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# Effect of Pressure on the Energy Levels of Impurities in Semiconductors. III. Gold in Germanium*†

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Gold can exist in substitutional positions in germanium in four states of ionization, with which are associated four energy levels in the forbidden energy gap. Appropriate doping and counterdoping with group V and group III elements allow each level to ionize independently of the others in certain temperature ranges. The separation in energy of the level from the band edges can thus be found. The pressure dependence of these separations can also be determined from the effect of the resultant change in carrier density on the resistivity. The measurements were carried out up to 6000 kg cm$^{-2}$ between 45 and 273°K. Equations for analyzing the multi-energy level systems are developed and calculations indicating how these equations can be used in actual situations are included in a set of appendices. Corrections for the effects of changes in mobility and density-of-states on the resistivity are also considered. The results indicate that the pressure coefficients of all four levels are much greater than for the hydrogenic impurities, and that the separation from the conduction band increases much more rapidly than that from the valence band.

## 1. INTRODUCTION

THE first paper[1] of this series reported the effects of high hydrostatic pressure on the "shallow" energy levels due to group III and group V impurities in silicon. The second[2] discussed a similar investigation of the so-called "deep-lying" levels produced by gold in silicon. In this third, and final, article the effects of pressure on the "deep-lying" levels produced by gold in germanium are considered.

Gold can exist in germanium in four different charge states[3,4] which are attainable through compensation of the gold in the sample with other impurities which normally produce shallow energy levels. The net charge on the gold atom in these states is known, although the distribution of the valence electrons among the states in the outermost shells has not been established with certainty.[5] The situation is illustrated in Fig. 1. The difference between the energy of the lowest state in the conduction band and the level Au(1) is that required to ionize the gold atom to give Au$^-$. Thus Au(1) is a donor level, since when it is occupied by an electron, the atom is electrically neutral. The corresponding energy differences involving Au(2), Au(3), and Au(4) represent the binding energies for the successive addition of one, two, and three electrons, and are additive. For ease of expression we refer to Au(2), Au(3), and Au(4) as energy levels of the solid, which are of the acceptor type, since they are electrically negative when filled with an electron. However, if the samples are suitably compensated, at low temperatures Au(1) and Au(2) can act as "sinks" for valence band electrons and Au(3) and Au(4) as "sources" for conduction-band electrons. Under appropriate experimental conditions, which will be explained, the free carrier density depends on only one of the four ionization energies. For the two shallower levels, Au(1) and Au(4), the temperature must be below 50°K. For Au(2) and Au(3) the temperature must be between about 100 and 170°K; the lower limit on the temperature is required since the occupation of one or other of the shallow levels can vary at low temperatures. In some samples the high resistance of the sample at very low temperatures imposes an experimental limitation.

The change in resistivity with pressure is measured

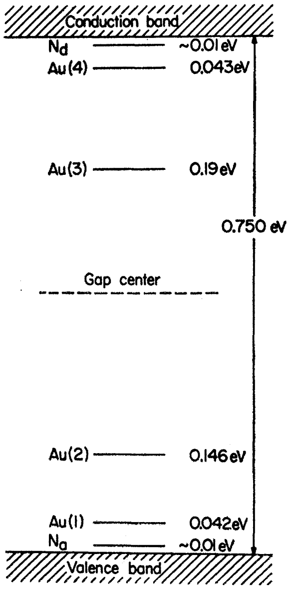

FIG. 1. Energy levels produced by gold impurity in germanium.

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† A summary of this work was presented at the Cambridge Meeting of the American Physical Society, March, 1959.

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[1] M. G. Holland and William Paul, this issue [Phys. Rev. **128**, 30 (1962)]. This paper will be referred to as I.

[2] M. I. Nathan and William Paul, preceding paper (Phys. Rev. **128**, 38 (1962)].

[3] W. C. Dunlap, Jr., *Proceedings of the Conference on Photoconductivity* (John Wiley & Sons, Inc., New York, 1956); W. C. Dunlap, Jr., Phys. Rev. **100**, 1619 (1955).

[4] W. W. Tyler and H. H. Woodbury, Phys. Rev. **102**, 647 (1957); H. H. Woodbury and W. W. Tyler, Phys. Rev. **105**, 89 (1957).

[5] G. W. Ludwig and H. H. Woodbury, Phys. Rev. Letters **5**, 98 (1960); Bull. Am. Phys. Soc. **3**, 135 (1958).

as in I. When pressure changes the ionization energy of Au(3) or Au(4), the change in carrier density is so large that the mobility corrections discussed in I are negligible, and further, changes in the density of states in the conduction (or valence) bands can be ignored when compared to changes in the ionization energy. When Au(1) or Au(2) are the controlling levels, the corrections must be considered.

## 2. APPARATUS AND METHODS

The methods and equipment described in I were also used in these experiments. Temperatures between 145 and 195°K were obtained by reducing and controlling the vapor pressure over finely powdered $CO_2$, which proved to be an easy and accurate way of maintaining constant temperatures in this range. A measurement at 111.7°K was made using a liquid methane bath. Stringent temperature control was not as necessary in these experiments as in I since the changes due to pressure were not masked by small temperature fluctuations, but in all cases the temperature was kept constant to $\pm 0.05$°K during a measurement between 100 and 170°K and to $\pm 0.01$°K below 50°K. The pressure was measured using a manganin wire gauge, calibrated by assuming that mercury freezes at 7640 kg $cm^{-2}$ at 0°C.[1]

Four contacts were soldered directly to each sample. The sample was first etched in CP4 and carefully washed after the metal contacts had been applied. The etching and washing are necessary to keep the surface conductivity low, since some of the samples have resistivities well above $10^5$ Ω cm.

## 3. EQUATIONS GOVERNING MULTIPLE ENERGY LEVELS

The expressions for carrier densities given by the Fermi statistics for deep energy levels are similar to those for shallow levels, when the impurity produces only one new level in the forbidden energy gap.[6] When the impurity can exist in several charge states, and these can be described by energy levels in the forbidden gap of increasing energy, it is no longer possible in general to write a simple Fermi factor for a particular level. Compensation of group V and group III impurities can bring the impurity atom into any of its several charge states. When the impurity levels in the gap are separated by several $kT$, a Fermi factor, which includes a degeneracy factor, accurately gives the probability of filling of the level.

Figure 1 illustrates the energy level spectrum. The lowest donor level, Au(1), can only be active when it is partially empty of electrons and it is acting as a sink for electrons from the valence band. If $N_a > N_d$ and $(N_a - N_d) > N_{\mathrm{Au}}$, the electrons in level Au(1) are emptied into the group III acceptor level at 0°K. As the temperature is raised, electrons are excited from the valence band, most easily into the remaining acceptor levels, but with increasing ease into the vacated Au(1) levels. If $N_{\mathrm{Au}} > (N_a - N_d)$, excitation of electrons occurs into the $(N_a - N_d)$ vacated gold levels. In either case, the gold donor states are entirely filled by 50°K and there remain $(N_a - N_d)$ holes in the valence band at this temperature; the crystal is $p$ type. If $N_d > N_a$, the gold donor level *will not be active at any temperature* and there will be no holes in the valence band due to this gold donor level.

The second gold level Au(2) is an acceptor nearer the valence band edge than the conduction band edge. It behaves similarly to group III acceptors, causing the sample to be $p$ type. If $N_{\mathrm{Au}} > (N_d - N_a) > 0$, there will be $[N_{\mathrm{Au}} - (N_d - N_a)]$ empty states in the level at 0°K; as the temperature is increased electrons from the valence band are excited into these states until the states are all filled, at approximately 200°K, leaving conducting holes in the valence band. If $(N_a - N_d) > 0$, the Au(1) donor is filled as described above, and an electron will not be excited into the Au(2) level of a particular gold atom until the Au(1) level for that atom is filled. Thus, as the temperature is increased, first the Au(1) level is filled with electrons from the valence band and then the Au(2) level is filled.

The third gold level Au(3) is an acceptor level nearer to the conduction band edge, and behaves as a source of electrons for the conduction band. If $2N_{\mathrm{Au}} > (N_d - N_a) > N_{\mathrm{Au}}$, the lower acceptor level Au(2) will be completely filled with electrons and the remaining $[(N_d - N_a) - N_{\mathrm{Au}}]$ electrons will be in Au(3) at 0°K. Then, the electrons from Au(3) can be thermally excited into the conduction band and the material is $n$ type.

The last of the gold levels Au(4) is an acceptor level very near the conduction band edge which behaves similarly to Au(3), acting as a source of electrons in $n$-type material. If $3N_{\mathrm{Au}} > (N_d - N_a) > 2N_{\mathrm{Au}}$, the two lower acceptor levels Au(2) and Au(3) will be filled and the remaining $[(N_d - N_a) - 2N_{\mathrm{Au}}]$ electrons will be in Au(4) at 0°K. These electrons are thermally excited into the conduction band, and the level is empty of electrons at temperatures above 50°K. At higher temperatures Au(3) supplies electrons to the conduction band.

If $(N_d - N_a) > 3N_{\mathrm{Au}}$, a situation similar to that for the Au(1) level occurs. The $[(N_d - N_a) - 3N_{\mathrm{Au}}]$ residual electrons in the group V donor states are excited to the conduction band between 0 and 15°K; the Au(4) level continues to supply electrons to the conduction band up to 50°K; the Au(3) level continues to supply electrons to the conduction band at higher temperatures.

The situation[7] can be described analytically using

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[6] H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. 7.

[7] Equation (2) was devised independently by Holland[8] and Khartsiev.[9] It should be pointed out that in one case (Holland) the number of electrons in each energy level is counted, and in the

the equations[6,8,9]

$$n+N_a+N_{\mathrm{Au}}f_T=p+N_d, \tag{1}$$

$$f_T=(f_1-1)+f_1f_2+f_1f_2f_3+f_1f_2f_3f_4, \tag{2}$$

$$f_i=\left(1+\frac{1}{g_i\exp[(E_F-E_i)/kT]}\right)^{-1} \tag{3}$$

where $N_{\mathrm{Au}}$ is the number of gold atoms, $E_i$ the ionization energy of level Au$(i)$ and the remaining symbols are defined in I. $N_{\mathrm{Au}}f_T$ is the total number of excess electrons on the neutral gold atoms. $g_i$ is a degeneracy factor which describes the number of ways in which the atom can be converted from one charge state to another higher charge state. The expression for $f_T$ is not rigorously correct. For the case in question, where any pair of the gold energy levels is separated by many times $kT$ at all temperatures under consideration, it gives an accurate formulation of the problem.

If only one level is active, the Fermi energy will be very near that level and the $f_i$ for other levels will be either 0 or 1. If two levels are active, the Fermi level can be between the levels or near one or the other levels, depending on the temperature. Using Eqs. (1) through (3) we can find the following four equations, giving the carrier densities when the Fermi level is close to one of the four levels:

$$\frac{p(p+N_{\mathrm{Au}}-N_a')}{N_a'-p}=g_1A_p\exp\left[\frac{(E_v-E_1)}{kT}\right]=g_1\phi_{1p}, \tag{4}$$

$$\frac{p(p-N_a')}{N_{\mathrm{Au}}+N_a'-p}=g_2A_p\exp\left[\frac{(E_v-E_2)}{kT}\right]=g_2\phi_{2p}, \tag{5}$$

$$\frac{n(n+2N_{\mathrm{Au}}-N_d')}{N_d'-N_{\mathrm{Au}}-n}=g_3^{-1}A_n\exp\left[\frac{(E_3-E_c)}{kT}\right]=g_3^{-1}\phi_{3n}, \tag{6}$$

$$\frac{n(n+3N_{\mathrm{Au}}-N_d')}{N_d'-2N_{\mathrm{Au}}-n}=g_4^{-1}A_n\exp\left[\frac{(E_4-E_c)}{kT}\right]=g_4^{-1}\phi_{4n}, \tag{7}$$

where $N_a'=N_a-N_d=-N_d'$, and the remaining symbols are defined in I.

These equations can be solved under certain conditions on $N_{\mathrm{Au}}$, $N_a'$, $n$, and $p$. The solutions will be discussed specifically for each sample.

Information on the number of carriers, and hence on the number of impurities is found from Hall coefficient and resistivity measurements as a function of temperature using the following relations[6,10]:

$$R=r/ne, \tag{8}$$

$$\rho=1/ne\mu, \tag{9}$$

$$r=\mu_H/\mu, \tag{10}$$

where $R$ is the Hall coefficient, $\mu_H$ the Hall mobility, $\rho$ the resistivity, $\mu$ the conductivity mobility, and $e$ the electronic charge. $r$, the Hall coefficient factor, is approximately equal to 1, but the values actually used are indicated for each sample.

These expressions will be used for $p$-type material as well as $n$-type material, since the value of $r$ has been experimentally determined[11,12] even though the mobilities are complicated due to the presence of two valence bands.

## 4. EXPERIMENTAL RESULTS AND INTERPRETATION

Under certain conditions on $N_{\mathrm{Au}}$, $N_a'$, $N_d'$, and the temperature, Eqs. (4) to (7) can be written

$$n=Ce^{-E/kT}, \tag{11}$$

where $C$ is a constant and $E$ the ionization energy. Then if $E=E_0+\alpha P$, the change in number of carriers with pressure at constant temperature gives the pressure coefficient $\alpha$.

$$d\ln n/dP=-\alpha/kT. \tag{12}$$

The condition on the temperature is that it be below some maximum value, this maximum being different for each case. It was not always possible to do a pressure measurement at the desired temperature due to limitations of the existing equipment. At temperatures at which the experiments are feasible the necessary corrections to Eq. (11) involve terms in $E_i$, $g_i$, and $N_{\mathrm{Au}}$, $N_d'$, and $N_a'$. The determination of these quantities is quite difficult and their values uncertain so that, where possible, we sought experimental conditions that give the pressure coefficients of the ionization energies without requiring precise knowledge of $E_i$ and $g_i$.

### a. Donor Level Au(1)

The Hall coefficient and Hall mobility of a sample of $p$-type gold-doped germanium, counterdoped so that the level Au(1) is only partially filled at 0°K, are shown in Figs. 2 and 3. In Appendix A we show that at tem-

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second (Khartsiev) the number of gold atoms in each state of ionization is counted. Both approaches fail to take into account the ionization of a level $E_i$ when $E_{i-1}$ is not completely filled. For the case of gold in germanium this ionization is negligible but for a case where the levels are within a few $kT$ of each other the above expressions are best replaced by other more complete expressions [C. A. Klein and P. P. Debye, *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960*), (Czechoslovakian Academy of Sciences, Prague, 1961), p. 278; C. A. Klein, P. P. Debye, and G. Rupprecht, Bull. Am. Phys. Soc. **5**, 62 (1960); Raytheon Company Research Division Technical Memorandum-T-213, 1960 (unpublished); H. Brooks (private communication)], which can be obtained from the grand canonical ensemble or simply by more careful counting of states.

[8] M. G. Holland, Technical Report HP4, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

[9] V. E. Khartsiev, Soviet Physics—Tech. Phys. **3**, 1522 (1958).

[10] H. Y. Fan, *Solid State Physics*, edited by F. Seitz and D. Turnbull, (Academic Press Inc., New York, 1955), Vol. 1.

[11] A. C. Smith, Technical Report HP2, Gordon McKay Laboratory, Harvard University, 1958 (unpublished).

[12] C. A. Klein and P. P. Debye, reference 7.

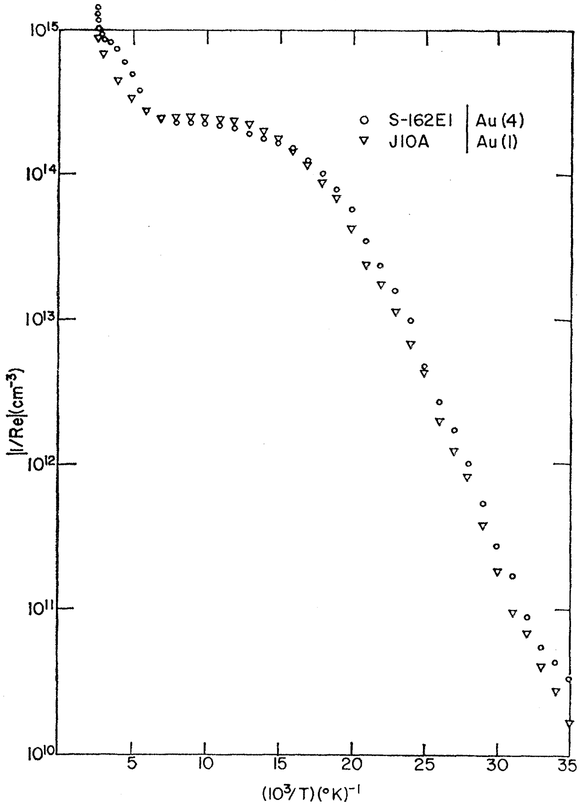

FIG. 2. Hall coefficient vs temperature for samples showing energy levels Au(1) and Au(4).

peratures below 50°K, the carrier density is given by

$$p=\frac{N_a'}{N_{\mathrm{Au}}-N_a'}g_1\phi_{1p}(1-\gamma_1+C_1\gamma_1^2), \qquad (13)$$

where

$$\gamma_1=\frac{N_{\mathrm{Au}}g_1\phi_{1p}}{(N_{\mathrm{Au}}-N_a')^2}, \quad C_1=\frac{N_{\mathrm{Au}}+N_a'}{N_{\mathrm{Au}}}.$$

At temperatures below 40°K, $\gamma_1\sim 0$, so that the energy $E_1-E_v$ can be obtained from the slope of the Hall coefficient curves of Fig. 2. A value of $0.042\pm0.002$ eV is found. This is in good agreement with the values of 0.041 and 0.05 eV found by other workers.[3,12]

In Appendix A we show that for temperatures near 50°K

$$\alpha_{1p}=\frac{d}{dP}(E_1-E_v)=kT\left[f_1(\gamma_1)\left(\frac{d\ln p}{dP}+\frac{d\ln\mu_p}{dP}\right)+\frac{d\ln A_p}{dP}\right], \qquad (14)$$

where

$$f_1(\gamma_1)=(1-\gamma_1+C_1\gamma_1^2)/(1-2\gamma_1+3C_1\gamma_1^2).$$

When $\gamma_1$ is negligible at low enough temperatures, $f_1(\gamma_1)=1$ and $\alpha_{1p}$ is accurately determined, provided the corrections for mobility and density-of-states factor can be applied. In our case the lowest temperature available, through pumping on liquid nitrogen, was about 50°K, and an estimation of $f_1(\gamma_1)$ was necessary. This is discussed in Appendix A.

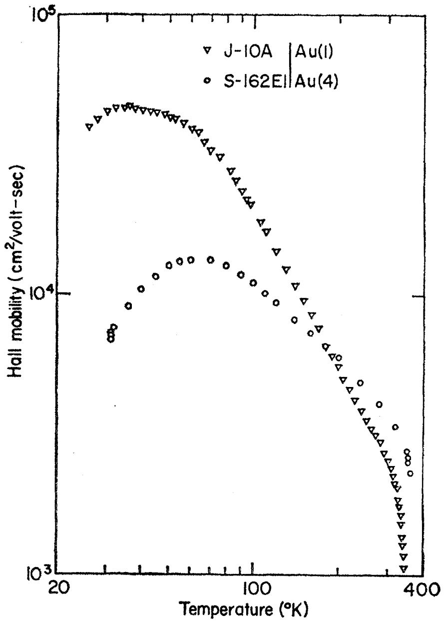

FIG. 3. Hall mobility vs temperature for samples showing energy levels Au(1) and Au(4).

The results of the pressure measurements at 49.5°K are shown in Fig. 4. The corrections for the second and third terms in Eq. (14) will now be discussed. The mobility $\mu_p$ is the average mobility of light and heavy holes and is determined by lattice and impurity scattering in an unknown combination.[6] We can, however, place limits on the pressure coefficient by observing the pressure coefficient of the mobility due to lattice scattering only, and to ionized impurity scattering only. These were determined by Smith[11] and Bridgman,[13] respectively. We can also calculate the

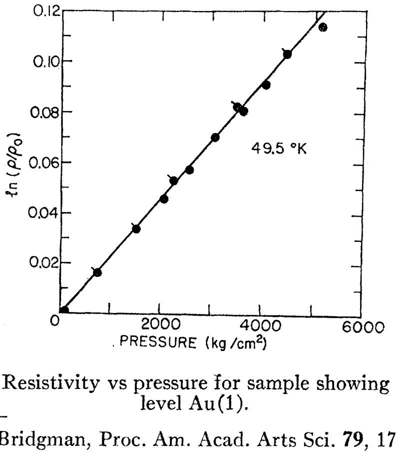

FIG. 4. Resistivity vs pressure for sample showing energy level Au(1).

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[13] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **79**, 177 (1951).

size of the effect from the known effect of pressure on the effective masses, elastic constants, and dielectric constant. The result is the estimate arrived at in Appendix A that

$$d\ln\mu_p/dP = -1.7\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

The change in $A_p$ with pressure is due to changes in both the light- and heavy-hole masses. Some of this evidence comes from experimental observation of effective-mass changes with pressure, other from theoretical argument. From Appendix A we quote

$$d\ln A_p/dP = 3.9\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

Figure 4 gives

$$d\ln\rho/dP = (23.0\pm0.7)\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

It is shown in Appendix A that $f_1(\gamma_1) = 1.0\pm0.1$ so that

$$\alpha_{1p} = (0.11\pm0.02)\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2,$$

where the 20% error represents the experimental error plus the crudely estimated errors in the correction factors to Eq. (14).

### b. Acceptor Level Au(2)

Curves of the Hall coefficient and Hall mobility versus temperature of a sample of $p$-type gold-doped germanium, counterdoped so that level Au(2) is partially filled at 0°K, are shown in Figs. 5 and 6. In Appendix B, we show that below 200°K the carrier density is given by

$$p = [(N_{\mathrm{Au}} - N_d')/N_d']g_2\phi_{2p}(1+\gamma_2)^{-1}, \qquad (15)$$

where

$$\gamma_2 = g_2\phi_{2p}/N_d', \quad N_d' = -N_a' = N_d - N_a.$$

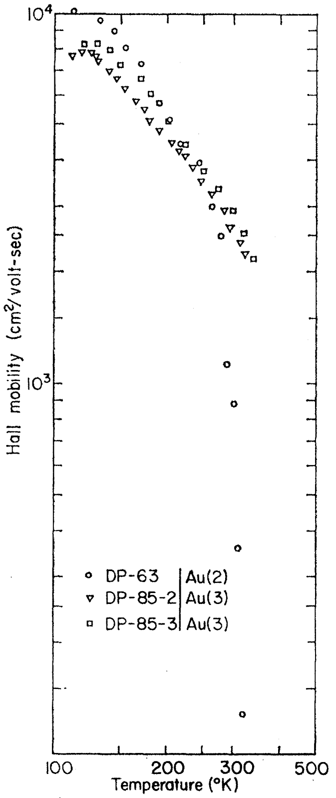

FIG. 6. Hall mobility vs temperature for samples showing energy levels Au(2) and Au(3).

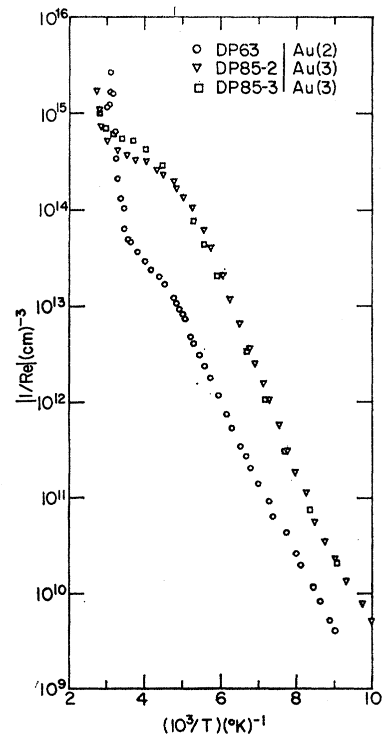

FIG. 5. Hall coefficient vs temperature for samples showing energy levels Au(2) and Au(3).

At temperatures below 170°K, $\gamma_2\sim0$ so that the energy $E_2-E_v$ can be obtained from the slopes of the Hall coefficient curves of Fig. 5. Using values for the Hall coefficient factor found for samples having a similar number of group III impurities[12] (i.e., having a similar mobility in the range 100 to 200°K, a value of $E_2-E_v = 0.146\pm0.005$ eV is derived, in good agreement with the values of 0.15 and 0.145 eV found by other workers.[3,4,12]

In Appendix B we show that for temperatures near 200°K

$$\alpha_{2p} = \frac{d}{dP}(E_2-E_v) = kT\left((1+\gamma_2)\left[\frac{d\ln\rho}{dP}+\frac{d\ln\mu_p}{dP}\right] + \frac{d\ln A_p}{dP}\right). \qquad (16)$$

When $\gamma_2$ is negligible at low enough temperatures, $\alpha_{2p}$ is accurately determined provided the corrections for mobility and density-of-states factor can be applied. In our case, a measurement was made at 170°K, where $\gamma_2$ is within 1% of unity. However, to check the

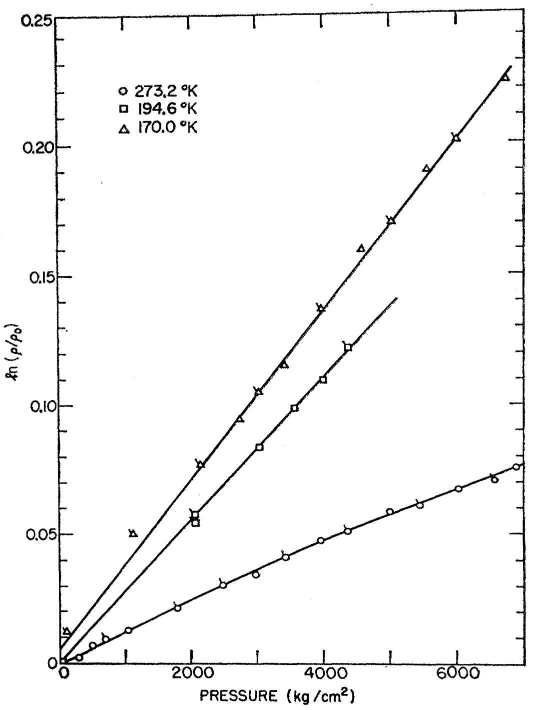

FIG. 7. Resistivity vs pressure for sample showing energy level Au(2). The points with ears were taken as the pressure was decreased.

procedure measurements were also made at 195 and 273°K. The results of these pressure measurements are shown in Fig. 7.

To explain the 273°K data we must use an equation which takes into account the presence of intrinsic electrons and holes. In Appendix B, we derive

$$\alpha_{2p}=\frac{d}{dP}(E_2-E_v)=kT\left\{\frac{(1+\gamma_2)}{(1-2\beta n_i^2/p^2)}\right.$$

$$\left.\times\left[\frac{d\ln\rho}{dP}+\frac{d\ln\mu_p}{dP}+\frac{\beta n_i^2}{p^2}\frac{d\ln(n_i^2)}{dP}\right]+\frac{d\ln A_p}{dP}\right\}, \quad (17)$$

where

$$\beta=\mu_n/\mu_p, \quad n_i^2=A_nA_p\exp[-E_g/kT].$$

There are of the order of $5\times10^{11}$ cm$^{-3}$ intrinsically derived electrons and holes in the sample at atmospheric pressure which contribute about 3% to the resistivity. The intrinsic contribution decreases rapidly as the pressure increases since the germanium energy gap increases at a rate of $5\times10^{-6}$ eV kg$^{-1}$ cm$^2$.[14,15]

To explain the data quantitatively we again consider the terms involving the mobility and density-of-states factor. In the temperature range used, the mobility is determined by lattice scattering. We use the values indicated in Appendix B.

TABLE I. Pressure coefficients for the acceptor level Au(2).

| $T$ (°K) | $kTd\ln\rho/dP$ (eV kg$^{-1}$ cm$^2$) | $\gamma_2$ | $\alpha_{2p}$ (eV kg$^{-1}$ cm$^2$) |
|---|---|---|---|
| 273.0 | $0.27\times10^{-6}$, $P<3000$<br>$0.22\times10^{-6}$, $P>3000$ | 1.12 | $0.61\times10^{-6}$<br>$0.61\times10^{-6}$ |
| 194.6 | $0.46\times10^{-6}$ | 0.057 | $0.57\times10^{-6}$ |
| 170.0 | $0.47\times10^{-6}$ | 0.013 | $0.55\times10^{-6}$ |

$$d\ln A_p/dP=3.9\times10^{-6}\text{ kg}^{-1}\text{ cm}^2,$$

$$d\ln\mu_p/dP=1.3\times10^{-6}\text{ kg}^{-1}\text{ cm}^2.$$

The parameters used in obtaining $\gamma_2$ are indicated in Appendix B. In Table I we have tabulated the calculated values of $\alpha_{2p}$.

For the 273°K data the value of $\alpha_{2p}$ for $p>3000$ kg cm$^{-2}$ is obtained with $\beta n_i^2/p^2=0$. The agreement is good considering the large range of temperatures and the approximations. The value of $\alpha_{2p}$ at 170°K is probably most accurate due to the low value of the correction for $\gamma_2$.

$$\alpha_{2p}=(0.55_{-0.02}^{+0.06})\times10^{-6}\text{ eV kg}^{-1}\text{ cm}^2.$$

### c. Acceptor Level Au(3)

Three samples of $n$-type gold-doped germanium, counterdoped so that level Au(3) was only partially filled at 0°K, were measured at high pressure. One sample which gave pressure results consistent with the other two was destroyed in an explosion of the pressure vessel before adequate data versus temperature had been taken. Figures 5 and 6 display the Hall coefficient and Hall mobility versus temperature dependences for the remaining two.

In Appendix C we show that below 170°K, and

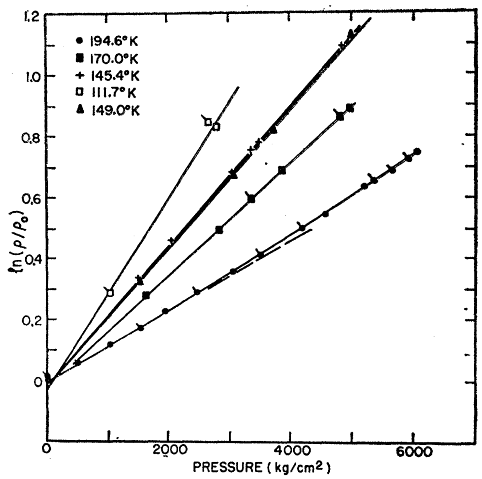

FIG. 8. Resistivity vs pressure for sample showing energy level Au(3). The points with ears were taken as the pressure was decreased.

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

[15] M. I. Nathan, W. Paul, and H. Brooks, Phys. Rev. **124**, 391 (1961).

possibly up to 195°K, the carrier density is given by

$$n=\{(N_d'-N_{\mathrm{Au}})/(2N_{\mathrm{Au}}-N_d')\}(\phi_{3n}/g_3)(1-\gamma_3), \quad (18)$$

where

$$\gamma_3=N_{\mathrm{Au}}\phi_{3n}/[g_3(2N_{\mathrm{Au}}-N_d')^2].$$

At low temperatures, $\gamma_3\sim 0$, and the ionization energy $E_c-E_3$ can be obtained from the slope of the Hall coefficient curve of Fig. 5. A value of 0.19±0.01 eV is found for both samples, in good agreement with the values of 0.20 eV found by other workers.[3,4]

From Eq. (18), and $\rho=(ne\mu_n)^{-1}$, we find

$$\alpha_{3n}=\frac{d}{dP}(E_c-E_3)=kT\left[\frac{1}{1-\gamma_3}\left(\frac{d\ln\rho}{dP}+\frac{d\ln\mu_n}{dP}\right)+\frac{d\ln A_n}{dP}\right]. \quad (19)$$

When $\gamma_3\rightarrow 0$, $\alpha_{3n}$ can be determined quite accurately. In Appendix C we show that the terms involving the mobility and density-of-states factor are relatively small for all temperatures below 200°K, and can be neglected.

The results of the pressure measurements are shown in Figs. 8 and 9. Figure 10 displays $kT(d\ln\rho/dP)$ vs $1/T$. From Eq. (19),

$$kT(d\ln\rho/dP)\gtrsim\alpha_{3n}(1-\gamma_3)$$
$$=\alpha_{3n}\{1-C\exp[(E_3-E_c)/kT]\}, \quad (20)$$

where $C$ is a constant.

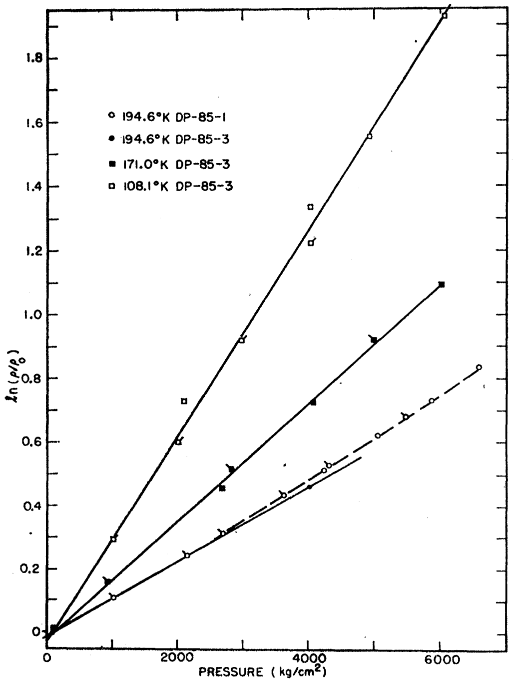

FIG. 9. Resistivity vs pressure for a second sample showing energy level Au(3). The points with ears were taken as the pressure was decreased.

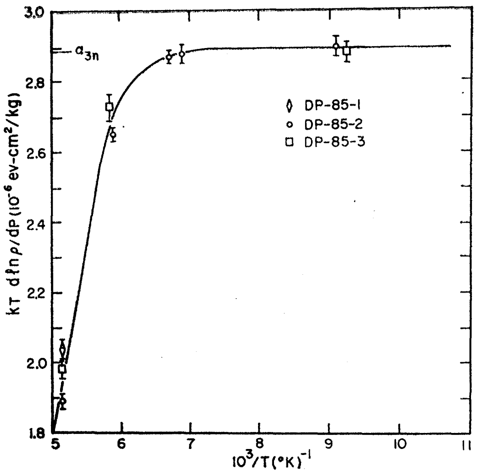

FIG. 10. Variation of $kT(d\ln\rho/dP)$ with temperature for samples showing energy level Au(3).

Figure 10 does have the form of Eq. (20). From the low-temperature asymptote ($\gamma_3\rightarrow 0$),

$$\alpha_{3n}=(2.90\pm 0.03)\times 10^{-6}\text{ eV kg}^{-1}\text{ cm}^2.$$

It is quite clear that it is preferable to deduce $\alpha_{3n}$ in the limiting case of low temperature, since corrections for $E_3$ and $g_3$ and the impurity densities are to some extent uncertain. The curvature in the data for 195°K is caused by a finite $\gamma_3$ in Eq. (19). As the pressure is raised, $E_c-E_3$ increases, $\phi_{3n}$ decreases, and $\gamma_3$ decreases. A pressure of 5000 kg cm$^{-2}$ is equivalent to a 10°K decrease in temperature at 200°K. Thus the smaller correction for $\gamma_3$ at high pressures in the 195°K data causes an increase in $(d\ln\rho/dP)$.

In principle, it is possible to determine the temperature dependence of $E_c-E_3$ from Fig. 10 and Eq. (20).[8] In practice, we are prevented from doing so by the inaccuracy of our estimates of impurity densities and degeneracy factors.

### d. Acceptor Level Au(4)

Two samples of $n$-type gold-doped germanium counterdoped so that the Au(4) level is partially filled at 0°K were obtained and measured. Analysis of one of the samples gave an activation energy of about 0.025 eV and did not obey the condition $3N_{\mathrm{Au}}>N_d'>2N_{\mathrm{Au}}$. This sample was discarded since the relation between $n$ and $E_c-E_3$ would be complex. The Hall coefficient and Hall mobility of the second sample are shown in Figs. 2 and 3. In Appendix D we show that near 50°K the carrier density is given by

$$n=\frac{N_d'-2N_{\mathrm{Au}}}{3N_{\mathrm{Au}}-N_d'}\frac{\phi_{4n}}{g_4}(1-\gamma_4+C_4\gamma_4^2), \quad (21)$$

where

$$\gamma_4=N_{\mathrm{Au}}\phi_{4n}/[g_4(3N_{\mathrm{Au}}-N_d')^2], \quad C_4=(N_d'-N_{\mathrm{Au}})/N_{\mathrm{Au}}.$$

TABLE II. Summary of pressure coefficients of the four energy levels due to gold in germanium.

| Level | Type | $E_i-E_v$ (eV) | $E_c-E_i$ (eV) | $\frac{d}{dP}(E_i-E_v)$ ($10^{-6}$ eV kg$^{-1}$ cm$^2$) | $\frac{d}{dP}(E_c-E_i)$ ($10^{-6}$ eV kg$^{-1}$ cm$^2$) | $\frac{d\ln(E_i-E_v)}{dP}$ ($10^{-6}$ kg$^{-1}$ cm$^2$) | $\frac{d\ln(E_c-E_i)}{dP}$ ($10^{-6}$ kg$^{-1}$ cm$^2$) |
|---|---|---|---|---|---|---|---|
| $E_v$ | | 0 | 0.75 | 0 | 5.0 | 0 | 6.7 |
| $E_1$ | donor | 0.042 | 0.71 | $0.11\pm0.02$ | 4.9 | 2.6 | 6.9 |
| $E_2$ | acceptor | 0.146 | 0.60 | $0.55_{-0.02}^{+0.06}$ | 4.4 | 3.8 | 7.3 |
| $E_3$ | acceptor | 0.56 | 0.19 | $2.1\pm0.1$ | 2.9 | 3.7 | 15.0 |
| $E_4$ | acceptor | 0.71 | 0.043 | $2.9\pm0.1$ | 2.1 | 4.1 | 49.0 |
| $E_c$ | | 0.75 | 0 | 5.0 | 0 | 6.7 | 0 |

At temperatures below 40°K, $\gamma_4\sim0$ so that the energy $E_c-E_4$ can be obtained from the slopes of the Hall coefficient curves of Fig. 2. Using a Hall coefficient factor $r=1$,[16] a value of $0.043\pm0.002$ eV is found, in good agreement with the values of 0.040 eV found by other workers.[4]

In Appendix D we show that

$$\alpha_{4n}=\frac{d}{dP}(E_c-E_4)=kT\left[f_4(\gamma_4)\left(\frac{d\ln\rho}{dP}+\frac{d\ln\mu_n}{dP}\right)+\frac{d\ln A_n}{dP}\right], \quad (22)$$

where

$$f_4(\gamma_4)=(1-\gamma_4+C_4\gamma_4^2)/(1-2\gamma_4+3C_4\gamma_4^2).$$

At low enough temperatures, $f_4(\gamma_4)\sim1$ and $\alpha_{4n}$ is accurately determined. In Appendix D we show that the terms involving the mobility and density-of-states factor are negligible for all temperatures considered.

Even at the lowest temperature of measurement, 45°K, $f_4(\gamma_4)$ is not approximately 1 at zero pressure, and can in fact be in error by a factor of two because of errors in $g_4$ alone. In order to avoid the necessity of knowing $f_4(\gamma_4)$ exactly, we note that near 5000 kg cm$^{-2}$, at 45°K, the decrease in $\gamma_4$, due to the increase with pressure of $E_c-E_4$, forces $f_4(\gamma_4)$ to become approximately unity.

In Appendix D we calculate that at 45°K and 5000 kg cm$^{-2}$ $f_4(\gamma_4)=1.01\pm0.01$.

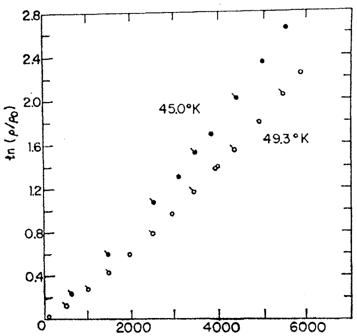

FIG. 11. Resistivity vs pressure for sample showing energy level Au(4). The points with ears were taken as the pressure was decreased.

Since, from Fig. 11,

$$kTd\ln\rho/dP=(2.1\pm0.1)\times10^{-6}\text{ eV kg}^{-1}\text{ cm}^2$$

at this temperature and pressure,

$$\alpha_{4n}=(2.1\pm0.1)\times10^{-6}\text{ eV kg}^{-1}\text{ cm}^2,$$

where the error represents the experimental error.

## DISCUSSION AND CONCLUSIONS

The pressure coefficients for the four gold levels are collected together in Table II. Since the energy gap in germanium increases with pressure in the pressure range studied, all the levels are found to move away from both the valence and conduction band edges with increasing pressure. The percentage change, $d\ln(E_i-E_v)/dP$, with respect to the valence band edge is the same within 10% for the three acceptor levels. The fractional changes in the separations of the four levels from the conduction band edge are considerably greater than the changes in the separations from the valence band. We can give no theoretical explanation for this.

It may also be noted that the pressure coefficients of the ionization energies of the gold impurities are much larger than those for the three "hydrogenic" impurities in silicon,[1] and also for the donor state produced by gold in silicon.[2] Gold also produces an acceptor level in silicon about midway in the energy gap. The separation between this level and the two band edges *decreases* with pressure, but again the absolute magnitude of the coefficient with respect to the conduction band is much the greater.[2]

## ACKNOWLEDGMENTS

We should like to acknowledge helpful discussions with Dr. Harvey Brooks, Dr. Marshall I. Nathan, Dr. Arthur C. Smith, and Dr. Douglas M. Warschauer. We are grateful to Charles Chase, James Inglis, and Alden Peavey for assistance with the high pressure apparatus, which was developed by the late Dr. P. W. Bridgman.

The samples were generously supplied by Dr. W. C. Dunlap, Jr., and Dr. W. W. Tyler of the General Electric Research Laboratory. We should like to thank Dr. Tyler and W. D. Straub of the Raytheon Research Division for Hall measurements on many of the samples.

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[16] F. J. Morin, Phys. Rev. **93**, 62 (1954).

## APPENDICES

In these Appendices we consider a miscellany of data and quantitative corrections necessary in deducing the pressure coefficients $\alpha_{ip}$ and $\alpha_{in}$ from the experimental determinations of $\ln\rho$ as a function of pressure.

## APPENDIX A. DONOR LEVEL Au(1)

(1) From the discussion in Sec. 3 and from Eqs. (4), (5), and (8) we see that the Hall coefficient near 100°K gives $N_a'$. From Fig. 2, the Hall coefficient is approximately constant between 80° and 150°K, so that, in the absence of a large temperature dependence of the Hall coefficient factor $r$, $N_a'$ is accurately determined. That is, the Au(1) level is completely filled with electrons and the Au(2) level has not yet started to fill, so that there are $N_a'$ holes (the 0°K population of Au(1)), in the valence band at these temperatures. Using $r=1.1$ at 100°K[12] we find $N_a'=2.6\times10^{14}$ cm$^{-3}$ independent of any assumptions on the $g_i$'s.

We also require $N_{\mathrm{Au}}$. Near room temperature the hole density $p$ is given by Eq. (5). Solving this equation for $N_{\mathrm{Au}}$, we find

$$N_{\mathrm{Au}}=(p-N_a')(1+(p/g_2\phi_{2p})]. \qquad \text{(A1)}$$

Using $r=1.8$ at 294°K and $\phi_{2p}$ determined with $(E_2-E_v)=0.146$ eV as found in Sec. 4b, we obtain

$$N_{\mathrm{Au}}=5.9\times10^{14}(1+5.4\times10^{-2}g_2^{-1})\ \mathrm{cm}^{-3}.$$

The values of $g_2^{-1}$ found in the literature vary from 2 [6] to 8.5.[12,17] For $2\leqq g_2^{-1}\leqq10$, we find $6.5\times10^{14}\leqq N_{\mathrm{Au}}\leqq9.1\times10^{14}$. If we now solve Eq. (4) for $p$ at 50°K we must keep all terms second order in $g_1\phi_{1p}/N_a'$ and $g_1\phi_{1p}/N_{\mathrm{Au}}$ since $g_1$ is greater than 1 [12] and $\phi_{1p}\sim2\times10^{13}$ at 49.5°K. In this way we find

$$2p=(N_{\mathrm{Au}}-N_a'+g_1\phi_{1p})\times\left[\left(1+\frac{4g_1\phi_{1p}N_a'}{(N_{\mathrm{Au}}-N_a'+g_1\phi_{1p})^2}\right)^{1/2}-1\right],$$

$$p=\frac{g_1\phi_{1p}N_a'}{N_{\mathrm{Au}}-N_a'}\left(1-\frac{N_{\mathrm{Au}}g_1\phi_{1p}}{(N_{\mathrm{Au}}-N_a')^2}+\frac{(N_{\mathrm{Au}}g_1\phi_{1p})^2}{(N_{\mathrm{Au}}-N_a')^4}\frac{N_{\mathrm{Au}}+N_a'}{N_{\mathrm{Au}}}\right), \qquad \text{(A2)}$$

$$p=\frac{g_1\phi_{1p}N_a'}{N_{\mathrm{Au}}-N_a'}(1-\gamma_1+C_1\gamma_1^2),$$

which is Eq. (13).

From

$$\rho=(pe\mu_p)^{-1},$$

we have

$$\frac{d\ln p}{dP}=-\frac{d\ln\mu_p}{dP}-\frac{d\ln p}{dP}$$

$$=-\frac{d\ln\mu_p}{dP}-\frac{1}{f_1(\gamma_1)}\frac{d\ln A_p}{dP}-\frac{1}{kTf_1(\gamma_1)}\frac{d}{dP}(E_v-E_1),$$

where

$$f_1(\gamma_1)=(1-\gamma_1+C_1\gamma_1^2)/(1-2\gamma_1+3C_1\gamma_1^2) \qquad \text{(A3)}$$

from a straightforward differentiation of Eq. (A2). This leads directly to Eq. (14).

We are left with the problem of setting limits on the function $f_1(\gamma_1)$. The experimental error on $E_1-E_v$ is enough to give wide variation in the calculation of $g_1$ and thus give large errors in $\gamma_1$. If $r=1.1\pm10\%$ at 49.5°K, we find $p=4.7\times10^{13}\pm10\%$ from the Hall coefficient (Fig. 2). Then, using Eq. (4) directly we can solve for $g_1$ using the two limiting values of $N_{\mathrm{Au}}$ found above. With this procedure we find for $N_{\mathrm{Au}}=6.5\times10^{14}$ cm$^{-3}$, $g_1=5.1$, $f_1(\gamma_1)=1.07$ and for $N_{\mathrm{Au}}=9.1\times10^{14}$ cm$^{-3}$, $g_1=8.1$, $f_1(\gamma_1)=1.09$. The value of $g_1$ quoted in the literature is approximately 2. If we use $g_1=2$ we find $f_1(\gamma_1)$ can be only as low as 0.90. Thus independent of $g_1$ and $g_2$ (since $N_{\mathrm{Au}}$ depends on $g_2$) we find $f_1(\gamma_1)=1.0\pm0.1$.

(2) The value of $d\ln A_p/dP$ is found from Smith's[11] estimated changes in the effective masses with pressure. These were obtained from the pressure dependence of the lattice scattering mobility and the elastic constants, and some approximations regarding the motion of the energy bands which interact with the valence bands being considered.

$$\frac{d\ln A_p}{dP}=\frac{3}{2}\frac{d\ln m_d}{dP}, \qquad (m_d)^{3/2}=m_1^{3/2}+m_2^{3/2}, \qquad \text{(A4)}$$

where $m_1$ is the heavy-hole mass and $m_2$ the light-hole mass.

$$\frac{d}{dP}\ln(m_d^{3/2})=\frac{d}{dP}\{\tfrac{3}{2}\ln m_1+\ln[1+(m_2/m_1)^{3/2}]\},$$

$$\frac{d\ln A_p}{dP}=\frac{3}{2}\frac{d\ln m_1}{dP}+\frac{1}{1+(m_2/m_1)^{3/2}}\frac{d(m_2/m_1)^{3/2}}{dP}, \qquad \text{(A5)}$$

$$\frac{d\ln A_p}{dP}=\frac{3}{2}\left[\frac{d\ln m_1}{dP}+\frac{1}{1+(m_1/m_2)^{3/2}}\left(\frac{d\ln m_2}{dP}-\frac{d\ln m_1}{dP}\right)\right].$$

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[17] C. A. Klein, P. P. Debye, and G. Rupprecht, reference 7.

Smith estimates

$$d\ln m_2/dP = 12\times 10^{-6}\ \mathrm{kg^{-1}\ cm^2},$$

$$d\ln m_1/dP = 2.2\times 10^{-6}\ \mathrm{kg^{-1}\ cm^2}.$$

$m_1/m_2 = 8.4$ for germanium so that

$$d\ln A_p/dP = 3.9\times 10^{-6}\ \mathrm{kg^{-1}\ cm^2}.$$

This value is due mostly to the change in heavy-hole mass.

We must assume that the change in effective mass with pressure is temperature independent so that these values found from room temperature data will apply between 49.5 and 300°K. Smith has shown that the effect of pressure on lattice scattering is temperature independent from 200 to 300°K, the region over which he made his measurements.

(3) To avoid the difficulties in estimating the correction due to the mobility in $p$-type material, found in paper I of the series, we shall neglect the change in mass of the light holes with pressure. Smith has shown that the change in lattice scattering mobility is due for the most part to the change in heavy-hole mass. Similarly, the heavy holes contribute most of the conduction when impurity scattering dominates. We assume

$$\mu^{-1} = \mu_L^{-1} + \mu_I^{-1},$$

so that

$$\frac{d\ln\mu}{dP} = \frac{\mu}{\mu_L}\frac{d\ln\mu_L}{dP} + \frac{\mu}{\mu_I}\frac{d\ln\mu_I}{dP}. \tag{A6}$$

$\mu_L$ is calculated from a formula of Morin and Maita,[16,18] $\mu$ is taken to be the measured Hall mobility at 49.5°K, and $\mu_I$ is calculated from the reciprocal relation between mobilities. From Smith[11] we have

$$d\ln\mu_L/dP = 1.3\times 10^{-6}\ \mathrm{kg^{-1}\ cm^2}.$$

From the Brooks–Herring formula[6] for ionized impurity scattering we have approximately

$$\frac{d\ln\mu_I}{dP} = 2\frac{d\ln K}{dP} - \frac{1}{2}\frac{d\ln m_1}{dP}, \tag{A7}$$

where $K$ is the dielectric constant. Using the value of $d\ln K/dP$ from Cardona, Paul, and Brooks[19] and the change in $m_1$ estimated by Smith, we obtain $d\ln\mu_I/dP$, and finally

$$d\ln\mu/dP = -1.7\times 10^{-6}\ \mathrm{kg^{-1}\ cm^2}.$$

### APPENDIX B. ACCEPTOR LEVEL Au(2)

(1) The Hall coefficient of the sample used to study Au(2) (Fig. 5) continues to increase for temperatures less than 125°K, indicating that a deep level is deionizing as the temperature is lowered in this range. From the discussion in Sec. 3,

$$N_d' = -N_a' = N_d - N_a > 0.$$

The number of current carriers and the number of impurities can be obtained by solving Eq. (5) using $-N_d' = +N_a'$. Without approximation, Eq. (5) gives

$$N_{\mathrm{Au}} - N_d' = p\left(1 + \frac{p+N_d'}{g_2\phi_{2p}}\right). \tag{B1}$$

At high temperatures, from Eq. (B1) it would appear that $p$ tends to the value $N_{\mathrm{Au}} - N_d'$, corresponding to filling of the Au(2) level from the valence band. In our samples, there is an appreciable density of intrinsic carriers at room temperature. Where possible the data are analyzed at low temperatures to avoid considering these.

The value of $g_2$ is not well established so that Eq. (B1) cannot be solved exactly. However, if we assume $p \ll N_d'$, a condition which will be fulfilled for the data analyzed, then

$$N_{\mathrm{Au}} - N_d' = p(1 + N_d'/g_2\phi_{2p}). \tag{B2}$$

The density $p$, at several temperatures, is found from the Hall coefficient data, using appropriate values of the Hall coefficient factor $r$. The quantity $\phi_{2p}$ can be calculated at these temperatures. Equation (B2) can thus be solved for $N_{\mathrm{Au}} - N_d'$, and $N_d'/g_2$. In this way we obtain

$$N_{\mathrm{Au}} - N_d' = 1.3\times 10^{14}\ \mathrm{cm^{-3}},$$

$$N_d'/g_2 = 8.4\times 10^{15}\ \mathrm{cm^{-3}}.$$

Thus, even if $g_2^{-1}$ is as high as 10, $N_d' \sim 10^{15}\ \mathrm{cm^{-3}}$ and $p$ is at most $0.1\times N_d'$ at 273°K and $p \ll N_d'$ for $T < 250$°K. The impurity densities are therefore known in Eq. (B2) which we rewrite as

$$p = \frac{N_{\mathrm{Au}} - N_d'}{N_d'} g_2\phi_{2p}(1+\gamma_2)^{-1}, \tag{B3}$$

where

$$\gamma_2 = g_2\phi_{2p}/N_d'.$$

The resistivity is given by

$$\rho = (pe\mu_p)^{-1},$$

so that

$$d\ln\rho/dP = -d\ln\mu_p/dP - d\ln p/dP, \tag{B4}$$

where

$$\frac{d\ln p}{dP} = \frac{1}{1+\gamma_2}\left[\frac{d\ln A_p}{dP} + \frac{d(E_v - E_2)}{kTdP}\right]. \tag{B5}$$

Thus,

$$\frac{d\ln\rho}{dP} = -\frac{d\ln\mu_p}{dP} - \left(\frac{1}{1+\gamma_2}\right) \times\left[\frac{d\ln A_p}{dP} + \frac{1}{kT}\frac{d}{dP}(E_v - E_2)\right] \tag{B6}$$

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[18] F. J. Morin and J. P. Maita, Phys. Rev. **96**, 28 (1954).

[19] M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

and

$$\alpha_{2p}=\frac{d}{dP}(E_2-E_v)=kT\left\{(1+\gamma_2)\left[\frac{d\ln\rho}{dP}+\frac{d\ln\mu_p}{dP}\right]+\frac{d\ln A_p}{dP}\right\}. \quad (16)$$

The values of $\gamma_2$ can be calculated without knowing $g_2$ directly since we need only $N_d'/g_2$ and $\phi_{2p}$. They are listed in Table I.

To explain the 273°K data we must include intrinsic carriers. The resistivity equation becomes

$$\rho=(pe\mu_p)^{-1}(1+\beta n_i^2/p^2)^{-1}, \quad \text{(B7)}$$

where

$$\beta=\mu_n/\mu_p$$

and

$$n_i^2=np=A_nA_p\exp(-E_g/kT)$$

$$=\text{square of the number of intrinsic carriers.}$$

In this case

$$-\frac{d\ln\rho}{dP}=+\frac{d\ln\mu_p}{dP}+\frac{d\ln p}{dP}+\frac{d}{dP}\ln(1+\beta n_i^2/p^2). \quad \text{(B8)}$$

The term involving the intrinsic carriers is small at 273°K:

$$\beta n_i^2/p^2=0.01.$$

Thus

$$\frac{d}{dP}\ln(1+\beta n_i^2/p^2)\approx\beta n_i^2/p^2\left[\frac{d\ln\beta}{dP}+\frac{d\ln(n_i^2)}{dP}-\frac{d\ln p^2}{dP}\right], \quad \text{(B9)}$$

where

$$\frac{d\ln\beta}{dP}=\frac{d\ln\mu_n}{dP}-\frac{d\ln\mu_p}{dP}\approx-5\times10^{-6}\text{ kg}^{-1}\text{ cm}^2$$

from the data of Smith[11] and Nathan, Paul, and Brooks.[15] Also

$$\frac{d\ln(n_i^2)}{dP}=\frac{d\ln(A_nA_p)}{dP}+\frac{d}{dP}\left(-\frac{E_g}{kT}\right)\approx\frac{-1}{kT}\frac{dE_g}{dP}$$

$$=2.1\times10^{-4}\text{ kg}^{-1}\text{ cm}^2, \quad \text{(B10)}$$

from the data of Paul and Brooks.[14] Thus we can neglect the $\beta$ term in Eq. (B9). From Eqs. (B8) and (B9),

$$-\frac{d\ln\rho}{dP}=\frac{d\ln\mu_p}{dP}+\left(1-\frac{2\beta n_i^2}{p^2}\right)\frac{d\ln p}{dP}+\frac{\beta n_i^2}{p^2}\frac{d\ln(n_i^2)}{dP}, \quad \text{(B11)}$$

or

$$d(E_2-E_v)/dP=\alpha_{2p}=kT\left[d\ln A_p/dP+\frac{(1+\gamma_2)}{1-2\beta n_i^2/p^2}\left(\frac{d\ln\rho}{dP}+\frac{d\ln\mu_p}{dP}+\frac{\beta n_i^2}{p^2}\frac{d\ln(n_i^2)}{dP}\right)\right]. \quad (17)$$

(2) The correction for the density-of-states factor is the same as found in Appendix A.

(3) At the temperatures of these measurements the carriers are scattered predominantly by the lattice vibrations, so that we can use Smith's value for the pressure coefficient of the lattice-scattering mobility, viz.,

$$d\ln\mu_L/dP=1.3\times10^{-6}\text{ kg}^{-1}\text{ cm}^2.$$

## APPENDIX C. ACCEPTOR LEVEL Au(3)

(1) The sign of the Hall coefficient, and its continuous increase as the temperature is lowered, show that for certain samples the condition $2N_{\text{Au}}>N_d'>N_{\text{Au}}$ is satisfied, so that level Au(3) is de-ionizing. Equation (6) gives

$$N_d'-N_{\text{Au}}=n[1+(n+2N_{\text{Au}}-N_d')g_3/\phi_{3n}]. \quad \text{(C1)}$$

When $\phi_{3n}/g_3(2N_{\text{Au}}-N_d')<1$, this expression can be approximated by

$$n=\frac{N_d'-N_{\text{Au}}}{2N_{\text{Au}}-N_d'}\frac{\phi_{3n}}{g_3}(1-\gamma_3), \quad (18)$$

with

$$\gamma_3=N_{\text{Au}}\phi_{3n}/g_3(2N_{\text{Au}}-N_d')^2.$$

In order to show that this approximation is justified, at least below 170°K, we note the following:

$\phi_{3n}$ is calculable at any temperature since $A_n$ is known from effective mass data, and $E_c-E_3$ can be found from the slope of the Hall coefficient curve at low temperatures to be 0.19±0.01 eV. $g_3$ is taken to be $\frac{1}{2}$.[6] Thus, at 294°K,

$$g_3/\phi_{3n}=1/(2\times5.6\times10^{15}),$$

and we can show self-consistently that

$$n=N_d'-N_{\text{Au}}\approx5\times10^{14}\text{ cm}^{-3}$$

for both samples measured. The value of $n$ is obtained from the asymptote of the Hall curve near room temperature in Fig. 5 with the assumption that $r=1$. Since $2N_{\text{Au}}>N_d'>N_{\text{Au}}$, this implies that

$$N_d'\geqq1\times10^{15}\text{ cm}^{-3},$$

and

$$N_{\text{Au}}\geqq5\times10^{14}\text{ cm}^{-3}.$$

Then, unless $2N_{\text{Au}}$ and $N_d'$ nearly balance, that is, if $2N_{\text{Au}}-N_d'$ is of the order of $10^{14}$ cm$^{-3}$ we can take $\phi_{3n}/g_3(2N_{\text{Au}}-N_d')<1$ below 170°K and probably at even higher temperature. For example, at 170°K $\phi_{3n}<1\times10^{13}$, and the approximation is correct.

The experimental error of 0.01 eV on the value of $E_3-E_c$ is sufficient to prevent accurate determination of $N_d'$, $N_{\mathrm{Au}}$, and $g_3$ from the Hall data. Our discussion is aimed at establishing the range of temperature where Eq. (18) will be a good approximation, even allowing for uncertainties in $N_{\mathrm{Au}}$ and $N_d'$. Using Eq. (18), we obtain Eq. (19) for the pressure coefficient by a straightforward differentiation.

$$\alpha_{3n}=\frac{d}{dP}(E_c-E_3)=kT\left[\left(\frac{1}{1-\gamma_3}\right)\left(\frac{d\ \ln\rho}{dP}+\frac{d\ \ln\mu_n}{dP}\right)+\frac{d\ \ln A_n}{dP}\right]. \quad (19)$$

(2) Paul and Brooks,[14] and Nathan, Paul, and Brooks[15] have determined the pressure coefficient at 195 and 77°K of the electron mobility due to lattice scattering.

$$(d/dP)\ \ln\mu_{Ln}=-4\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

Since at all the temperatures considered the gold-doped samples have predominantly lattice scattering mobility this value can be used. Nathan, Paul and Brooks[15] have also deduced the pressure change in the density-of-states effective mass

$$d\ \ln m_d/dP\sim4\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

Thus,

$$d\ \ln A_n/dP\sim6\times10^{-6}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2.$$

However, at 200°K we find

$$d\ \ln\rho/dP=1\times10^{-4}\ \mathrm{kg}^{-1}\ \mathrm{cm}^2$$

and this value increases as the temperature decreases. By 170°K the terms in $A_n$ and $\mu_n$ will contribute less than 0.5% to $\alpha_{3n}$ and thus they have been neglected.

### APPENDIX D. ACCEPTOR LEVEL Au(4)

(1) From the discussion in Sec. 3 and from Eqs. (6), (7), and (8) we see that the Hall coefficient near 100°K gives $N_d'-2N_{\mathrm{Au}}$. Figure 2 shows that the Hall coefficient is almost constant between 110 and 140°K. If we ignore any (probably small) temperature dependence of the Hall coefficient factor $r$, $N_d'-2N_{\mathrm{Au}}$ is accurately determined. Setting $r=1$ at 125°K we find $N_d'-2N_{\mathrm{Au}}=2.2\times10^{14}$ cm$^{-3}$; this is independent of any assumption about the $g_i$'s.

At higher temperatures Au(3) starts to ionize and Eq. (6) is appropriate. We rewrite it as

$$N_d'-N_{\mathrm{Au}}=n[1+(2N_{\mathrm{Au}}-N_d'+n)/g_3^{-1}\phi_{3n}] \quad (\mathrm{C1})$$

and evaluate $N_d'-N_{\mathrm{Au}}$, taking $r=1$ at 294°K, and determining $\phi_{3n}$ with $E_c-E_3=0.19$ eV. We get

$$N_d'-N_{\mathrm{Au}}=8.5\times10^{14}(1+0.009g_3)\ \mathrm{cm}^{-3}.$$

Unless $g_3>10$, $N_d'-N_{\mathrm{Au}}=8.5\times10^{14}$ cm$^{-3}$ within 10%. Hence,

$$N_{\mathrm{Au}}=6.3\times10^{14}\ \mathrm{cm}^{-3} \quad \text{and} \quad N_d'=1.5\times10^{15}\ \mathrm{cm}^{-3}.$$

We can calculate $g_4$ from the Hall data below 40°K using these values of $N_{\mathrm{Au}}$ and $N_d'$, $r=1$, and $E_c-E_4=0.043$ eV. From the data at 33.3°K we find $g_4=0.22$. There is a factor of 2 error in $g_4$ due to the 5% error in $E_c-E_4$ alone.

If we now solve Eq. (7) for $n$ near 45°K we note that $\phi_{4n}\approx1\times10^{13}$ so that we must keep terms second order in $\phi_{4n}/g_4(3N_{\mathrm{Au}}-N_d')$. In this way we find

$$n=\left(\frac{3N_{\mathrm{Au}}-N_d'+\phi_{4n}g_4^{-1}}{2}\right)\times\left[\left(1+\frac{4(N_d'-2N_{\mathrm{Au}})\phi_{4n}g_4^{-1}}{(3N_{\mathrm{Au}}-N_d'+\phi_{4n}g_4^{-1})^2}\right)^{\frac{1}{2}}-1\right], \quad (\mathrm{D1})$$

$$n=\left(\frac{N_d'-2N_{\mathrm{Au}}}{3N_{\mathrm{Au}}-N_d'}\right)\frac{\phi_{4n}}{g_4}\left[1-\frac{N_{\mathrm{Au}}\phi_{4n}}{g_4(3N_{\mathrm{Au}}-N_d')^2}+\frac{N_{\mathrm{Au}}^2\phi_{4n}^2}{g_4^2(3N_{\mathrm{Au}}-N_d')^4}\left(\frac{N_d'-N_{\mathrm{Au}}}{N_{\mathrm{Au}}}\right)\right],$$

which is Eq. (21).

From

$$\rho=(ne\mu_n)^{-1},$$

we have

$$\frac{d\ \ln\rho}{dP}+\frac{d\ \ln\mu_n}{dP}=-\frac{d\ \ln n}{dP}, \quad (\mathrm{D2})$$

$$\frac{d\ \ln n}{dP}=\left(\frac{1-2\gamma_4+3C_4\gamma_4^2}{1-\gamma_4+C_4\gamma_4^2}\right)\frac{d\ \ln\phi_{4n}}{dP}=\frac{1}{f_4(\gamma_4)}\left[\frac{d\ \ln A_n}{dP}+\frac{1}{kT}\frac{d(E_4-E_c)}{dP}\right]. \quad (\mathrm{D3})$$

These lead directly to Eq. (22).

We are left with the problem of setting limits on the function $f_4(\gamma_4)$. Using the value of $g_4$ calculated above we find $f_4(\gamma_4)=1.13$ but this can be in error by over 10% due to errors in $g_4$ and $E_c-E_4$.

To eliminate the need for an accurate value of $f_4(\gamma_4)$ we consider the expression for $f_4(\gamma_4)$ at 5000 kg cm$^{-2}$.

$$\gamma_4=\frac{N_{\mathrm{Au}}\phi_{4n}}{g_4(3N_{\mathrm{Au}}-N_d')^2},$$

$$\phi_{4n}=A_n\exp(E_4-E_c)/kT.$$

If we write

$$E_c-E_4=(E_c-E_4)_0+\alpha_{4n}P, \quad (\mathrm{D4})$$

where the subscript 0 refers to atmospheric pressure, we find

$$\gamma_4=\gamma_{40}e^{-\alpha_{4n}P/kT}. \qquad \text{(D5)}$$

A value of $\gamma_{40}=0.16$ is calculated, again in error by a factor of 2 due to errors in $g_4$ and $(E_c-E_4)$.

Now, if we assume $f_4(\gamma_4)=1$ at 45°K and 5000 kg $\text{cm}^{-2}$, we can find a first approximation for $\alpha_{4n}$ using Eq. (22), neglecting terms in $\mu_n$ and $A_n$. In this way $\alpha_{4n}=2.1\times10^{-6}$ eV $\text{kg}^{-1}$ $\text{cm}^2$. Substituting this in Eq. (D5) at $P=5000$ kg $\text{cm}^{-2}$ we find $\gamma_4=\gamma_{40}\times0.08\sim0.013$.

Hence, at this pressure and temperature, $f_4(\gamma_4)=1.01\pm0.01$ where the 0.01 error represents an error of a factor of 2 in $\gamma_{40}$.

At 45°K and atmospheric pressure, we find that

$$kTd\ln\rho/dP=1.6\times10^{-6}\ \text{eV kg}^{-1}\ \text{cm}^2,$$

and using

$$f_4(\gamma_4)=1.13\pm10\%,$$

we get

$$\alpha_{4n}=1.8\times10^{-6}\pm10\%\ \text{eV kg}^{-1}\ \text{cm}^2,$$

which is in agreement with the value found near 5000 kg $\text{cm}^{-2}$. Thus this approach is reasonable.

(2) At 45°K we find

$$d\ln\rho/dP\sim10^{-3}\ \text{kg}^{-1}\ \text{cm}^2.$$

We have seen in Appendix C that

$$d\ln A_n/dP\sim6\times10^{-6}\ \text{kg}^{-1}\ \text{cm}^2.$$

Thus, the density-of-states factor represents a negligible correction in Eq. (22).

(3) At 45°K the carriers are scattered both by lattice vibrations and ionized impurities. In Appendix C we have seen that the change in lattice scattering mobility with pressure is of the same magnitude as the change in the density-of-states factor and is therefore negligible.

The pressure coefficient of the ionized impurity scattering mobility can be expressed as

$$\frac{d\ln\mu_I}{dP}=\frac{2d\ln K}{dP}+\frac{d\ln}{dP}\left(\frac{m_2}{m_1^{1/2}}\right).$$

However, since the changes in $K$ and in the masses are also of the order of $10^{-6}$ $\text{kg}^{-1}$ $\text{cm}^2$, the pressure coefficient of this scattering mechanism can also be neglected.

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# Force on a Moving Dislocation*

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A Lagrangian formulation is used to discuss the nature of the force on a moving dislocation. Whether or not a Lorentz force appears depends on the definition of force adopted, but it is shown that this force can give rise to no physical effects; a definition which does not introduce it is therefore recommended. The force is given by the usual static expression ($F=\sigma b$) and is independent of the motion of the dislocation.

## 1. INTRODUCTION

THE nature of the force on a moving dislocation, and especially the existence of the so-called Lorentz force, is still a matter of discussion.[1] We shall argue here that the difficulties associated with the force concept arise because no clear definition of force applicable to a moving dislocation has been given. A definition will be proposed which leads to an unambiguous expression for the force and is consistent with its use in other fields. Before starting on the constructive part of this program, however, we must consider some of the complications which arise when this point is neglected.

The nature of the force on a dislocation at rest has been fully discussed by Eshelby,[2] who has particularly emphasized the need for thorough treatment. His conclusions are that (a) the force should be defined as the derivative of the energy with respect to dislocation displacement; from this it follows that (b) the force in the slip plane is just $\sigma b$ per unit length of the dislocation, where $\sigma$ is the resolved shear stress. It seems to have been accepted quite uncritically that both statements (a) and (b) apply also in the dynamical case, without realizing that here they are in fact inconsistent. (The question of a Lorentz force does not arise here as it acts normally to the slip plane if it is present at all.) To illustrate this, consider two parallel screw dislocations $P$ and $Q$ in an isotropic medium, $P$ at rest and $Q$ moving with a uniform velocity $v$ in the direction $PQ$. At any instant the interaction energy of $P$ and $Q$ can depend only on their distance apart and not on their absolute positions; hence, if statement (a) is adopted, the forces each dislocation exerts on the other are equal and opposite. On the other hand, the stress produced by the

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[1] F. R. N. Nabarro, Phil. Mag. **6**, 1261 (1961).

[2] J. D. Eshelby, Phil. Trans. Roy. Soc. London **A244**, 87 (1951); *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79.