *vs* pressure measurements on Mg_2Sn show that the energy gap widens with increasing pressure by roughly 0.01 ev between one and 2000 atmospheres.

1. INTRODUCTION

THIS paper presents the results of measurements of the effects of a hydrostatic pressure on the electrical properties of several well-known semiconductors. Such measurements have become of interest lately, since they can give information about the lattice-spacing dependences of semiconductor energy band schemes. Paul and Brooks have made rather extensive studies of the effects of pressure on the electrical properties of germanium[1,2] and silicon.[3] The writer has done similar experiments on indium antimonide,[4] and Keyes[5] has studied the pressure dependence of electrical conductivity in InSb. Bridgman[6] made some early conductivity *vs* pressure measurements on tellurium.

In the present work experiments have been done which for the most part represent extensions of previous studies. We shall present in Sec. 2 the results of the several different types of experiments which have been done on germanium, indium antimonide, indium arsenide, gallium antimonide, tellurium and magnesium stannide. Then in Sec. 3 we shall discuss these results with regard to their relations to pressure dependences of carrier concentrations, mobilities, energy gaps, and effective masses.

2. EXPERIMENTAL RESULTS

A. Experimental Apparatus

The apparatus consisted of a stainless steel bomb with seven electrical leads and capable of producing by a fluid a pressure up to 2000 atmospheres. Measurements of the Hall effect, electrical conductivity, and in a few cases magnetoresistance were made. The apparatus and experimental methods employed were generally the same as described in a previous paper.[4] For further details see the author's thesis.[7]

B. Hall Reversal in Germanium

The germanium experiment consisted of a measurement of the effect of a pressure of 2000 atmospheres on the temperature at which the Hall coefficient of a *p*-type sample reversed sign. The sample used was a single crystal of 21 ohm-cm *p*-type Ge obtained from the Philco Corporation whose atmospheric pressure Hall reversal temperature was 64.5°C. The experiment was done by obtaining portions of the Hall coefficient *vs* temperature curves above and below the reversal temperature at one and 2000 atmospheres using a field of 1000 gauss. The results are plotted in Fig. 1, where we see that the reversal occurred at 68.9°C at the high pressure, representing an increase of 4.4 degrees between one and 2000 atmospheres. There is a ± 5 percent probable error in the measured value of the reversal temperature shift due to inaccuracies in temperature and pressure measurements and slight uncertainty as to the proper curves to be drawn through the experimental points in Fig. 1.

C. Magnetoresistance of Indium Antimonide

The results of measurements of the pressure dependences of the conductivity and Hall coefficient of a *p*-type sample of InSb were reported in the previous paper.[4] It was found that the energy gap widened with increasing pressure at a rate of about 14×10^{-6} ev/atmosphere and that the electron mobility was smaller by about 12 percent at 2000 atmospheres than at atmos-

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† This paper summarizes part of a thesis presented to the Graduate School, University of Pennsylvania, in partial fulfillment of the requirements for the Ph.D. degree.
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[1] W. Paul, Phys. Rev. **90**, 336 (1953).
[2] W. Paul and H. Brooks, Phys. Rev. **94**, 1128 (1954).
[3] W. Paul and G. Pearson, Phys. Rev. **98**, 1755 (1955).
[4] D. Long, Phys. Rev. **99**, 388 (1955).
[5] R. Keyes, Phys. Rev. **99**, 490 (1955).
[6] P. W. Bridgman, Proc. Am. Acad. Sci. **68**, 95 (1933); **72**, 159 (1938).
[7] D. Long, Ph. D. thesis, University of Pennsylvania, 1955 (unpublished).

pheric pressure. Keyes[5] found similar results and also showed that the hole mobility was not changed by pressure. In the present work a measurement was made of the effect of pressure on the transverse magnetoresistance of the same sample used in our previous experiments on InSb. The experiment was done at a temperature of 23°C with a magnetic field of 6900 gauss. It was found that the value of $(\Delta\rho/\rho_H)$ at atmospheric pressure was 0.364; whereas, at 2000 atmospheres it was 0.344. The impurity hole density in the sample was 3.3×10^{15} per cc.

D. Conductivity and Hall Effect in Indium Arsenide and Gallium Antimonide

Measurements of conductivity and Hall coefficient *vs* pressure were made on an *n*-type sample of InAs ob-

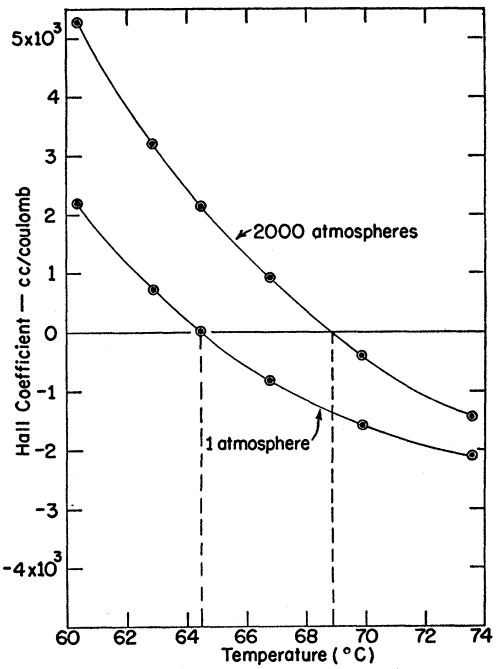

FIG. 1. Pressure shift of Hall coefficient reversal temperature in *p*-type Ge.

tained from the Naval Ordnance Laboratory at 24.0°C and 44.3°C. This sample was completely extrinsic at these temperatures and had an impurity electron density of 6×10^{16} per cc. The conductivity decreased in an apparently linear fashion with increasing pressure and was about 7 percent smaller at 2000 atmospheres than at atmospheric pressure. The Hall coefficient was unaffected by pressure. Exactly the same types of measurements were made on an *n*-type sample of GaSb obtained from Bell Telephone Laboratories at 23.0°C. The conductivity and Hall coefficient of the GaSb sample were both found to be independent of pressure up to 2000 atmospheres. This sample was also completely extrinsic at the temperature of the experiment.

TABLE I. Pressure dependence of conductivity of tellurium (sample TA).

Temperature °C	Conductivities ($ohm^{-1}-cm^{-1}$) σ_1	σ_{2000}	σ_{2000}/σ_1
58.8	6.44	13.7	2.12
73.2	8.24	17.1	2.07
90.1	10.63	21.6	2.03
101.8	12.58	25.1	2.00
119.4	15.9	31.0	1.95

E. Tellurium

An extensive study has been made of the effects of pressure on the conductivity and Hall effect of tellurium. Tellurium has an anisotropic crystal structure[8] consisting of long chains of atoms arranged in hexagonal array. The measurements to be described here have *all* been made on single-crystal samples in which the direction of current flow was parallel to the one unique crystallographic axis, the *c*-axis. The samples were all *p*-type at low temperatures, and were prepared by the author.

First of all, conductivity *vs* pressure measurements were made on sample TA at 58.8°C, 73.2°C, 90.1°C, 101.8°C, and 119.4°C. This sample was completely intrinsic at these temperatures and had an impurity hole density of about 2.5×10^{15} per cc. The values of the conductivity at one and 2000 atmospheres at each of the temperatures are listed in Table I, and the conductivity *vs* pressure data at 58.8°C (which are typical) are plotted semilogarithmically in Fig. 2. An interesting feature in Fig. 2 is the slight curvature in the plot of log (conductivity) *vs* pressure. Measurements of Hall coefficient *vs* pressure were also made on sample TA at 73.2°C, 90.1°C, and 101.8°C at the same times as the corresponding conductivity measurements. The ratios of the Hall coefficient at 2000 atmospheres to that at one atmosphere are listed in Table II, and the Hall coefficient *vs* pressure data at 90.1°C (which are typical) are plotted semilogarithmically in Fig. 3.

Measurements of conductivity and Hall coefficient *vs* pressure were made on sample TC at 0°C and 26.3°C.

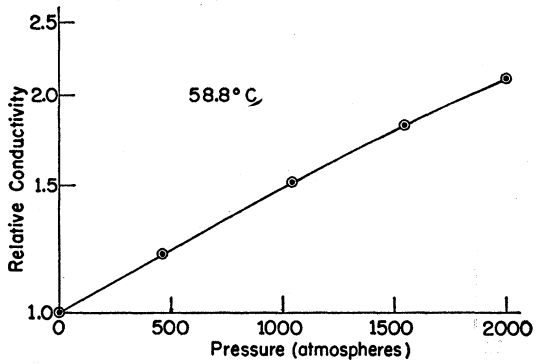

FIG. 2. Conductivity *vs* pressure for tellurium, sample TA.

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

TABLE II. Pressure dependence of Hall coefficient of sample TA.

Temperature, °C	R_{2000}/R_1
73.2	0.57
90.1	0.59
101.8	0.60

This sample was doped with antimony to make it extrinsic at these temperatures and had an impurity hole density of about 1.3×10^{18} per cc. The conductivity increased approximately linearly with increasing pressure at both temperatures and was 1.23 times as large at 2000 atmospheres as at atmospheric pressure. The Hall coefficient of sample TC was unaffected by pressure

The Hall coefficient of tellurium exhibits two sign reversals, the high-temperature one always occurring at about 500°K, and the low-temperature reversal occurring at a temperature which varies from sample to sample and depends upon the impurity concentration. A measurement was made of the pressure-induced shift of the lower Hall reversal temperature on sample TD, which had an impurity hole density of 2.1×10^{16} per cc. This experiment was done in the same way as the germanium experiment described earlier, and the results are plotted in Fig. 4. We see that the reversal shifted to lower temperatures with increasing pressure, and that it occurred at 41.0°C, 29.5°C, and 19.2°C at one, 1000, and 2000 atmospheres respectively. A similar experiment was attempted on the high-temperature (500°K) Hall reversal, but no pressure shift was detected.

F. Magnesium Stannide

Measurements were made at 0°C and 21.7°C of the pressure dependence of the conductivity of an intrinsic sample of Mg_2Sn from one to 2000 atmospheres. The results are plotted in Fig. 5. This sample was n-type at low temperatures and had an impurity electron density of about 2×10^{16} per cc. We see that the resistivity (inverse of conductivity) increased with increasing pressure at both temperatures in an apparently exponential manner. This sample was provided by Dr. R. G. Breckenridge of the National Bureau of Standards. Electrical leads of copper wire were attached to it with ordinary soft solder.

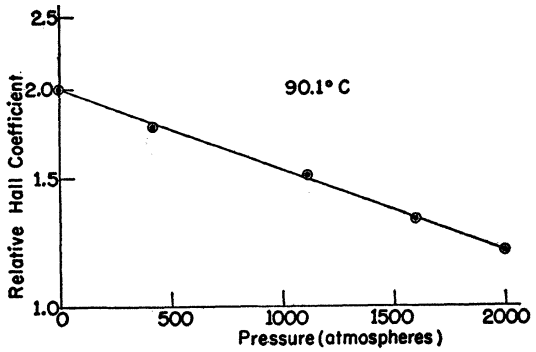

FIG. 3. Hall coefficient *vs* pressure for tellurium, sample TA.

3. DISCUSSION

A. Germanium

We shall see that the observed shift of the Hall reversal temperature of our p-type Ge sample is due almost entirely to a widening of the energy gap with increasing pressure. Paul[1] has found that the gap in Ge widens linearly with increasing pressure at a rate of just about 5.5×10^{-6} ev/atmosphere, which then gives a value at 2000 atmospheres which is 0.011 ev larger than the atmospheric pressure gap. Paul and Brooks[2] have found that the electron and hole mobilities in Ge are practically independent of pressure up to 2000 atmospheres. In the following analysis of our results we shall allow for the existence of two distinct types of holes in the valence band.[9]

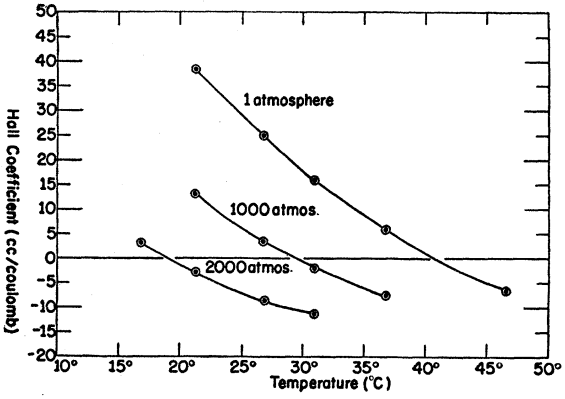

FIG. 4. Pressure shift of low Hall coefficient reversal temperature in tellurium, sample TD.

The condition for the Hall coefficient to pass through a zero is that

$$n\mu_n^2-p_1\mu_1^2-p_2\mu_2^2=0, \tag{1}$$

where the subscripts n, 1, and 2 refer to electrons, "fast" holes, and "slow" holes respectively. Let us now define a and b as the fractions of the total hole density p which have the mobilities μ_1 and μ_2 respectively. Also,

$$p=n+p_0, \tag{2}$$

since the impurities are all ionized at the temperature of the Hall reversal. Then the reversal condition can be written as

$$n=\frac{p_0(a\mu_1^2+b\mu_2^2)}{\mu_n^2-(a\mu_1^2+b\mu_2^2)}. \tag{1a}$$

The carrier densities at the Hall reversal are related to the energy gap (at absolute zero) E_g^0, the reversal

[9] See, for example, Willardson, Harman, and Beer, Phys. Rev. 96, 1512 (1954).

temperature T_r, the temperature rate of change β of the gap width, and the effective masses by the following equation:

$$np=4\left(\frac{2\pi kT_r}{h^2}\right)^3(m_nm_p)^{\frac{3}{2}}\exp\left(\frac{\beta}{k}\right)\exp\left(\frac{-E_g^0}{kT_r}\right). \quad (3)$$

The mobilities, and therefore also the effective masses, are pressure-independent up to 2000 atmospheres. β must certainly also be nearly independent of pressure. Furthermore, we can safely assume that the relative numbers of "fast" and "slow" holes remain constant with respect to temperature and pressure because of the smallness of the spin-orbit splitting in the valence band.[9] Then, the values of n and p for which the Hall coefficient is zero must be unchanged by 2000 atmospheres. We neglect the slight difference in the temperature dependences of the electron and hole mobilities,[9] since the effect of this on our results would certainly be insignificant. From (3), for small pressure changes of T_r and E_g^0, we obtain finally the following equation:

$$\delta E_g^0=E_g^0\frac{\delta T_r}{T_r}+3k\delta T_r. \quad (4)$$

Substituting average values of $E_g^0=0.755$ ev and $T_r=340°$K into (4) along with $\delta T_r=+4.4$ degrees, we find that $\delta E_g^0=+0.0109$ ev. This result compares very well with the value of 0.011 ev obtained from Paul's work; it thus indicates that the shift of the Hall reversal to higher temperatures is caused only by the pressure-induced increase of the energy gap, and also lends verification to our assumptions of constancy of the effective masses, etc.

B. Intermetallic Compounds

Willardson, Harman, and Beer[9] give the following expression for the transverse magnetoresistance of a two-carrier semiconductor:

$$\frac{\Delta\rho}{\rho_H}=1-\frac{(aK_n+K_p)^2+\frac{1}{4}\pi\gamma_p(acL_n-L_p)^2}{(a+1)(aK_n+K_p)}. \quad (5)$$

K and L are dimensionless integrals over carrier energies and the γ's are defined as

$$\gamma_n=(9\pi/16)\mu_n^2H^2\times10^{-16},$$
$$\gamma_p=(9\pi/16)\mu_p^2H^2\times10^{-16},$$

where the mobilities μ_n and μ_p are in cm²/volt-sec, and the magnetic field H is in gauss. Also,

$$a=\sigma_n^0/\sigma_p^0, \quad \text{where} \quad \sigma_n^0+\sigma_p^0=\sigma^0,$$
$$c=\mu_n^0/\mu_p^0,$$

where the superscript zeros mean that the conductivities σ and the mobilities are for zero magnetic field. The subscripts n and p refer to electrons and holes respectively.

In order to apply Eq. (5) to our experimental results on InSb, we must substitute the values of the various parameters for the sample studied. From the previous Hall and resistivity measurements,[4] we find that at atmospheric pressure, $a=28.5$ and $c=32.0$, and at 2000 atmospheres, $a=25.4$ and $c=28.6$. Now, when γ is of the order of 25 the following asymptotic expansions for K and L can be used with accuracy:

$$K=\frac{2!}{\gamma}-\frac{3!}{\gamma^2}+\cdots,$$
$$L=\frac{1\cdot3}{2\gamma}-\frac{1\cdot3\cdot5}{2^2\gamma^2}+\cdots. \quad (6a)$$

When γ is less than about 0.025, the approximations are

$$K=1-\gamma-\gamma^2(0.577+\ln\gamma),$$
$$L=1-2\gamma-2\pi^{\frac{1}{2}}\gamma^{\frac{3}{2}}, \quad (6b)$$

The electron mobility in our sample at 23°C and atmospheric pressure was about 50 000 cm²/volt-sec, and was 12 percent smaller at 2000 atmospheres.[4] Because of the difficulty of measuring the magnitude of the mobility accurately, the following procedure was followed in order to determine the value of γ_n. For a mobility in the vicinity of 50 000 cm²/volt-sec and a field of 6900 gauss, γ_n lies somewhere between 20 and 25, so that the approximations of (6a) can be used. Also, γ_p is then less than 0.025, so that we can use the approximations of (6b) for the holes. A series of values of γ_n between 20 and 25 were substituted into Eq. (5)

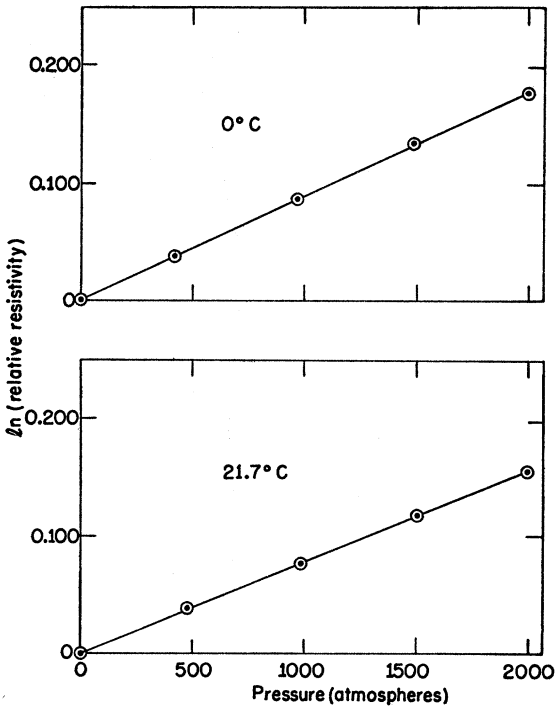

FIG. 5. Conductivity *vs* pressure for Mg_2Sn.

along with the values of a, c, and γ_p until one was found which gave a $(\Delta\rho/\rho_H)$ equal to the experimental result of 0.364 at atmospheric pressure. The proper choice proved to be $\gamma_n=23$, requiring then that $\gamma_p=0.0226$. Then, a decrease of electron mobility of 12 percent leads to a value of $\gamma_n=18.4$ at 2000 atmospheres. Repeating the calculation with this γ_n, we find that $(\Delta\rho/\rho_H)=0.346$ at 2000 atmospheres which compares well with the experimental value of 0.344. We thus see that the transverse magnetoresistance is smaller at 2000 atmospheres than at one atmosphere by approximately the amount expected for the known decrease of electron mobility.

The decrease of conductivity with increasing pressure in the extrinsic n-type sample of InAs must be caused by a pressure-induced decrease of the electron mobility of 7 percent for 2000 atmospheres, since the lack of change of the Hall coefficient means that the extrinsic electron density was unaffected by pressure. Thus, there is a rather large decrease of the electron mobility in InAs just as there is in InSb, and this decrease is probably due to an increase of the effective mass with increasing pressure in the same manner as in InSb. The absence of a pressure change of either the conductivity or the Hall coefficient of GaSb leads to the conclusion that the electron mobility in this material is practically independent of pressure.

C. Tellurium

In discussing the results of the tellurium experiments, we shall use the double-conduction-band model developed by Callen[10] and Naussbaum,[11] since it appears to be the best so far proposed. In this model the conduction band consists of two overlapping bands whose bottom edges are separated from the lower conduction band by a forbidden gap about 0.33 ev wide. The density of states in the lower conduction band is smaller than in the upper, and the density of states at the top of the valence band has a value somewhere in between the conduction band densities. The mobilities are then related in the reverse fashion, with the mobility in the upper conduction band the smallest. It has not yet been possible to determine the quantitative relations among these quantities, but it is probable that the contributions to the conductivity and Hall coefficient of those electrons occupying states in the upper (low-mobility) conduction band are rather small.

We then deal with a three-carrier model in tellurium. Account must also be taken of the anisotropic crystal structure. The conductivities parallel and perpendicular to the crystalline c-axis are related to the carrier densities and mobilities in these directions by

$$\begin{aligned}\sigma_{\parallel}&=|e|(p\mu_{p\parallel}+n_1\mu_{1\parallel}+n_2\mu_{2\parallel}),\\ \sigma_{\perp}&=|e|(p\mu_{p\perp}+n_1\mu_{1\perp}+n_2\mu_{2\perp}),\end{aligned}\tag{8}$$

where p, 1, and 2 refer respectively to holes in the valence band, electrons in the lower conduction band, and electrons in the upper conduction band. For the Hall effect it can be shown[7] that if the primary current flows parallel to the c-axis, the Hall coefficient is given by

$$R=+\frac{3\pi}{8|e|}\times\frac{p\mu_{p\parallel}\mu_{p\perp}-n_1\mu_{1\parallel}\mu_{1\perp}-n_2\mu_{2\parallel}\mu_{2\perp}}{(p\mu_{p\parallel}+n_1\mu_{1\parallel}+n_2\mu_{2\parallel})(p\mu_{p\perp}+n_1\mu_{1\perp}+n_2\mu_{2\perp})}.\tag{9}$$

Let us consider now a completely intrinsic sample well below 500°K, and also assume that the contributions of the upper band electrons to the conductivity and Hall effect are negligible. We can then write Eqs. (7), (8), and (9) as

$$\sigma_{\parallel}=|e|n\mu_{p\parallel}(fc_{\parallel}+1),\tag{7a}$$

$$\sigma_{\perp}=|e|n\mu_{p\perp}(fc_{\perp}+1),\tag{8a}$$

$$R=\frac{-3\pi}{8|e|}\frac{1}{n}\frac{fc_{\parallel}c_{\perp}-1}{(fc_{\parallel}+1)(fc_{\perp}+1)},\tag{9a}$$

where n is the total electron density, f is the fraction of the total electrons which occupy the lower conduction band, and the c's are the mobility ratios parallel and perpendicular to the crystalline c-axis.

The first problem is to determine the direction and magnitude of the pressure-induced energy gap change in tellurium. This can be done from our conductivity *vs* pressure data on sample TA. The procedure is to find the energy gap at one and 2000 atmospheres pressure from plots of $\ln\sigma$ *vs* $1/T$ at these two pressures, which can of course be made from our data. In this way we find that the gap is about 0.032 ev smaller at 2000 atmospheres than at atmospheric pressure, where the gap width is about 0.336 ev. Bardeen[12] also found such a gap decrease from Bridgman's data,[6] but he obtained a larger value because of an incorrect extrapolation of his curve of energy gap *vs* pressure to 0.38 ev at one atmosphere. It can incidentally be shown[7] that the $\ln\sigma$ *vs* $1/T$ procedure gives the correct value of the forbidden zone in the double conduction-band model of Te.

Our experimental results on the extrinsic sample TC indicate that the hole mobility parallel to the c-axis is about 1.23 times as large at 2000 atmospheres as at atmospheric pressure, since the interpretation is obviously the same as for the InAs and GaSb experiments. It should be pointed out that Bridgman[6] found a conductivity increase of about 26 percent between one and 2000 atmospheres on a sample in which the direction of current flow was almost perpendicular to the c-axis. It seems likely that this was caused by an increase of hole mobility, since the experiment was done at −78.3°C at which the sample was completely extrinsic. The domin-

[10] H. B. Callen, J. Chem. Phys. 22, 518 (1954).
[11] A. Nussbaum, Phys. Rev. 94, 337 (1954).
[12] J. Bardeen, Phys. Rev. 75, 1777 (1949).

ant scattering process in tellurium at −78.3°C and above appears to be lattice-scattering,[7] so that the mobilities involved in these pressure experiments are lattice-scattering limited.

Now, let us multiply Eq. (7a) by (9a) to obtain

$$\sigma_{\parallel}R=\frac{-3\pi}{8}\mu_{p\parallel}\left[\frac{fc_{\parallel}c_{\perp}-1}{(fc_{\perp}+1)}\right], \tag{10}$$

and (8a) by (9a) to obtain

$$\sigma_{\perp}R=\frac{-3\pi}{8}\mu_{p\perp}\left[\frac{fc_{\parallel}c_{\perp}-1}{(fc_{\perp}+1)}\right]. \tag{11}$$

We can find the effect of pressure on the term in square brackets in (10) by substituting our experimental values of the changes of $\sigma_{\parallel}$ and R between one and 2000 atmospheres on sample TA at 90.1°C and our value of the change of $\mu_{p\parallel}$ found on sample TC. When this is done, it turns out that the value of the bracket at 2000 atmospheres is 0.98 times its value at one atmosphere. The bracketed term must then be practically independent of pressure. Similarly, it is possible to show that the bracketed term in (11) is also nearly pressure-independent, provided that we use Bridgman's conductivity *vs* pressure result at 95°C on his sample in which the current flowed perpendicular to the c-axis[6] along with our result for R and Bridgman's change of $\mu_{p\perp}$ of 26 percent. In this case the bracketed term is also about 0.98 times as large at 2000 atmospheres as at one. It is clear that the bracketed terms in Eqs. (10) and (11) can *both* be *completely* independent of pressure only if f, $c_{\parallel}$, and $c_{\perp}$ independently are. More evidence for this will appear in the following paragraphs.

Let us next consider the measurements of conductivity *vs* pressure on sample TA in a different manner. Equation (7a) applies. The total electron concentration depends on the energy gap, temperature, and densities of states as

$$n\propto(g_pg_n)^{\frac{3}{4}}e^{-E_g/2kT}, \tag{12}$$

where g_n is an "effective" density of states for electrons. Take the logarithm of (7a) and evaluate it at one and 2000 atmospheres to obtain

$$\ln\left(\frac{\sigma_{\parallel 2000}}{\sigma_{\parallel 1}}\right)=\frac{-\Delta E_g}{2kT}+\tfrac{3}{4}\ln\left[\frac{(g_pg_n)_{2000}}{(g_pg_n)_1}\right]+\ln\left(\frac{\mu_{p\parallel 2000}}{\mu_{p\parallel 1}}\right). \tag{13}$$

We have assumed that the term $(fc_{\parallel}+1)$ in (7a) does not change with pressure, as indicated by the results of the preceding paragraph. We already have experimentally determined values of all the terms in (13) except the one involving the densities of states. Substituting these values, we find that the density of states product changes by less than one percent between one and 2000 atmospheres, and can therefore be considered pressure-independent.

In order to check the validity of our result of the preceding paragraph (that the density of states product is pressure-independent), let us now consider the measurements of Hall coefficient *vs* pressure on sample TA at 90.1°C. Equation (9a) applies. At this stage of the analysis we know that the only dependence of R on pressure must be through the dependence of n on the energy gap. Then, we have the relation that

$$\ln(R_{2000}/R_1)=\Delta E_g/2kT. \tag{14}$$

To see whether this is so, we substitute our experimental value of $\Delta E_g=-0.032$ ev and $T=363$°K into (14). We find from this a value of 0.60 for the Hall coefficient ratio of Eq. (14). This compares very well with the experimental value of 0.59, and thus lends verification to the previous results of this section.

It is of interest now to attempt to explain the slight curvature in the plot of $\ln\sigma$ *vs* P in Fig. 2. Suppose that E_g decreases linearly with increasing pressure. The contribution of this gap change to the total change of conductivity will then give a straight line on the semilogarithmic plot. Now suppose that $\mu_{p\parallel}$ increases linearly with increasing pressure. The plot of this on the semilogarithmic graph will have a slight curvature (convex upward). The sum of these two plots then will give a slightly curved $\ln\sigma$ *vs* P line in the same fashion as given by our experimental results. Actually, part of the curvature in the experimental plots may be caused by slightly nonlinear pressure-dependence of the gap width, but our measurement of the gap change did not show this.

We next consider the experiment to determine the lower Hall reversal *vs* pressure for tellurium. The reversal condition is

$$n_1\mu_{1\parallel}\mu_{1\perp}-p\mu_{p\parallel}\mu_{p\perp}=0, \tag{15}$$

which can be rewritten as

$$n=\frac{p_0}{fc_{\parallel}c_{\perp}-1}, \tag{16}$$

since $p=n+p_0$ and $n_1=fn$. Let us first assume that f does not change as the reversal temperature shifts, postponing a discussion of this until later. Then, the analysis is essentially the same as for the germanium experiment, since the right-hand side of (16) is independent of pressure by our results of the preceding sections. We then obtain again the following relation:

$$\frac{\delta E_g}{E_g}=\frac{\delta T_r}{T_r}+\frac{3k\delta T_r}{E_g}. \tag{4}$$

Now, in this experiment it is most convenient to sub-

stitute the experimental magnitudes of δT_r and T_r into the equation and compare the resulting value of δE_g with -0.032 ev, since T_r depends upon the average reversal temperature around which the experiment was done. From one to 2000 atmospheres the average reversal temperature was 303°K and the average value of E_g about 0.32 ev. Also, $\delta T_r = 21.8$ degrees. Substituting these quantities into Eq. (15), we find that $\delta E_g = -0.029$ ev.

Our assumption that f remains constant as the reversal point shifts to lower temperatures with increasing pressure is not quite justified. Consideration of the meaning of f reveals that it increases as the temperature is lowered, leading in turn to an increase of the term on the right-hand side of Eq. (16). It is easy to see that this would cause the reversal temperature to shift by slightly more than if f were constant, and would then lead to a value of δE_g slightly greater than the correct one if Eq. (16) is used in the analysis. Lacking knowledge of the magnitudes of the various terms on the right-hand side of (16), we cannot evaluate the size of this effect. However, it does not seem likely that f changes by as much as 5 percent as the reversal temperature shifts.[7] In any case, the value of δE_g found from this lower Hall reversal experiment agrees reasonably well with our value of -0.032 ev.

The last experiment to be considered is the one in which we found that pressure had little or no effect on the upper (500°K) Hall reversal temperature, Here we shall *not* neglect the contribution of the upper-band electrons. The reversal condition then is

$$n_1\mu_{1\parallel}\mu_{1\perp}+n_2\mu_{2\parallel}\mu_{2\perp}-p\mu_{p\parallel}\mu_{p\perp}=0. \qquad (17)$$

The sample was of course completely intrinsic at 500°K, so that we can rewrite (17) as

$$fc_{\parallel}c_{\perp}+(1-f)c_{\parallel}'c_{\perp}'=1, \qquad (17a)$$

where the primed c's are the ratios of the electron mobilities in the upper conduction band to the hole mobilities. Now, our results of the preceding sections require that the terms of $fc_{\parallel}c_{\perp}$ and $(1-f)$ be independent of pressure. Any pressure change of $c_{\parallel}'c_{\perp}'$ would then have to be compensated for by a change in the reversal temperature, which is involved in f, but the term $(1-f)c_{\parallel}'c_{\perp}'$ is much smaller than $fc_{\parallel}c_{\perp}$, so that we would not expect much of a change in the reversal temperature even if $c_{\parallel}'c_{\perp}'$ changed considerably. The one effect which could cause a marked change in the reversal temperature would be a change of ΔE. Nussbaum's experiments[11] on selenium-doped Te samples illustrate this very clearly. He found that the upper Hall reversal temperature shifted markedly to lower values as more selenium was added to the tellurium lattice. In a sample containing 13.2 percent Se the reversal occurred at 450°K, compared to 500°K for pure Te. Selenium atoms substitute for tellurium in the lattice and cause a decrease in the lattice spacing because of their smaller size. The fact that the upper reversal temperature does not shift then leads us to believe that ΔE is practically unaffected by pressure.

Neuringer[13] has measured the effect of pressure on the optical absorption edge which corresponds to the wider energy gap and finds that the gap width decreases with increasing pressure at a rate of about -1.5×10^{-5} ev/atmosphere. This can be considered as further verification of our deduction that ΔE is nearly pressure-independent, since we see that both gaps decrease at about the same rates. Neuringer's result has been found from preliminary measurements; a more accurate result should be obtained from his more extensive experiments which are now in progress.

We have been able to deduce from the results of the pressure experiments done in the present work and two of those done by Bridgman that: (a) the forbidden energy zone in tellurium narrows by 0.032 ev under the application of 2000 atmospheres pressure, (b) the hole mobilities parallel and perpendicular to the c-axis increase by about 23 and 26 percent respectively under 2000 atmospheres, (c) the electron mobilities in the lower conduction band increase at about the same rates as the corresponding directional hole mobilities since the mobility ratios were constant, (d) the densities of states in the valence and conduction bands are quite insensitive to pressure, and (e) the separation between the bottoms of the two conduction bands does not change much under 2000 atmospheres. We do not wish to give the impression that our deductions are rigorously correct, but merely say that our relatively simple model describes all the experimental results. (That is, there is in no case an effect which is radically inconsistent with all the other effects if the above deductions are assumed correct.) More complicated models may also apply. A more extensive discussion of the tellurium experiments is given in the author's thesis.[7]

D. Magnesium Stannide

The decreases of conductivity with increasing pressure on our Mg_2Sn sample appear to be caused primarily by a widening of the energy gap. By applying the same method used to find the gap change in tellurium, we find that the gap is roughly 0.01 ev wider at 2000 atmospheres than at atmospheric pressure. In this case, however, it is necessary to make a slight correction for the contribution of the impurities to the conductivity at the temperatures of the pressure experiments. The details of the calculation are given in the author's thesis.[7]

Another method of calculating the gap change is to substitute the values of the conductivity at one and 2000 atmospheres at a single temperature into the usual

[13] L. Neuringer (private communication).

expression relating σ to E_g and then find the change in the gap. This is essentially the method used by the author for InSb.[4] In this way, we find again that the gap widens by roughly 0.01 ev. The rather small effect of pressure on the conductivity of Mg_2Sn prevents us from measuring the magnitudes of these changes very accurately, but we can be quite sure that the gap does increase under pressure.

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Effect of Neutron Bombardment on a Zinc Sulfide Phosphor

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It was previously shown that neutron bombardment produced new traps in a zinc sulfide phosphor. These were interpreted as electron traps on the model of Klasen and Schoen. The new model proposed by Lambe and Klick for cadmium sulfide may be used here. This new model gives a better interpretation of the dielectric constant changes observed on neutron-irradiated samples, and is consistent with the rest of the data.

THE effect of neutron bombardment on a zinc sulfide phosphor, reported by Smith and Turkevich,[1] made use of the Klasen-Schoen model of luminescence.[2] In a recent paper, Lambe and Klick[3] propose a slightly different model. It is the purpose of this paper to show that the latter model explains the data obtained by Smith and Turkevich more simply than does the model of Klasen and Schoen. This is, thus, a further confirmation of the Lambe-Klick model.

The particular set of data which is difficult to explain on the Klasen-Schoen model concerns the dielectric constant change on illumination. If we follow Garlick,[4] the dielectric constant change is due to trapped electrons. This is not attractive since the dielectric constant change is nearly the same for samples which have a large difference in the number of traps.[1] Verwey[5] has pointed out that powdered or sintered materials can be treated as two materials in series. An increase in the conductivity of one can lead to an apparent increase in the dielectric constant. This would be the case in powdered zinc sulfide since illumination increases the conductivity greatly. In this case there should be no increase in the dielectric constant change when new traps are produced by neutron bombardment. However, the rise and decay characteristics of the dielectric constant change do not make sense using the Klasen-Schoen model. The new model of Lambe and Klick removes this difficulty.

With the Klasen-Schoen model, electron traps are produced by neutron bombardment. These traps allow nonradiative transitions to the ground state but with a long decay time. The luminescent act consists of an electron going from the conduction band to an empty luminescence center. In this model the number of electrons in the conduction band should build up on illumination and decay with about the same rate as the luminescence. The dielectric constant change should do likewise, being dependent on the number of conduction electrons. In the actual case of neutron-bombarded materials, the luminescence rises slowly and decays quickly. The dielectric constant change does just the opposite.

On the Lambe-Klick model, the luminescent act involves the holes going from the filled band to a luminescence center. The traps produced by neutron bombardment would then be hole traps. Thus, the number of electrons in the conduction band would build up quickly upon illumination, but the luminescence would build up slowly since the hole traps must be filled up first. On the other hand, the number of holes would decay from the filled band quickly and with them the luminescence, while the number of electrons in the conduction band and the dielectric constant change would decay slowly since the recombination with holes in the hole traps is assumed to be slow. This is what was observed.

[1] A. W. Smith and John Turkevich, Phys. Rev. **94**, 857 (1954).
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[5] H. K. Henish, in *Semiconducting Materials* (Butterworths Scientific Publications, London, 1951), p. 151.