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Intervalley scattering in n type Ge from a Hall effect experiment to high pressures

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Abstract. Hall effect measurements on n type Ge to 65 kbar are described. The Hall mobility of electrons through the transfer from ⟨111⟩ to ⟨100⟩ states has been measured and an assessment of the scattering parameters for the different intervalley and intravalley processes has been made following the analysis of Nathan and co-workers in 1961. Results are compared with the more complete theory of Fawcett and Paige, and reasonable agreement is found. The Hall mobility of electrons in the ⟨100⟩ valleys is determined as $1020 \pm 170\ \mathrm{cm^2\ V^{-1}\ s^{-1}}$, the ⟨100⟩ effective mass is estimated to be ~ 50% greater than for n type Si and the ⟨100⟩–⟨111⟩ energy sub-band gap is $0{\cdot}186 \pm 0{\cdot}010$ eV. Nonequivalent intervalley scattering between the ⟨111⟩ and ⟨100⟩ valleys is shown to reduce the mobility by a factor of two near band cross-over. Results are directly relevant in determining coupling constants between valleys in high electric field calculations, involving ⟨100⟩ and ⟨111⟩ minima, as in InP.

1. Introduction

The low electric field properties of n type Ge at atmospheric pressure are now well understood. The electrons occupy four ellipsoidal minima at L_1 points at the ⟨111⟩ zone edge. At high pressures, however, an electron transfer to a higher lying set of minima takes place. The work of Bridgman and Paul (unpublished; results are reported in Nathan *et al.* 1961) and Nathan *et al.* (1961) was instrumental in showing that these minima were in the ⟨100⟩ direction at Δ_1 points in from the zone edge, similar to the occupied minima in n type Si at atmospheric pressure. Thus n type Ge can be converted by the application of high pressure into a semiconductor whose properties resemble those of Si. This effect allows us to make some interesting comparisons concerning the scattering properties and effective masses in the equivalent minima for the two semiconductors.

The high electric field properties of n type Ge are the subject of some discussion. The problem is discussed in an exhaustive Monte Carlo calculation by Fawcett and Paige (1971), who suggest that electron transfer to the higher density of states Δ_1 minima at high fields can explain all the reported data, including the negative differential mobility below 150 K observed by McGroddy and Nathan (1967). Pressure measurements are extremely useful in providing some idea of the parameters, such as sub-band energy gaps, effective masses, and deformation potentials, which can be used in these high field calculations to give a better understanding of high field transferred electron devices.

The pressure experiments reported to date have been confined to simple resistivity measurements below 30 kbar (Nathan *et al.* 1961) or p–n junction measurements (Jayaraman and Kosicki 1968). In neither case was the pressure high enough to eliminate scattering to the L_1 minima. Further recent high field, high pressure measurements are adequately discussed by Fawcett and Paige (1971). This paper describes Hall measurements to pressure (65 kbar) which are high enough to isolate electrons in the Δ_1 minima, well past L_1–Δ_1 band cross-over. Also for the first time, the mobility of electrons during band cross-over and in the ⟨100⟩ valleys has been measured. This has allowed us to observe directly how

the intense L_1–Δ_1 nonequivalent intervalley scattering can lead to a large reduction in the effective electron mobility near band cross-over.

The observed resistivity and Hall data are both fitted following the approach of Nathan *et al.* (1961). In section 6, the parameter values obtained are compared with those derived from our resistivity data alone by Fawcett and Paige (1971) in the course of a Monte Carlo study of the high field properties of germanium.

2. Conduction band structure of Ge at high pressures

The measured effective masses in the longitudinal and transverse directions for the L_1 minima are approximately $m^*_{lL} = 1{\cdot}58\, m_e$ and $m_{tL} = 0{\cdot}08\, m_e$ respectively, giving a density of states effective mass $m^*_{DL} = (m^*_{lL} m^{*2}_{tL})^{1/3} \nu_L^{2/3} = 0{\cdot}54\, m_e$, where ν_L represents the number of minima. The pressure coefficient of the L_1 minima is $+5 \times 10^{-6}$ eV bar^{-1}, away from the central Γ_{25} valence band maximum (Paul 1961). Early measurements by Bridgman (1952) showed that the resistance passed through a maximum near 30 kbar, and then decreased in a manner similar to that observed in n type Si at lower pressures. Although these measurements were probably carried out under significantly nonhydrostatic conditions, further measurements on Ge–Si alloys (Bridgman and Paul unpublished) confirmed that it was a real effect. The analysis of Nathan *et al.* (1961) showed that intense intervalley scattering, giving rise to a reduction in mobility, between the L_1 and Δ_1 valleys was the principal cause of the maximum in the resistance. Later Jayaraman and Kosicki (1968) repeated the experiment to 50 kbar and estimated a pressure coefficient for the Δ_1 minima to be between -1×10^{-6} and $-1{\cdot}5 \times 10^{-6}$ eV bar^{-1}, which may be compared with that for Si of $-1{\cdot}5 \times 10^{-6}$ eV bar^{-1} (Paul 1961). They also determined the sub-band energy gap $E(\Delta_1$–$L_1)$ as $0{\cdot}18 \pm 0{\cdot}01$ eV.

To fit the Ge data previous workers have used either the Si effective mass $m^*_{l\Delta} = 0{\cdot}92\, m_e$, $m^*_{t\Delta} = 0{\cdot}19\, m_e$, that is $m_{D\Delta} = 1{\cdot}06\, m_e$ where $\nu_\Delta = 6$ (Hensel *et al.* 1965), or theoretical estimates which tend to be near the Si value. In attempting to fit our data we have started by taking the theoretical masses of Dresselhaus and Dresselhaus (1967), which give $m^*_{D\Delta}$ considerably less than for Si, and Cardona and Pollak (1965), where $m^*_{D\Delta}$ is comparable to the Si mass.

At atmospheric pressure the $\Gamma_{2'}$ conduction band minimum lies $\sim 0{\cdot}15$ eV above the L_1 minima (Zwerdling and Lax 1951), and hence below the Δ_1 minima. The pressure coefficient has been measured as $+14{\cdot}0 \times 10^{-6}$ eV bar^{-1} (Melz unpublished). Even at low pressures the minimum will have moved well above the Δ_1 minima and will have little effect on the results. Also because of the small density of states a negligible number of electrons will be transferred. Thus while the effect of the minimum might perhaps be considered in high field calculations it can be safely ignored in these high pressure experiments.

Nonparabolicity of the bands can also be ignored since the electrons will at all times be near the bottom of the minima at the low electric fields used here. Interesting effects might occur at high fields, however, but it is expected that transfer of the $\langle 100 \rangle$ valleys will occur before nonparabolicity in the $\langle 111 \rangle$ minima has any large significant effect (Fawcett and Paige 1971).

3. Experimental method and results

The apparatus and techniques have already been described in detail (Pitt 1968). The n type Ge crystal used for this study had the following electrical parameters: resistivity at atmospheric pressure $\rho_0 = 2{\cdot}65\, \Omega$ cm; carrier concentration $(N_D - N_A) = 8{\cdot}1 \times 10^{14}$ cm^{-3}; Hall mobility $\mu_{H_0} = 3340$ cm^2 V^{-1} s^{-1}. The crystals were cut and polished in $\langle 100 \rangle$ and $\langle 111 \rangle$ orientated slices and tin contacts soldered to the Van der Pauw samples cut from the slices.

The stresses on the crystal sample below 30 kbar in this apparatus are nonhydrostatic and, since electron transfer in Ge involves two sets of degenerate off centre minima near the zone edge, the nonhydrostatic stress would show large effects in resistivity and Hall

constant due to splitting of the minima. The analysis of the results would then be extremely complicated. To circumvent this problem crystals with both ⟨100⟩ and ⟨111⟩ orientations were used. The conductivity versus pressure curve for our sample is shown in figure 1, and compared with the truly hydrostatic measurements of Nathan *et al.* (1961) to 27 kbar. Excellent agreement was obtained for the ⟨100⟩ samples (ie ⟨100⟩ direction perpendicular to the opposed anvils). This might be expected since the degeneracy of the occupied ⟨111⟩ minima is not removed by the stress differences inherent in the apparatus in this pressure

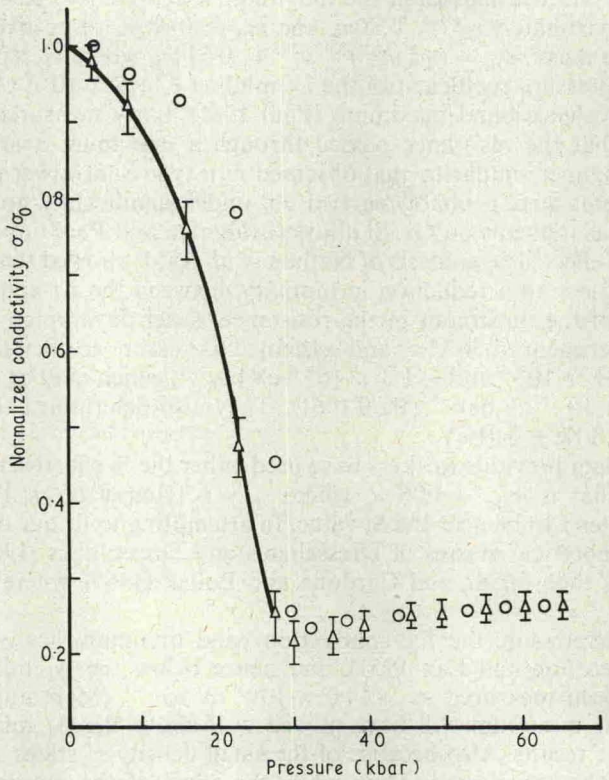

Figure 1. Normalized conductivity (σ/σ_0) results with pressure to 65 kbar in n type Ge at 295 K; △ for ⟨100⟩, and ○ for ⟨111⟩ orientations. Comparison is made with the truly hydrostatic measurements of Nathan *et al.* (1961) to 27 kbar. Indications of the errors on the ⟨100⟩ samples for four runs are given; the magnitudes for the ⟨111⟩ samples are similar at corresponding pressures. Full curve from Nathan *et al.* (1961).

range. The ⟨111⟩ samples, however, show a resistivity variation quite different from the hydrostatic results, as expected. By 30 kbar the two results have converged and pass through a minimum near 33 ± 1 kbar. The spread of results for five runs on both orientations are shown by the error bars. The largest variations occur in the highly nonhydrostatic pressure region below 20 kbar, in agreement with our previous results (Pitt 1968). Above 30 kbar the coalescing of results for both orientations further confirms that our conditions are reasonably hydrostatic. By 65 kbar the resistivity has almost levelled off at a value of $\rho/\rho_0 = 4{\cdot}0 \pm 0{\cdot}3$.

Figure 2 shows mean plots of the Hall constant R_H/R_{H_0} and Hall mobility μ_H/μ_{H_0}. Dimensional changes of the crystal have been allowed for by taking the compressibility

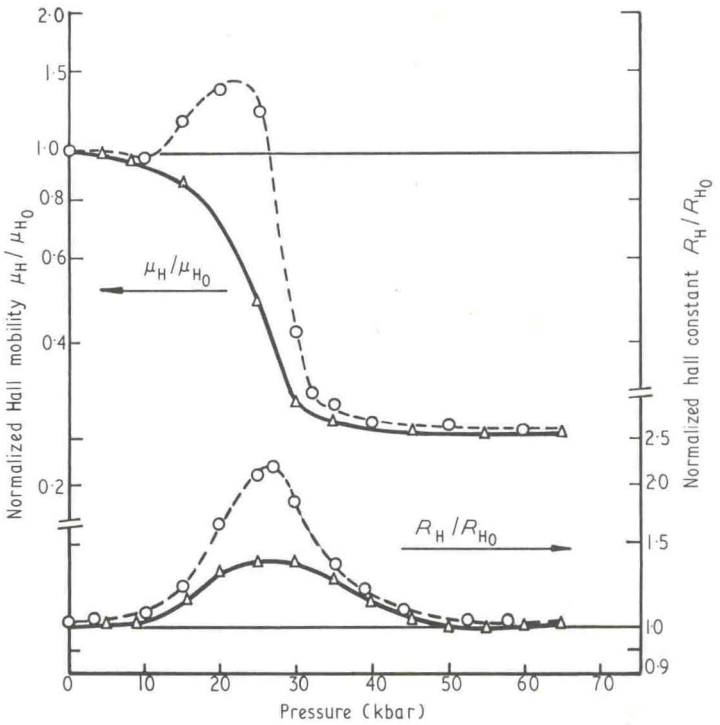

Figure 2. Normalized Hall constant (R_H/R_{H_0}) and Hall mobility (μ_H/μ_{H_0}) to 65 kbar in n type Ge at 295 K; △ for ⟨100⟩ and ○ for ⟨111⟩ orientations. Results converge above 30 kbar indicating hydrostatic conditions. Also R_H/R_{H_0} returns to the original normalized value by 60 kbar, and $\mu_H(60)$ is 850 $cm^2\ V^{-1}\ s^{-1}$.

determined from measurements on the elastic constants by Bond *et al.* (1950). It is seen that R_H/R_{H_0} passes through the characteristic band transfer maximum near band cross-over. This effect has been seen before in transfers from high to low mobility bands in several materials (Pitt and Lees 1970). The curves for both orientations in R_H/R_{H_0} return to the original normalized value, within experimental error, by 65 kbar and level off. This implies that transfer has been fully completed with no carrier loss to deep lying impurity levels which might exist at atmospheric pressure above the L_1 minima. Such resonance states have been observed in several III–V compounds (Paul 1968). Perhaps the fact that they have not been observed in Ge to date reflects the advanced state of the technology in growing the crystals (ie the existence of these nonhydrogenic levels in the III–V compounds may be associated with crystal defects).

The Hall mobility falls gradually at low pressures probably because of an increase in effective mass as the L_1 band moves away from the valence band. Before band cross-over the drop in mobility is largely due to intervalley scattering between the L_1 and Δ_1 minima and also transfer to the lower mobility band. We note that the mobility does not pass through a minimum at band cross-over. This is because maximum scattering between the minima will occur when the L_1 minima are lower in energy than the Δ_1 minima owing to the smaller density of states in the L_1 minima.

4. Analysis of Hall and resistivity data

The formulation of the equations including the scattering and electrical parameters will be described first, followed by an analysis of the assumptions that have been made. We use the same symbols, where possible, as employed by Nathan *et al.* (1961), and con-

sider only the two sets of minima. The L_1 minima situated in energy ΔE_0 below the Δ_1 minima. Electrons occupying the L_1 minima are represented by the subscript g and Δ_1 by the subscript s.

For g electrons we may write the scattering time in the form

$$\frac{1}{\tau_g(E)} = A_g C'_g E^{\frac{1}{2}} + B_g C'_s (E - \Delta E)^{\frac{1}{2}} v_s \qquad E \geqslant \Delta E$$
$$= A_g C'_g E^{\frac{1}{2}} \qquad E < \Delta E \tag{1}$$

and similarly for the s electrons

$$\frac{1}{\tau_s(E)} = A_s C'_s (E - \Delta E)^{\frac{1}{2}} + B_s C'_g E^{\frac{1}{2}} v_g \qquad \Delta E \geqslant 0 \tag{2}$$

where

$$A_g \text{ and } A_s = \frac{2\pi}{\hbar} \left| \text{equivalent intervalley or intravalley scattering matrix in the g and s minima respectively} \right|^2,$$

$$B_g \text{ and } B_s = \frac{2\pi}{\hbar} \left| \text{nonequivalent intervalley scattering matrix element} \right|^2$$

and

$$C'_x = m_{lx}^{\frac{1}{2}} m_{tx} 4\pi \times \frac{2^{\frac{1}{2}}}{h^3}$$

where x refers to either g or s.

The zero point energy is taken at the g band edge, but when $\Delta E < 0$ (ie the Δ_1 valleys lie below the L_1 valleys) then the subscripts must be interchanged and the zero of energy taken at the s band edge.

The electron mobilities in the two valleys are given by (Herring 1955)

$$\mu_g = \frac{e\langle \tau_g(E) \rangle}{3} \left(\frac{1}{m_{lg}} + \frac{2}{m_{tg}} \right)$$
$$\mu_s = \frac{e\langle \tau_s(E) \rangle}{3} \left(\frac{1}{m_s} + \frac{2}{m_{ts}} \right) \tag{3}$$

where

$$\langle \tau_x^n(E) \rangle = \frac{4}{3\pi^{1/2}} \int_0^\infty \tau_x^n(y)\, y^{3/2} \exp(-y)\, dy \tag{4}$$

where $y = E/kT$ and Maxwell–Boltzmann statistics are assumed.

The two carrier resistivity as a function of pressure is

$$\rho(P) = \frac{1}{\sigma(P)} = \frac{1}{e\{n_g(P)\,\mu_g(P) + n_s(P)\,\mu_s(P)\}} \tag{5}$$

where n_g and n_s are the number of electrons in the g and s minima, and hole conduction has been neglected. The $\mu_x(P)$, where x refers to either g or s, may be expressed in terms of a mobility associated with equivalent intervalley and intravalley process only, $\mu_x^*(P)$. The resulting relaxation time may be obtained directly from equation (1) by allowing ΔE to go to infinity, in which case only these processes contribute to $\tau_g(E)$. Hence from equation (3) we can write

$$\frac{\mu_g(P)}{\mu_g^*(P)} = \frac{\langle \tau_g(\Delta\epsilon) \rangle}{\langle \tau_g(\infty) \rangle} \tag{6}$$

where we have written $\langle\tau(E)\rangle$ as explicity dependent on the band gap $\Delta\epsilon$ (ie $\Delta E/kT$) at a particular pressure. A similar relation holds for the s valleys, and so equation (5) becomes

$$\rho(P) = \frac{1}{e\left\{n_g(P)\,\mu_g^*(P)\,\frac{\langle\tau_g\,\Delta\epsilon)\rangle}{\langle\tau_g(\infty)\rangle} + n_s(P)\,\mu_s^*(P)\,\frac{\langle\tau_s(\Delta\epsilon)\rangle}{\langle\tau_s(\infty)\rangle}\right\}} \tag{7}$$

We now examine the Hall constant for the two carrier model which can be written as

$$R_H(P) = \frac{-e^3}{3\sigma^2(P)}\left\{n_s(P)\,\langle\tau_s^2(\Delta\epsilon)\rangle\,\frac{(K_s+2)\,K_s}{m_{lg}^2} + n_g(P)\,\langle\tau_g^2(\Delta\epsilon)\rangle\,\frac{(K_g+2)\,K_g}{m_{lg}^2}\right\} \tag{8}$$

This is the same formula as that given by Nathan *et al.* (1961) apart from an extra e^2 factor. If we substitute for $K_x = m_{lx}/m_{tx}$ then from equations (3)

$$\mu_x = e\langle\tau_x(E)\rangle\,\frac{(1+2K_x)}{3m_{lx}} \tag{9}$$

and a further substitution in equation (8) yields

$$R_H(P) = \frac{-e}{\sigma^2(P)}\left\{n_s(P)\,\mu_s^{*2}(P)\,r_s^*\,\frac{\langle\tau_s^2(\Delta\epsilon)\rangle}{\langle\tau_s^2(\infty)\rangle}\,\frac{3K_s(K_s+2)}{(1+2K_s)^2}\right.$$

$$\left. + n_g(P)\,\mu_g^{*2}(P)\,r_g^*\,\frac{\langle\tau_g^2(\Delta\epsilon)\rangle}{\langle\tau_g^2(\infty)\rangle}\,\frac{3K_g(K_g+2)}{(1+2K_g)^2}\right\} \tag{10}$$

where $r_x^* = \langle\tau_x^2(\infty)\rangle/\langle\tau_x(\infty)\rangle^2$.

Now let $F_x = r_x^* 3K_x(K_x+2)/(1+2K_x)^2$ and take the values of K_g from the measured Ge ($\sim$20) and K_s from the measured Si ($\sim$5) results (Glickman (1956) found little variation in K_s in Ge–Si alloys before band cross-over) to give $F_g \sim 0{\cdot}78\,r_g^*$ and $F_s \sim 0{\cdot}87\,r_s^*$. It can be shown that for intravalley acoustic mode scattering $r_g^* = r_s^* = 1{\cdot}18$ (and hence $F_g = 0{\cdot}29$), $F_s = 1{\cdot}02$ and equation (10) becomes

$$R_H = \frac{-e}{\sigma^2(P)}\left\{0{\cdot}92n_g(P)\,\mu_g^{*2}(P)\,\frac{\langle\tau^2(\Delta\epsilon)\rangle}{\langle\tau_g^2(\infty)\rangle} + 1{\cdot}02n_s(P)\,\mu_s^{*2}(P)\,\frac{\langle\tau_s^2(\Delta\epsilon)\rangle}{\langle\tau_s^2(\infty)\rangle}\right\} \tag{11}$$

To take account of the intervalley scattering Nathan *et al* (1961) used the further scattering parameters S and S' defined by

$$S = \frac{B_g C_s' v_s}{A_g C_g'} \qquad \text{and} \qquad S' = \frac{B_s C_g' v_g}{A_s C_s'} \tag{12}$$

which give the relative strengths of the inter- to intra-valley scattering for the L_1 and Δ_1 states. The relaxation times to be used in equations (7) and (11) then become modified in the manner shown in the appendix.

We are left with a number of parameters which can be used to fit the data:

(*a*) ΔE_0 the atmospheric pressure $\Delta_1 - L_1$ sub-band energy gap

(*b*) N_0 the ratio of the density of states

$$\frac{N_{\Delta_1}}{N_{L_1}} \propto \left(\frac{m_{D\Delta_1}^*}{m_{DL_1}^*}\right)^{3/2}.$$

We have used initially the experimental value of $m_{DL}^* = 0{\cdot}54\,m_e$, and for $m_{D\Delta}^*$ have used predicted theoretical values (see table 1).

(*c*) The pressure coefficient of the sub-band gap $dE(\Delta_1 - L_1)/dP$ was taken as $5{\cdot}9 \times 10^{-6}$ eV bar^{-1}. This implies that the Δ_1 minima are moving towards the valence band maximum with a pressure coefficient of $-0{\cdot}9 \times 10^{-6}$ eV bar^{-1}, if the L_1 minima have the

accepted coefficient of $5{\cdot}0 \times 10^{-6}$ eV bar^{-1}. The small negative coefficient of the Δ_1 minima was estimated from the slopes of the resistivity and mobility curves beyond 55 kbar. These were less than have been observed for Si which has a pressure coefficient of $-1{\cdot}5 \times 10^{-6}$ eV bar^{-1}. Our result is in agreement with the coefficient later used by Howard (1961) of $-1{\cdot}0 \times 10^{-6}$ eV bar^{-1} for unpublished magnetoconductivity measurements in n type Ge.

(*d*) The pressure coefficients of mobilities in the two bands. In the low pressure region, where the effect of the Δ_1 minima is small, the best fit for $\mu_g^*(P)$ was

$$\frac{\mu_g^*(0)}{(1 + 0{\cdot}008P)}$$

where P is in kbar. This 0·008 variation is larger than the result of 0·004 used by Nathan *et al.* (1961), but it gave the best fit in the 0–10 kbar range. The relatively large error in our results in this pressure range, however, (figure 1) limits the accuracy of such a fit, and the discrepancy should not be considered as serious. Our variation in μ_g^* is used for the whole pressure range. The variation in the Δ_1 mobility was ignored. This is reasonable in view of the small pressure coefficient of these minima.

(*e*) The anisotropy K_s of the Δ_1 minima is unknown, and to a first approximation we have used the Si value, $K_s \sim 5$. We have assumed that the anisotropies of both the L_1 and Δ_1 minima will not change with pressure. Early Hall and magnetoresistance measurements to 10 kbar by Benedek *et al.* (1955) implied that a change in K_g with pressure was taking place, but this was before any effect due to the Δ_1 minima was considered. W. E. Howard and W. Paul (unpublished) have found that K_g varies to a negligible extent from magnetoconductivity measurements at pressure, and Glickman and Christian (1956) found little variation in K_s on Si–Ge alloys before band cross-over.

5. Curve fitting

The two sets of results, resistivity and Hall mobility, were fitted separately. In the diagrams

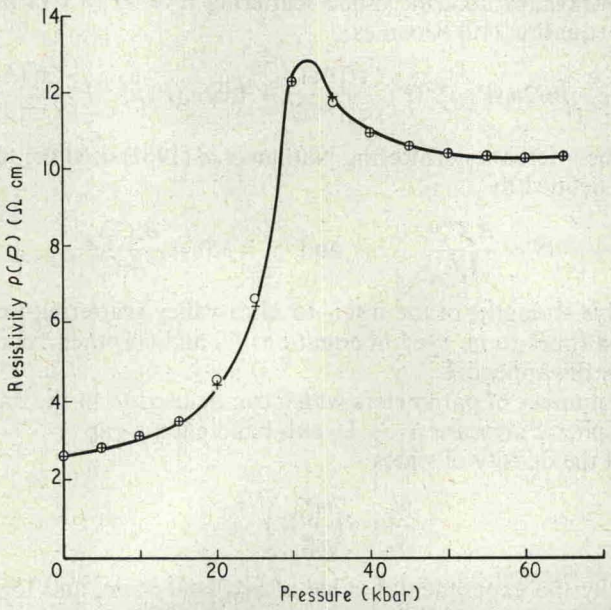

Figure 3. Theoretical fits of high pressure resistivity data in n type Ge which illustrates how higher values of N_0 lead to a greater sub-band gap ΔE_0 and scattering parameter S', when S (=4) is constant. Full curve, experimental: + $N_0 = 1{\cdot}55$, $S' = 0{\cdot}34$, $\Delta E_0 = 0{\cdot}177$ eV; ○ $N_0 = 4{\cdot}2$, $S' = 0{\cdot}123$, $\Delta E_0 = 0{\cdot}185$ eV.

in order to illustrate the fits of the various parameters, the curves corresponding to the $\langle 111 \rangle$ orientation are omitted.

5.1. *Resistivity curve*

The fits to the resistivity curves were made by fixing the experimental point at 30 kbar and varying ΔE_0 and S' for a particular value of S. It can be seen from figures 3 and 4 that the height and shape of the maximum depends sensitively on S, and shows that a reasonable value would lie between 3 and 5 (ie 4 ± 1). This is in excellent agreement with Jayaraman and Kosicki (1968). The value of S' corresponding to this value of S can be seen to

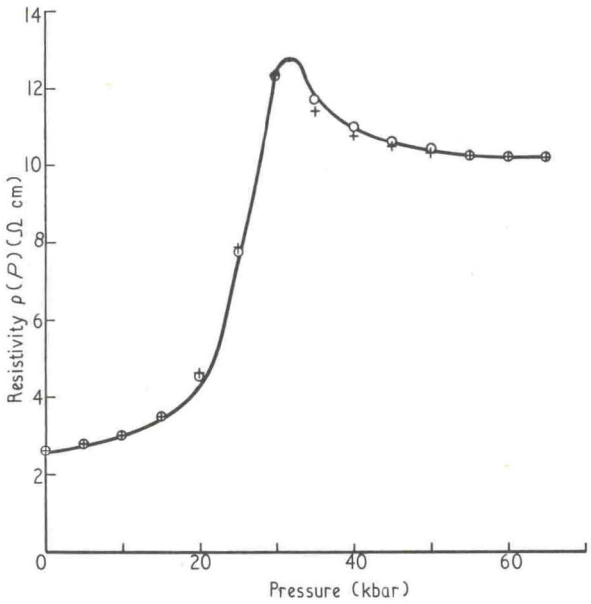

Figure 4. Theoretical fits of high pressure resistivity data in n type Ge for $N_0 = 5{\cdot}5$, $\Delta E_0 = 0{\cdot}186$ eV, and values of S from 3 to 5. Full curve, experimental; $\bigcirc S = 3, S' = 0{\cdot}188$; $+ S = 5, S' = 0{\cdot}099$.

be near 0·1 to 0·2, provided N_0 is greater than 2·7. Jayaraman and Kosicki (1968) obtained S' between 0·1 and 0·36 for $N_0 \sim 2{\cdot}7$. We further find that any increase in N_0 must be accompanied by an increase in ΔE_0 to obtain the best resistivity fit, and for $N_0 = 5{\cdot}5$ we have ΔE_0 is $0{\cdot}186 \pm 0{\cdot}01$ eV.

The resistivity theoretical fits have the same deviations as found by Fawcett and Paige (1971) for their determination of the L_1–Δ_1 nonequivalent intervalley scattering coupling constant, that is a steeper rise in resistivity at a lower pressure than observed experimentally, and more pronounced saturation in the very high pressure region.

5.2. *Hall mobility curve*

These were obtained from R_H/ρ (figures 5 and 6) and proved to be extremely sensitive to the chosen value of S'. It was extremely difficult to obtain a wholly accurate fit taking different values of S and S' in the region just before and at band cross-over. The integrals in this case were solved exactly since the approximate expressions of Nathan *et al.* (1961) produced even worse fits. To obtain reasonable fits for $S = 4$, it is evident that N_0 must be much greater than 2·7 (taking the Cardona and Pollak (1965) Δ_1 effective mass). Figure 5 illustrates how the mobility is particularly sensitive to S' near band cross-over, in the 25–35 kbar range. Figure 6 shows also how an increase in N_0 lowers the points near 25 kbar and

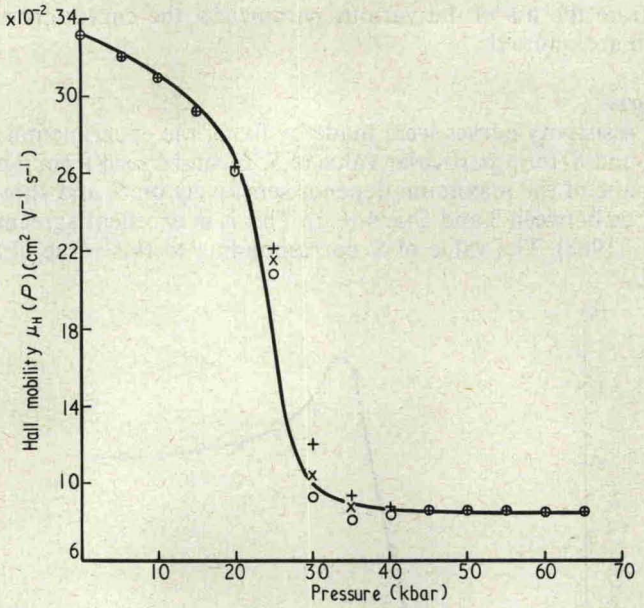

Figure 5. Theoretical fits of high pressure mobility data in n type Ge for $N_0 = 5{\cdot}5$, $S = 5$, and $\Delta E_0 = 0{\cdot}186$ eV for: + $S' = 0$; × $S' = 0{\cdot}1$; ○ $S' = 0{\cdot}2$. Note that the largest changes occur near band cross-over in the 25–35 kbar range. Full curve, experimental.

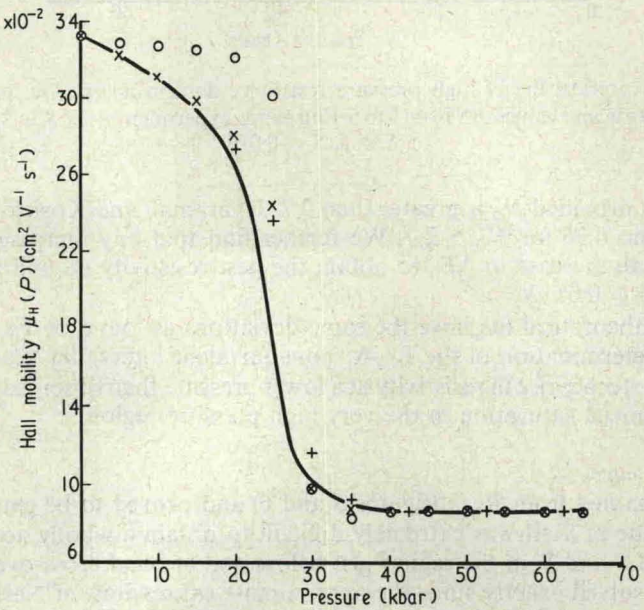

Figure 6. Theoretical fits of high pressure mobility data in n type Ge for constant S (=4) and S' (=0), which illustrates that a high value of N_0 is required ($N_0 = 1{\cdot}55$ is obviously too low). Full curve, experimental; ○ $N_0 = 1{\cdot}55$, $\Delta E_0 = 0{\cdot}177$ eV; × $N_0 = 2{\cdot}7$, $\Delta E_0 = 0{\cdot}18$ eV; + $N_0 = 4{\cdot}2$, $\Delta E_0 = 0{\cdot}185$ eV.

tends to reduce the discrepancy between experiment and theory, while S and S' are kept constant. It is very apparent that $N_0 = 1{\cdot}55$ is incorrect. We find that for $N_0 = 5{\cdot}5$ and $S' = 0{\cdot}2$ the fit is reasonable. The combinations of parameters used in attempting to fit the experimental results are given in table 1.

Table 1. Parameters used to fit the high pressure data.

Density of states ratio at atmospheric pressure	Sub-band energy gap at atmospheric pressure and 295 K	Scattering parameters used in the simple theory of section 4	
$N_0 \frac{\langle 100\rangle}{\langle 111\rangle}$	ΔE_0 eV	S	S'
1·55 (Dresselhaus and Dresselhaus 1967)	0·177 ± 0·010	4·0	0·03
2·7 (Cardona and Pollak 1965)	0·180 ± 0·010	4·0	0·10
4·2	0·185 ± 0·010	4·0	0·13
5·5	0·186 ± 0·010	4·0	0·19

6. Discussion and conclusions

It becomes obvious from the curve fitting that we require N_0 to be considerably larger than has been previously theoretically advanced. The conclusion that the $\langle 100\rangle$ effective mass was considerably larger than for Si was obtained independently, but the particular value $N_0 = 5{\cdot}5$ was taken for the curve fitting since Fawcett and Paige (1971) had carried out calculations for a density of states ratio of this magnitude, and comparisons could be made.

Provided the coupling constants are known, it is possible from a determination of S to fix S' (equations 12). This enables us to compare our scattering parameters with those expected from the coupling constants used by Fawcett and Paige (1971).

For $N_0 = 5{\cdot}5$, we find $S = 4 \pm 1$ and $E_0 = 0{\cdot}186 \pm 0{\cdot}010$ eV. The coupling constants of Fawcett and Paige would give $S = 4$, which is excellent agreement. For S' however, agreement is not so good—we obtained $S' = 0{\cdot}2$, while the Fawcett and Paige theory gives $S' = 0{\cdot}5$. This discrepancy may be accounted for in the following way. The formulation developed and used to describe the L_1–Δ_1 intervalley scattering has omitted to include the phonon energy involved in the scattering event. This was noted by Nathan *et al.* (1961) but no calculations were performed. The effect of the inelastic nature of this process results in a modified expression for $\tau_g(E)$, the total relaxation time for all scattering processes in valley g

$$\frac{1}{\tau_g(E)} = A_g C'_g E^{1/2} + B_g C'_{ss} \{(E - \Delta E + \hbar\omega)^{1/2} + \exp(\hbar\omega/kT)(E - \Delta E - \hbar\omega)^{1/2}\} \times \{1 + \exp(\hbar\omega/kT)\}^{-1} \tag{13}$$

In the limit of elastic scattering the above expression reduces to equation (1) Since $\mu_H \propto \langle\tau^2(\Delta\epsilon)\rangle/\langle\tau(\Delta\epsilon)\rangle$, while $\rho \propto (\langle\tau(\Delta\epsilon)\rangle)^{-1}$ we might expect the above correction to alter the mobility fits more than the resistivity. Hence our method of fixing the point at 30 kbar in fitting the resistivity, should not incorporate a large error, and the value of $S = 4 \pm 1$ given above will reasonably allow for this. The mobility curve is particularly sensitive to S' near band cross-over, however, and here we have the largest discrepancies.

The lengthy calculations involving the use of equation (13) and the equivalent expression for $\tau_s(E)$ have not been carried out here, however, certain observations concerning the

effect of using the modified relaxation times can be made. Firstly we see that the absorption term $(E - \Delta E + \hbar\omega)^{1/2}$ makes a larger contribution to the integral derived from equation (4) than $\exp(\hbar\omega/kT)\ (E - \Delta E - \hbar\omega)^{1/2}$ where section 4 required a term $(E - \Delta E)^{1/2}$ only. Near band crossover, however, both terms become important and it is in this region that our theoretical fits disagree most with the experimental results (ie near 25 kbar). Secondly, the use of equation (13) will tend to increase the band separation at which nonequivalent intervalley scattering becomes important. The consequent reduction of the theoretical mobility before cross-over would improve the fits. Finally, the factor

$$\{1 + \exp(\hbar\omega/kT)\}^{-1}$$

may be expected to cause the calculated value of S' to be less than that defined by equation (12). The two independent results for S' are therefore converging, and perhaps a reasonable estimate is $0{\cdot}30 \pm 0{\cdot}15$.

The calculations also ignore any effect due to ionized impurity scattering. The mobility in our sample is lower than might be expected in pure Ge, and impurity scattering will probably be present. Measurements have been carried out on samples of different resistivities, however, with little variation in results. This is supported by Nathan *et al.* (1961) who found little variation at pressure for resistivities from 0·15–5 Ω cm. The results for

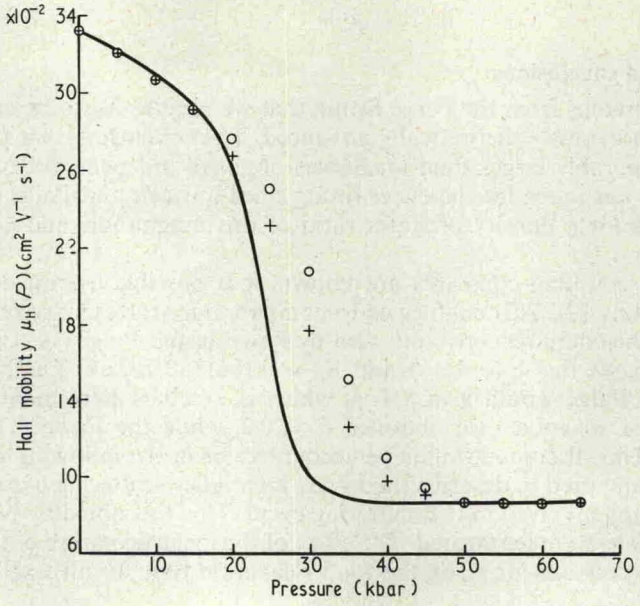

Figure 7. Theoretical fits of high pressure mobility data in n type Ge with no intervalley scattering taken into account. The largest discrepancy occurs near 30 kbar, where the true mobility is reduced by almost one half. Full curve, experimental; ○ $N = 1{\cdot}55$, $\Delta E_0 = 0{\cdot}177$ eV; + $N = 4{\cdot}2$, $\Delta E_0 = 0{\cdot}185$ eV.

our material and their samples are in excellent agreement to 30 kbar. It is reasonable to assume therefore that the mobility ratio $\mu_{H\Delta}/\mu_{H_\Sigma} = 4{\cdot}0 \pm 0{\cdot}3$, will hold for pure Ge. This implies a ⟨100⟩ mobility of $1100 \pm 150\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ at 65 kbar. At atmospheric pressure, by analogy with the Si mobility increase with pressure and taking account of the small Ge ⟨100⟩ pressure coefficient we have $\mu_H(\Delta_1) = 1020 \pm 170\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$.

Finally, we list our conclusions. The effective mass in the Ge conduction band Δ_1 valleys is considerably greater than for Si; an estimate of 50% greater gives reasonable fits to the

high pressure and high field data. The $(\Delta_1 - L_1)$ sub-band energy gap is $0{\cdot}186 \pm 0{\cdot}010$ eV. The scattering parameters defined by Nathan *et al.* (1961) are estimated to be $S = 4 \pm 1$, $S' = 0{\cdot}30 \pm 0{\cdot}15$. This is excellent support for their original work which used only resistivity data to 27 kbar. The Hall mobility through band cross-over has been measured directly for the first time. Figure 7 illustrates how the mobility near band cross-over at 30 kbar is drastically reduced compared with theoretical calculations which assume no nonequivalent intervalley scattering. The $\langle 100 \rangle$ Hall mobility in pure n type Ge is $1020 \pm 170\ \mathrm{cm^{-2}\ V^{-1}\ s^{-1}}$ at room temperature and atmospheric pressure.

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Appendix. Considerations of relaxation times

The normal expression is from equation (4)

$$\langle \tau_x^n(E) \rangle = \frac{4}{3\pi^{1/2}} \int_0^\infty \tau_x^n(y)\, y^{3/2} \exp(-y)\, dy \qquad y = E/kT$$

Now

$$\langle \tau_g(\infty) \rangle = \frac{4}{3\pi^{1/2}} \int_0^\infty \frac{E^{-1/2}}{A_g C_g' (kT)^{5/2}} E^{3/2} \exp(-E/kT)\, dE$$

and

$$\langle \tau_g^n(\infty) \rangle = \frac{4}{3\pi^{1/2}} \int_0^\infty \frac{E^{(3-n)/2}}{(A_g C_g')^n (kT)^{5/2}} \exp(-E/kT)\, dE$$

$$= \frac{4}{3\pi^{1/2}} M_g^n \int_0^\infty y^{(3-n)/2} \exp(-y)\, dy$$

where

$$M_g^n = \{A_g C_g' (kT)^{1/2}\}^{-n}.$$

Then

$$\langle \tau_g^n(\Delta E) \rangle = \frac{4}{3\pi^{1/2}} M_g^n \left\{ \int_0^{\Delta E} y^{(3-n)/2} \exp(-y)\, dy + \int_{\Delta E}^\infty \frac{y^{(3-n)/2} \exp(-y)\, dy}{\{1 + S(1 - \Delta E/y)^{1/2}\}^n} \right\}$$

and similarly for $\langle \tau_s^n(\infty) \rangle$ and $\langle \tau_s^n(\Delta E) \rangle$, where S' substitutes for S. When the s band becomes lower than the g then the subscripts are reversed.

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