Quantitative Piezospectroscopy of the 1s and 2p States of Arsenic Impurity in Germanium

A. D. Martin, P. Fisher and P. E. Simmonds

Department of Physics, University of Wollongong, P.O. Box 1144, Wollongong, N.S.W. 2500.

Abstract

The results are presented of a study of the behaviour under uniaxial compression of absorption lines due to transitions from the ground state manifold of states of arsenic impurities in germanium to excited p states. It is found that the shear deformation potential constant Ξ_u of the excited p states and conduction band minima of germanium is $16 \cdot 4 \pm 0 \cdot 2$ eV. The equivalent deformation potential constant of the ground state, here designated as Ξ'_u , is determined to be essentially the same (one analysis giving $\Xi'_u = 16 \cdot 5 \pm 0 \cdot 4$ eV), a result in contrast to that found for donors in silicon. The results are compared with those obtained by other workers who use a variety of techniques. Good agreement is found between the present results and a number of the others although several discrepancies remain.

1. Introduction

The deformation potential constants of a solid are important parameters since they affect a number of the properties of the material. This is particularly the case for semiconductors where the transport properties are very sensitive to the state of strain of the solid. For n-type germanium and silicon the rate at which the conduction band minima separate under a shear strain is very large, as was first observed from piezoresistance measurements on these materials (Smith 1954). The origin of this lies in the multivalley nature of the conduction bands of both substances. Quantitative values for Ξ_n , the shear deformation potential constant of the conduction band of germanium or silicon (Herring 1955; Herring and Vogt 1956), were obtained from piezoresistance measurements by several workers. The value which was considered to be the most reliable for germanium near liquid helium temperature, deduced from piezoresistance measurements, was $\Xi_u = 19 \cdot 2 \pm 0 \cdot 4 \text{ eV}$ per unit strain (Fritzsche 1959). Since then a large number of different properties have been studied to yield quantitative values of Ξ_n for both silicon and germanium at various temperatures and over a wide range of impurity concentrations. A number of these results are summarized in Table 1 and will be discussed later. The experimental values obtained for germanium are seen to range from approximately 15 to 19 eV.

One of the most direct and precise methods for determining Ξ_u at low temperatures is from an observation of the stress dependence of the splittings of the optical absorption lines of donor impurities in the solid; this will be called the piezospectroscopy of donors. This method has been used to determine Ξ_u for silicon (Tekippe *et al.* 1972; Butler *et al.* 1975). The results indicate that Ξ_u lies between 8.7 and 8.8 eV, in excellent agreement with values obtained by other methods, except for that deduced from piezo-spin-resonance (Wilson and Feher 1961; Watkins and Ham 1970) and 512

piezobirefringence (Schmidt-Tiedemann 1962). However, a later measurement using the piezobirefringence method (Riskaer 1966) yielded $\Xi_u = 8.5 \pm 0.4$ eV for silicon although this was more recently corrected to 8.1 ± 0.4 eV (Balslev 1972).

The present paper gives the results of the quantitative piezospectroscopy of donors in germanium; the results will be compared with those obtained by other methods (see Table 1). Preliminary results have been published elsewhere (Martin *et al.* 1979, 1980); previous observations of this type have been made but with unknown stresses (Reuszer and Fisher 1965, 1968).*

2. Experimental Apparatus and Procedure

The spectrometer, consisting of a Perkin-Elmer single-pass monochromator (Model 210B) with added entrance and exit optics, was essentially that described elsewhere (Soepangkat and Fisher 1973). The differences were in the optical filtering used, the bolometer detector and the sample cryostat. In the present case the detector was a Molectron silicon bolometer with a noise equivalent power (NEP) of approximately 5×10^{-12} W Hz⁻¹ at the operating frequency of 320 Hz; several modifications were made which improved the optics of the detector. The sample cryostat, equipped with a stress centrepiece, has been discussed before (Tekippe et al. 1972). The pressure head was calibrated two ways. Initially it was calibrated using the same method and platform scale previously specified (Tekippe *et al.*), while more recently it was recalibrated against a proving ring (manufactured by Wykham-Farrance, U.K.) which had itself been calibrated against known weights. The two calibrations so obtained gave $F = 2 \cdot 118 P \pm 0.004$ and $2 \cdot 112 P \pm 0.004$ respectively, where F is the resultant force in kg due to a pressure of P in p.s.i. (1 p.s.i. $\equiv 6.89$ kPa) being applied to the pressure head. Alternatively, a small tray of known mass could be fitted to the top of the push tube of the stress centrepiece to hold known weights. A maximum force of 12 kg could be applied in this way to permit observations to be made at forces smaller than those that could be obtained reliably using the pressure head. In addition, the two precision helicoid gauges (see Tekippe et al. 1972) were also recalibrated, a dead weight tester being used for this purpose. The dial readings of the two gauges were found to be within $\pm 0.5\%$ of the value of the calibrating pressure.

The samples were cut from suitably doped single crystal ingots of germanium and their orientations verified by an X-ray technique. The optical surfaces were prepared by lapping with Carborundum of successively finer grit followed by alumina and finally chemically polished in CP-4. Typical sample dimensions were $20 \times 4 \times 4$ mm. The cross sectional area was determined by direct measurement and then compared with that obtained from measuring the length of the sample and its mass and using the known density of germanium (Smakula and Sils 1955); the areas obtained by these two measurements agreed to better than 1%. Each sample was appropriately wedged along its length to suppress interference fringes.

The samples were mounted in the stress centrepiece using the same technique as that described elsewhere (Butler 1974; Butler *et al.* 1975). The only modification was in the use of lead instead of indium in the copper cups in which the ends of the samples were held; this modification appeared to produce a more uniform stress. A great deal of care was necessary in mounting the samples in order to avoid inhomo-

^{*} In the work of Reuszer and Fisher (1964, 1965, 1968), due to a historical error, the triplet ground state is designated by T_1 of T_d , rather than T_2 of T_d which is used in the present paper.

Piezospectroscopy of As Impurity in Ge

geneities in the applied stress. Such inhomogeneities were obtained initially due to a defect in the push tube which produced broadening of the optical absorption lines and gave large spurious values of Ξ_u . The temperature of the sample could be altered by inserting a stainless steel spacer between the bottom of the push tube and the sample and/or using a stainless steel tailpiece in place of the low temperature copper tailpiece.

The transmission data were collected either in analogue form on a strip-chart recorder or by storing on a floppy disc via a digital interface to a Nova 3/12 computer.



Fig. 1. The relationship between an applied compressive force F, the crystal axes X, Y, Z, and the four $\langle 111 \rangle$ energy ellipsoids characterizing the conduction band minima of germanium. One half of each ellipsoid is shown dashed as a reminder that it has been translated from the opposite boundary of the Brillouin zone.

3. Theoretical Considerations

The conduction band minima of a multivalley semiconductor shift relative to one another under an applied uniaxial force. The total shift in energy of the *j*th minimum is given by

$$\varepsilon_{j}^{t} = \sum_{\alpha} \sum_{\beta} \left(\Xi_{d} \,\delta_{\alpha\beta} + \Xi_{u} \,K_{\alpha}^{(j)} \,K_{\beta}^{(j)} \right) u_{\alpha\beta} \,, \tag{1}$$

where $K_{\alpha}^{(j)}$ and $K_{\beta}^{(j)}$ are components of a unit vector directed from the centre of the Brillouin zone to the *j*th minimum in *k* space. The indices α and β designate components along the cubic axes of the crystal while the $u_{\alpha\beta}$ are the strain tensor components. The quantity Ξ_d is the dilatational deformation potential constant (Herring 1955; Herring and Vogt 1956). For germanium, the conduction band minima lie along the $\langle 111 \rangle$ directions and fall at the zone boundary. If we label the four valleys along [111], [111], [111] and [111] as 1, 2, 3 and 4 respectively (see Fig. 1), under uniaxial compression equation (1) reduces to (Keyes and Sladek 1962)

$$\varepsilon_{j} = -\frac{1}{2}\Xi_{u} T s_{44} \{ (\hat{z}_{j}, \hat{F})^{2} - \frac{1}{3} \}$$
⁽²⁾

for the shift of the *j*th minimum relative to the centre of gravity of the minima. Here T is the magnitude of the compressive uniaxial stress, \hat{F} is the unit vector in the direction of the compressive force F and \hat{z}_j is the unit vector along the axis of the

*j*th valley. The quantity s_{44} is one of the elastic compliance constants. For **F** in a general direction, we have

$$\varepsilon_1 = -A - B - C, \quad \varepsilon_2 = +A - B + C, \quad \varepsilon_3 = -A + B + C, \quad \varepsilon_4 = +A + B - C, \quad (3)$$

where

$$A = \frac{1}{3}\Xi_{\rm u} T s_{44} \sin \theta \cos \theta \sin^2 \phi, \qquad B = \frac{1}{3}\Xi_{\rm u} T s_{44} \sin \theta \cos \phi \sin \phi, \quad (4a, b)$$

$$C = \frac{1}{3} \Xi_n T s_{44} \cos \theta \sin \phi \cos \phi \,. \tag{4c}$$

The angles θ and ϕ are defined with respect to the cubic axes as shown in Fig. 1. Fig. 2 shows the variation of ε_i as a function of θ and ϕ .*



Fig. 2. Energy shifts ε_j of the conduction band valleys of germanium from the centre of gravity as a function of θ and ϕ (defined in Fig. 1) under a compressive force. The plane carrying the scales for θ and ϕ corresponds to the centre of gravity of the valleys. The energy sheets labelled 1, 2, 3, 4 correspond to valleys located in the directions so designated in Fig. 1.

If it is assumed that the effective masses characterizing the bottom of the conduction band and the dielectric constant are unaltered by strain then, for a given valley, the effective-mass energy level scheme of a group V donor (Kohn 1957) will be unaffected by the stress since the effective mass equation of the *j*th valley is unaltered. The energy levels bearing different valley labels, however, will be shifted relative to each other by the amounts given in equations (3) and (4). Thus, those donor states which are well described by the effective mass theory, viz. the excited p states, will be split, in general, into four sublevels the spacings of which will be identical for all the excited

* This is an unpublished result of V. J. Tekippe, H. R. Chandrasekhar, P. Fisher and A. K. Ramdas; see also Tekippe (1973).

p states and the same as those of the shifted conduction band valleys. A measurement of these spacings will provide a means to determine the value of Ξ_u . For F parallel to $\langle 100 \rangle$, $\varepsilon_j = 0$ for all j, while for both $F \parallel \langle 111 \rangle$ and $F \parallel \langle 110 \rangle$ two sublevels are produced for each excited state. For $F \parallel \langle 110 \rangle$, the orientation chosen for the present measurements, the shifts are

$$\varepsilon_{2,4} = -\varepsilon_{1,3} \equiv \varepsilon_{\rm b} = \frac{1}{6} \Xi_{\rm u} T s_{44}, \qquad (5)$$

where the b subscript is inserted for historical reasons (Reuszer and Fisher 1965, 1968).



Fig. 3. Splittings and shifts of group V donor s and p states in germanium for a compressive force $F \parallel [110]$ and propagation vector $q \parallel [110]$. Also shown are the allowed transitions from the ground state manifold to the p states for radiation polarized with its electric vector E parallel to F (dashed arrows) or E perpendicular to F (full arrows). The additional labels on the energy states specify the symmetry of the states with and without stress (see Reuszer and Fisher 1968).

The ground state of group V impurities, unlike the excited states, is not well described by the effective mass formalism. For $F \parallel \langle 110 \rangle$, the effect of stress on this state is given by (Price 1956)

$$E(A_1) = -\Delta_{\rm c} - (4\Delta_{\rm c}^2 + \varepsilon_{\rm b}'^2)^{\frac{1}{2}}, \quad \text{for } 1s(A_1); \tag{6}$$

$$E(A_{1}) = -\Delta_{c} + (4\Delta_{c}^{2} + \varepsilon_{b}^{\prime 2})^{\frac{1}{2}},$$
(7a)

$$E(B_2) = \Delta_{\rm c} + \varepsilon_{\rm b}', \tag{7c}$$

Here $4\Delta_c$ is the chemical splitting of the ground state due to corrections to the effective mass potential. For the unperturbed crystal, the site symmetry of the impurity is T_d . The ground state, without spin included, consists of a singlet (A_1 state) and a triplet (T_2 state). For $F \parallel \langle 110 \rangle$, the site symmetry becomes C_{2v} , and A_1 and T_2 of T_d decompose into A_1 and $A_1 + B_1 + B_2$ of C_{2v} respectively. In equations (6) and (7),

the zero of energy has been chosen to coincide with the centre of gravity of the unperturbed ground states. Also in these equations,

$$\varepsilon_{\mathbf{b}}' = \frac{1}{6} \Xi_{\mathbf{u}}' T s_{\mathbf{44}}, \tag{8}$$

where Ξ'_{u} , the deformation potential constant of the ground states, is analogous to Ξ_{u} and does not necessarily equal Ξ_{u} . An observation of the shifts and splittings of the ground states will provide a measure of Ξ'_{u} .

The selection rules for transitions from the ground states to p states using polarized radiation for $F \parallel [110]$ and $q \parallel [\overline{1}10]$ are shown in Fig. 3 (Reuszer and Fisher 1968). Here q is the wave vector of the exciting radiation.



Fig. 4. Part of the absorption spectrum of arsenic impurity in germanium (Ge(As) 326A No. 2) due to transitions from the lower ground state. The spectra are for compressive forces $F \parallel [110]$ with E perpendicular to F and radiation propagating along [I10]. The dashed curve corresponds to a stress T = 0.15 kbar while the full curve is for 0.30 kbar. The vertical lines show the zero stress positions of the transitions. The two transitions labelled with a P designate phosphorus, present as a contaminant; the remaining transitions belong to arsenic. Total donor concentration is 1.1×10^{15} cm⁻³, with liquid helium used as coolant and a sample temperature of ≈ 7 K.

4. Experimental Results

Essentially all the experimental results were obtained with $F \parallel [110]$ and $q \parallel [\overline{1}10]$. From Fig. 2, it is seen that the splitting of the states is least sensitive to misorientation of the sample for $F \parallel \langle 111 \rangle$. The choice of orientation was made taking account of constraints on the sample area, the minimum reliable force at which the pressure head could be used and the relative intensities of the components of the various excitation lines. Fig. 4 shows the relative transmission of an arsenic-doped germanium sample for $F \parallel \langle 110 \rangle$. The radiation is polarized such that the electric field E is perpendicular to F. Results are shown for two values of T. The sample has been selected to enhance in transmission the relatively isolated $2p_0$ excitation line to permit its splitting to be followed over a large range of stress. Spectra at zero stress are to be found elsewhere (Reuszer and Fisher 1964, 1965, 1968). In Fig. 5, the positions of the two components of the $2p_0$ line are plotted as a function of stress for $F \parallel \langle 110 \rangle$. The difference in energy between the two components is predicted by equation (5) to be $\Delta \varepsilon = 2\varepsilon_b = \frac{1}{3}\Xi_u Ts_{44}$. Fig. 6 shows $\Delta \varepsilon$ plotted as a function of stress using data obtained from four runs on two separate samples. The data at very low stress were taken using weights while the rest of the data were obtained with the pressure head. The solid line represents a least-squares fit to the data. From the value of 6.877×10^{11} dyn cm⁻² (1 dyn cm⁻² = 10^{-9} kbar $\equiv 10^{-4}$ kPa) for s_{44} at 4.2 K (deduced from Fine 1955), Ξ_u is found to be 16.4 ± 0.2 eV; this value is entered in Table 1. The error includes those arising from the sample cross section, the pressure-head calibration and the fit to the data of Fig. 6.



Fig. 5. Energies of the 2p₀ components of arsenic impurity in germanium (Ge(As) 326A no. 2) due to transitions from the lower ground state for $F \parallel \langle 110 \rangle$. Data points in many cases are composites of a number of points which were obtained at the same stress. Solid straight lines represent shifts of the 2po excited states and are drawn by adding and subtracting one-half the 2po splitting to the zero stress energy at each stress. The bottom curve shows the shift of the lower $1s(A_1)$ state as a function of stress. The curves through the data points are drawn for $\Xi_{\rm u} = 16.4 \, {\rm eV}$ (see text and Fig. 6).

Some data taken at an early stage of the investigation resulted in values of \mathcal{E}_u ranging from 18 to 22 eV. In each case, however, the stress-induced components were considerably broader than those shown in Fig. 4 and their widths increased with stress. This effect was attributed to non-uniform stress. As mentioned earlier, the stress push tube was found to be out of alignment and when re-aligned, together with careful alignment of the sample, sharp components were obtained whose widths showed little variation with stress. Under these conditions very consistent results were obtained.

Also shown in Fig. 5 (solid straight lines) are the energy shifts of the two stressinduced substates of the $2p_0$ excited state. These have been drawn using the value of ε_b obtained from each stress and assuming that these two substates are equidistant from the centre of gravity. The difference between either one of these straight lines and its corresponding $2p_0$ component is a measure of the shift of the $1s(A_1)$ ground



Fig. 6. The splitting $\Delta \varepsilon (=2\varepsilon_b)$ of the lower ground state to $2p_0$ transition of arsenic impurity in germanium (Ge(As) 326A No. 2) under a compressive force $F \parallel \langle 110 \rangle$. The line through the data points is the result of a linear least squares fit to the data and yields a value of $\Xi_u = 16.4 \text{ eV}$.

state $\varepsilon_{g.s.}$ It is clear that $\varepsilon_{g.s.}$ can be determined experimentally from the difference between the average of the energies of the $2p_0$ components and the energy of $2p_0$ at zero stress. The lower part of Fig. 5 shows how $\varepsilon_{g.s.}$ varies with stress. The solid curve through these data has been drawn using $\Xi'_{u} = 16.4$ eV, substituted into

$$\varepsilon_{g,s_{\star}} = \Delta_{c} \{ 2 - (4 + \varepsilon_{b}^{\prime 2} / \Delta_{c}^{2})^{\frac{1}{2}} \}, \tag{9}$$

an expression that can be derived from equation (6). The value used for $4\Delta_c$ in these calculations was 4.23 meV as determined by Reuszer and Fisher (1964) (see also Buzdin *et al.* 1973; Mayer and Lightowlers 1979; Aggarwal *et al.* 1980). It is also possible to display the shift of the $1s(A_1)$ state in a linear fashion by using the technique of Wilson and Feher (1961); see also Wilson (1964). In this procedure the quantity x is defined by $\Xi'_u Ts_{44}/4\Delta_c$ and equation (9) is manipulated to give

$$x = 3\{(\varepsilon_{g.s.}/2\varDelta_{c} - 1)^{2} - 1\}^{\frac{1}{2}}.$$
(10)

From the experimental value of $\varepsilon_{g.s.}$ at each stress an experimental value for x is determined. These values of x are plotted as a function of the stress T to give the result shown in Fig. 7. The solid line through the data represents a least-squares fit and leads to a value of $\Xi'_{u} = 16.5 \pm 0.4 \text{ eV}$; this value is included in Table 1.



Fig. 7. The stress dependence of x (see equation 10) for the lower $1s(A_1)$ ground state for $F \parallel \langle 110 \rangle$ (see text). The straight line through the data is a linear least squares fit and yields a value of $\Xi'_{\mu} = 16.5$ eV.

Transitions from the upper ground state $1s(T_2)$ are obtained by raising the temperature of the sample (Reuszer and Fisher 1964). With a stainless steel tailpiece and a stainless steel spacer inserted (mentioned earlier), the transition $1s(T_2) \rightarrow 2p_{\pm}$, designated as $2p_{\pm}^{(3)}(0)$ (the notation is that of Reuszer and Fisher 1965, 1968), was found to be sufficiently intense to study its behaviour under uniaxial compression. From Fig. 3, it is seen that for $F \parallel [110]$ and $q \parallel [\overline{110}]$, this absorption line should split into three components if $\varepsilon'_b = \varepsilon_b$. Two of these components should move 'rapidly away' from the zero stress position, one $(1s(A_1) \rightarrow 2p_{\pm}(-))$ to lower energy and the other $(1s(A_1) \rightarrow 2p_{\pm}(+))$ to higher energy. The remaining component, designated $2p_{\pm}^{(3)}$, consists of the superposition of the two transitions $1s(B_1) \rightarrow 2p_{\pm}(-)$ and $1s(B_2) \rightarrow 2p_{\pm}(+)$. As the stress is increased the former will provide the greater contribution due to thermal depopulation (thermalization) of the $1s(B_2)$ substate. The difference in energy between this transition and $2p_{\pm}^{(3)}(0)$ will be a measure of the difference between ε_b and ε'_b and hence Ξ_u and Ξ'_u .

The stress dependence of the transition from the lower $ls(A_1)$ state to $2p_0(-)$, designated $2p_0^{(1)}(-)$, and the $2p_{\pm}^{(3)}$ component, using polarized radiation is given in Fig. 8. The fact that the energy of the $2p_{\pm}^{(3)}$ component coincides with that of the $2p_{\pm}^{(3)}(0)$ line for stresses up to approximately 0.5 kbar demonstrates that at least the $ls(B_1)$ state of equation (7b) moves parallel to the $2p_{\pm}(-)$ state. Consequently, it is deduced that Ξ'_{u} , the deformation potential constant of the $ls(T_2)$ state, is the same as that of the excited states, viz. 16.4 ± 0.2 eV; this value is also included in Table 1. This result is consistent with that obtained previously for $F \parallel \langle 111 \rangle$ using qualitative stresses (Reuszer and Fisher 1968).

In Fig. 8, it is seen that for stresses in excess of approximately 0.5 kbar both the $2p_0^{(1)}(-)$ and $2p_{\pm}^{(3)}$ excitations split into doublets. Within experimental error this splitting was the same for each component up to the maximum stress applied (≈ 0.9 kbar). At this stress the splitting was 0.3 meV, less than 4% of $2\epsilon_b$. This additional splitting was attributed to a slight misalignment of **F** with respect to the $\langle 110 \rangle$ direction.



Fig. 8. The stress dependence of the $2p_0^{(1)}(-)$ and $2p_{\pm}^{(3)}$ components of arsenic impurity in germanium at a sample temperature of approximately 18 K for $F \parallel \langle 110 \rangle$. Appropriate superscripts designate E parallel to or perpendicular to F. The fine structure at stresses greater than approximately 0.5 kbar is attributed to a slight misorientation of the sample.

5. Discussion

In Table 1, a summary has been made of the various values of Ξ_{μ} obtained by a number of different methods of measurements. The first column of the table gives an abbreviated description of the method involved; the results of the present paper are given as its first entry. The next two methods are also piezospectroscopic, one using modulation spectroscopy to observe the splitting of the indirect exciton under stress (Balslev 1965, 1966, 1967; Walton et al. 1971), while the other gives the result obtained from studying the Raman transitions within the $1s(A_1)$ and $1s(T_2)$ ground state manifold under stress (Gorman and Solin 1977). The exciton data directly measure Ξ_u while the Raman observations give a value for Ξ'_u . The next method listed involves a study of the stress dependence of the hyperfine splitting of the donor electron spin resonance line of the impurity (Wilson 1964; Pontinen and Sanders 1966). This technique determines $\Xi'_{\rm u}/\Delta_{\rm c}$ and thus a knowledge of $\Delta_{\rm c}$ is required to obtain Ξ'_{u} (Reuszer and Fisher 1964). The fifth method listed provides a direct measurement of $\Xi_{\rm u}$. It depends upon the change in the elastic constants with concentration of conduction electrons and requires that the material be degenerate (Keyes 1961; Bruner and Keyes 1961; Mason and Bateman 1964; Hall 1965; Keyes 1967; Drabble and Fendley 1967; Baranskii et al. 1974). Next follows an optical method in which the birefringence of a doped sample is monitored as a function of stress for $F \parallel \langle 111 \rangle$. The change in the birefringence under stress is due to the redistribution of electrons between the shifted conduction band minima (Schmidt-Tiedemann 1962; Feldman 1966; Riskaer 1966). The results of some of the piezoresistance measurements are also given (Fritzsche 1959; Koenig 1963; Lopez and Koenig 1968; Schetzina and McKelvey 1969; Baranskii and Kolomoets 1971*a*). (Other publications of note on this topic are those of Morin *et al.* (1957), Fritzsche (1960, 1962), Katz (1962, 1965), Cuevas and Fritzsche (1965) and Baranskii and Kolomoets (1971*b*).) The second last method contains the value of Ξ_u obtained from measuring the stress dependence of the mobility of electrons in p-type material (Schetzina and McKelvey 1969). This effect also depends upon the transfer of electrons from upward shifting valleys to those shifting downward. The final entry is the value of Ξ_u obtained using the pseudo-potential method for band structure calculations (Saravia and Brust 1969).

In addition to the value of Ξ_{u} (or Ξ'_{u}) reported by the original investigators, a separate column is included containing, where justified, either an adjusted or an estimated value of Ξ_u . In some cases, the adjusted value of Ξ_u has been simply obtained by using Fine's (1955) values of c_{44} rather than those chosen or measured by the original worker. In the case of Feldman's (1966) piezobirefringence measurement, the value of c_{44} used to adjust Ξ_{u} was that appropriate to the carrier concentration of the degenerate sample used, the correction being estimated from the data of Bruner and Keyes (1961). In the cases where large carrier concentrations and large stresses are involved, it would appear as if the stress dependence of c_{44} should be incorporated into the data analysis since the deviation of c_{44} from the intrinsic value due to the electronic contribution is completely recovered at very high stress (Fjeldly 1972). In the review by Balslev (1972), corrected values of Ξ_{μ} are given for the piezobirefringence measurements of Schmidt-Tiedemann (1962) and Riskaer (1966) and for the piezoresistance result of Koenig (1963). The value of 16.9 eV listed under 'adjusted value' and attributed to Bruner and Keyes (1961) has been estimated from their data using the carrier concentration quoted there; similarly for the result of $16 \cdot 2 \text{ eV}$ attributed to Mason and Bateman (1964). In a later review paper, Keyes (1967) refers to the same data but quotes a different carrier concentration (see also Mason and Bateman 1964); it is not clear which of these two concentrations is the correct one, although Drabble and Fendley (1967) report the Bruner and Keyes value of Ξ_u as 17.0 ± 0.6 eV. For the indirect exciton measurements of Walton et al. (1971), no reference was given to the value of c_{44} used and thus this result for Ξ_u could not be adjusted. Since the values of $\Xi_{\rm u}$ obtained by Schetzina and McKelvey (1969) showed no variation from 77 to 297 K, adjustment of Ξ_u in this instance has been made using the values of c_{44} at 80 K.

It is believed by the present authors that the piezospectroscopy of donors provides the most direct and precise way of determining Ξ_u . It relies on the simple prediction that under a uniaxial force all the effective mass-like excited states shift in exactly the same way as do the conduction band minima and it requires a straightforward observation of the splitting of a spectral line under stress. The method also provides a means whereby the Ξ'_u appropriate to the ground state can be determined. It might be noted that the value obtained here for Ξ'_u for arsenic donors in germanium is the same as that obtained for Ξ_u for these donors, whereas for all the group V donors in silicon (Tekippe *et al.* 1972; Butler *et al.* 1975) $\Xi'_u < \Xi_u$, with Ξ'_u for arsenic being the second smallest.

Comparable in simplicity with the present technique is the determination of Ξ_u from c_{44} for degenerate material at very low temperature. Keyes (1961) has shown that at T = 0 K the electronic contribution to c_{44} of germanium is

$$(\delta c_{44})_0 = -(\frac{4}{3})^{5/3} \pi^{2/3} m^* \Xi_u^2 N^{1/3} / h^2$$

Deformation potential constants	ninima of Ge and for \mathcal{Z}'_u of the ground state of group V impurities in Ge
Table 1. D	Values are given for Ξ_u of the conduction band min

Method	Direction of F	Donor impurity	Energy state	Donor conc. (cm ⁻³)	Temp. (K)	Reported value of E_{u} or E'_{u} (eV)	Adjusted ^B value of E_{u} or E'_{u} (eV)	Origin of data ^A
Piezo- spectroscopy of donors	<110>	As	$2p_0$ $1s(A_1)$ $1s(T_2)$	1015	~7 ~7 ~18	$16.4\pm0.2 \\ 16.5\pm0.4 \\ 16.4\pm0.2 \\ 16.4\pm0.2 \\$		Present work
Piezo- spectroscopy of indirect exciton	(111), (110) (110) (110) (111) (111)	 	Conduction band (CB)	(40 Ω cm) —	80 80 297 290	$\begin{array}{c} 16\cdot2\pm0\cdot4\\ 16\cdot3\pm0\cdot2\\ 15\cdot85\pm0\cdot3c\\ 15\cdot2\pm0\cdot5\\ 14\cdot6\pm1\end{array}$	16-27 16-37 15-92	- 0 0 n n
Piezo- Raman spectroscopy	<111>,<110>	As	1s manifold	$\sim 10^{16}$	12	17.8 ± 0.5	17.76	4
Piezo electron spin resonance	<110>	P As Sb	1s manifold	8×10^{14} 5×10^{15} 5×10^{15} $4 \times 10^{14} \rightarrow 10^{16}$	$\begin{array}{c} 1\cdot 2\\ 1\cdot 2\\ 1\cdot 2\\ 1\cdot 2 \rightarrow 15\end{array}$	18.5±1.6 19.2±1.2 19.5±1.3 15.4±1.3		5, 6 6, 7
Elastic constants		As Sb As Sb As	B	$\begin{array}{c} 3\cdot 5\times 10^{19} \\ 1\cdot 5\times 10^{18} \\ 2\cdot 4\times 10^{19} \\ 2\cdot 8\times 10^{19} \\ 2\cdot 3\times 10^{19} \\ 2\cdot 3\times 10^{18} \\ 10^{18} \rightarrow 1\cdot 5\times 10^{19} \end{array}$	4 · 2 4 · 2 298 77→298 300	$\begin{array}{c}$	16.9	8 10 11 12

522

Piezo-	<111>	Sb As Sh	CB	$(0 \cdot 2 \rightarrow 1 \cdot 33) \times 10^{18}$ $(1 \cdot 24 \rightarrow 4 \cdot 66) \times 10^{18}$	90 1·4	18.9 ± 1.7 18.0	$17 \cdot 3 \pm 1 \cdot 5^{\mathrm{D}}$ $17 \cdot 7$	13 14
		Sb		$\approx 3.5 \times 10^{17}$	LL L	18.0 ± 0.5	15.8 ± 0.5^{D}	15
Piezo- resistance	⟨110⟩	As		7.8×10^{15} $\rightarrow 3.5 \times 10^{16}$	6·58 →8·93	19.2 ± 0.4		16
	I É	- As	CB	3.6×10^{14}	- L	— 16 <u>+</u> 1	$17 \cdot 0 \pm 1 \cdot 0^{D}$	17 18
	ÌI		CB	3×10^{14}	<i>71</i> →296	$16.0 \rightarrow 16.6$	$16.07 \rightarrow 16.67$	19
	<1111>		Ü	9.8×10^{11} $\rightarrow 6.5 \times 10^{13}$	<i>LL</i>	16.4 ± 0.2	16.55	20
Piezo- mobility	!!	Minority carriers in Ga- doped Ge	B	3×10^{14} and 7×10^{14} (gallium)	77→297	16.3±0.3	16.37	19
Pseudo- notential			C			14.0		21
calculation			in in Station					
								5 10101

Baranskii et al. (1974); 13, Schmidt-Tiedemann (1962); 14, Feldman (1966); 15, Riskaer (1966); 16, Fritzsche (1959); 17, Koenig (1963); 18, Lopez and Koenig ^A References: 1, Balslev (1966); 2, Balslev (1967); 3, Walton *et al.* (1971); 4, Gorman and Solin (1977); 5, Wilson (1964); 6, Reuszer and Fisher (1964); 7, Pontinen and Sanders (1961, 1966); 8, Bruner and Keyes (1961); 9, Mason and Bateman (1964); 10, Hall (1965); 11, Drabble and Fendley (1967); 12, (1968); 19, Schetzina and McKelvey (1969); 20, Baranskii and Kolomoets (1971a); 21, Saravia and Brust (1969) ^B See text for explanation of adjusted (estimated) values.

^c Average of two values.

^D Taken from Balslev (1972).

523

where $m^* = (m_1 m_t^2)^{1/3}$ and N is the concentration of conduction electrons derived from the donor atoms; m_1 and m_t are the longitudinal and transverse effective masses respectively of the conduction band energy ellipsoids. At higher temperatures this expression needs to be modified by the appropriate Fermi integrals. A somewhat similar expression exists for the change in the third order elastic constant c_{456} . However, even at T = 0 K, this method requires a knowledge of N while at higher temperatures the Fermi integrals (and their derivatives) are needed. The results obtained by Baranskii *et al.* (1974) indicate that Ξ_u is independent of impurity concentration but appears to depend upon temperature, this latter dependence being in the same sense as that determined by Balslev (1967) and Walton *et al.* (1971) although, as already mentioned, Schetzina and McKelvey's (1969) observations show essentially no temperature dependence from 77 to 297 K.

It might be expected that the Raman technique (Gorman and Solin 1977) should yield the same value of Ξ'_{u} as that obtained by the present method. There is, however (as is seen from Table 1), a significant difference between the results obtained by these two methods. The observations of Baranskii et al. (1974) indicate that the difference observed cannot be accounted for by the different impurity concentrations in the samples used. Since the observations have been carried out at essentially the same temperature the ambiguity mentioned above regarding the temperature dependence of Ξ_{u} does not provide an explanation. On the information available, the origin of the discrepancy between the present value of Ξ'_u and that obtained from the Raman spectra is not understood. A similar discrepancy exists between the present results and those obtained by piezo-spin-resonance (see Table 1). This latter discrepancy is also found for the case of silicon (Tekippe et al. 1972) where the difference between the Ξ'_u obtained by the two methods is relatively larger though in the same sense. Recently, Tan and Castner (1980) have reconsidered the results of Wilson and Feher (1961) for P and Sb donors in silicon assuming that $\Xi'_{u} = 8.6 \text{ eV}$. This assumption requires the Bohr radius of the donor ground state to be stress dependent contrary to the assumption made by Wilson and Feher, who attributed all the changes in hyperfine splitting to mixing of the upper ground state wavefunction into the singlet Is state without any changes in the effective-mass hydrogenic wavefunctions. The conclusions of Tan and Castner appear to be reasonable and may very well explain this long-known discrepancy. It would seem, however, that the values of 8.1 and 8.3 eV obtained by Tekippe et al. (1972) for Ξ'_{μ} of P and Sb respectively should be used rather than $8 \cdot 6$ eV which is essentially that of the conduction band minima of Si. It should be noted that the larger values of Ξ'_{u} are obtained by techniques involving transitions within the donor ground state manifold, whereas the present method involves transitions from the ground state complex to excited p states. From this point of view, a study of the direct transitions between the $1s(A_1)$ and $1s(T_2)$ states in optical absorption (Buzdin et al. 1973; Aggarwal et al. 1980) under stress would be of interest.

The indirect exciton studies initiated by Balslev (1966, 1967) and repeated by Walton *et al.* (1971) appear to suffer from the usual ambiguity associated with differential spectroscopy. The analysis performed by Walton *et al.* argues for the use of a different point on the differential curve than that claimed by Balslev for extracting splittings under stress. The two results obtained are significantly different although Walton *et al.* do state that their results are in agreement with Balslev's if they use the latter's criterion. It is interesting to note that Walton *et al.* do not refer to Balslev's (1967) later work, where stress modulation is used instead of the wavelength modula-

tion employed earlier by Balslev (1966). Balslev's results are in excellent agreement with the present values, implying that his criterion for this data analysis is preferable to that specified by Walton et al.

The remaining three techniques, piezobirefringence, piezoresistance and piezomobility measurements, all depend upon the transfer of electrons from one set of conduction band minima to another where these are energetically separated by applying uniaxial compression along a $\langle 111 \rangle$ direction. This direction is chosen in germanium since one minimum is depressed, while the other three, as a group, are raised in energy. This is, of course, the same effect as that involved in the study of c_{44} or c_{456} . However, in analysing the data obtained by the piezobirefringence, piezoresistance and piezomobility measurements, curve fitting with several parameters, one of which is Ξ_{u} , is usually used although Baranskii and Kolomoets (1971a) have improved on this somewhat and also obviated the need to make transverse piezoresistance measurements. Another parameter involved is the scattering anisotropy which either needs to be determined independently or adjusted along with $\Xi_{\rm u}$. The scattering anisotropy parameter is notoriously difficult to pin down since it depends not only on impurity concentration and temperature but also on the compensation. It is remarkable that when all these aspects are taken into account, the values of $\Xi_{\rm u}$ obtained are in such good agreement with those obtained by the more unambiguous techniques. The results of Schetzina and McKelvey (1969) and Baranskii and Kolomoets (1971a, 1971b), obtained later than the others using the same methods, are in particularly good agreement with the present value and those deduced from the elastic constants.

6. Conclusions

The results of the present investigations yield a value of $16 \cdot 4 \pm 0 \cdot 2 \text{ eV}$ for the shear deformation potential constant of the conduction band edge of germanium and the same value for the ground state manifold of arsenic donors in germanium. This value for Ξ_u is in excellent agreement with the latest results obtained by other methods, except those from piezo-Raman studies.

The piezospectroscopy of donors permits a reliable measurement to be made of Ξ_u at low temperatures and over a limited range of impurity concentrations. It is estimated that observations could be made up to approximately 30 K and for impurity concentrations as large as 10^{16} cm⁻³.

Acknowledgments

The authors would like to thank Dr N. F. Kennon for verifying the orientations of the samples used in the investigation and Mr R. Tanner of the Instruments Services Laboratory (N.S.W. Department of Productivity) for calibrating the pressure gauges. They also gratefully acknowledge support from the ARGC and the University of Wollongong's Special Research Grant Committee and to Purdue University for the loan of some of the equipment and samples used in the studies.

References

Aggarwal, R. L., People, R., Wolff, P. A., and Larsen, D. M. (1980). Proc 15th Int. Conf. on the Physics of Semiconductors, Kyoto; J. Phys. Soc. Jpn 49, Suppl. A, p. 197.

Balslev, I. (1965). Solid State Commun. 3, 213. Balslev, I. (1966). Phys. Rev. 143, 636.

- Balslev, I. (1967). Phys. Lett. A 24, 113.
- Balslev, I. (1972). In 'Semiconductors and Semimetals', Vol. 9, 'Modulation Techniques' (Eds R. K. Willardson and A. C. Beer), p. 403 (Academic: New York and London).
- Baranskii, P. I., Elizarov, A. I., and Kolomoets, V. V. (1974). Sov. Phys. Semicond. 8, 519.
- Baranskii, P. I., and Kolomoets, V. V. (1971a). Phys. Status Solidi (b) 45, K55.
- Baranskii, P. I., and Kolomoets, V. V. (1971b). Phys. Status Solidi (b) 46, 791.
- Bruner, L. J., and Keyes, R. W. (1961). Phys. Rev. Lett. 7, 55.
- Butler, N. R. (1974). Ph.D. Thesis, Purdue University.
- Butler, N. R., Fisher, P., and Ramdas, A. K. (1975). Phys. Rev. B 12, 3200.
- Buzdin, V. V., Demeshina, A. I., Kurskii, Yu. A., and Murzin, V. N. (1973). Sov. Phys. Semicond. 6, 1792.
- Cuevas, M., and Fritzsche, H. (1965). Phys. Rev. 137, A1847; 139, A1628.

Drabble, J. R., and Fendley, J. (1967). J. Phys. Chem. Solids 28, 669.

- Feldman, A. (1966). Phys. Rev. 150, 748.
- Fine, M. E. (1955). J. Appl. Phys. 26, 862.
- Fjeldly, T. A. (1972). Proc. 11th Int. Conf. on the Physics of Semiconductors, Warszawa, Vol. 1, p. 245 (PWN Polish Scientific Publishers: Warsaw).
- Fritzsche, H. (1959). Phys. Rev. 115, 336.
- Fritzsche, H. (1960). Phys. Rev. 120, 1120.
- Fritzsche, H. (1962). Phys. Rev. 125, 1552.
- Gorman, M., and Solin, S. A. (1977). Phys. Rev. B 16, 1631.
- Hall, J. J. (1965). Phys. Rev. 137, A960.
- Herring, C. (1955). Bell Syst. Tech. J. 34, 237.
- Herring, C., and Vogt, E. (1956). Phys. Rev. 101, 944.
- Katz, M. J. (1962). Helv. Phys. Acta 25, 511.
- Katz, M. J. (1965). Phys. Rev. 140, A1323.
- Keyes, R. W. (1961). IBM J. Res. Develop. 5, 266.
- Keyes, R. W. (1967). 'Solid State Physics' (Eds F. Seitz and D. Turnbull), Vol. 20, p. 37 (Academic: New York).
- Keyes, R. W., and Sladek, R. J. (1962). Phys. Rev. 125, 478.
- Koenig, S. H. (1963). 'Semiconductors' (Ed. R. Louden), p. 515 (Academic: New York).
- Kohn, W. (1957). In 'Solid State Physics' (Eds F. Seitz and D. Turnbull), Vol. 5, p. 257 (Academic: New York).
- Lopez, A. A., and Koenig, S. H. (1968). Proc. 9th Int. Conf. on the Physics of Semiconductors, Moscow, Vol. 2, p. 1061 (Nanka: Leningrad).
- Martin, A. D., Fisher, P., and Simmonds, P. E. (1979). Phys. Lett. A 73, 331.
- Martin, A. D., Fisher, P., and Simmonds, P. E. (1980). Bull. Am. Phys. Soc. 25, 11.
- Mason, W. P., and Bateman, T. B. (1964). Phys. Rev. 134, A1387.
- Mayer, A. E., and Lightowlers, E. C. (1979). J. Phys. C 12, L945.
- Morin, F. J., Geballe, T. H., and Herring, C. (1957). Phys. Rev. 105, 525.
- Pontinen, R. E., and Sanders, T. M., Jr (1961). Bull. Am. Phys. Soc. 6, 426.
- Pontinen, R. E., and Sanders, T. M., Jr (1966). Phys. Rev. 152, 850.
- Price, P. J. (1956). Phys. Rev. 104, 1223.
- Reuszer, J. H., and Fisher, P. (1964). Phys. Rev. 135, A1125.
- Reuszer, J. H., and Fisher, P. (1965). Phys. Rev. 140, A245.
- Reuszer, J. H., and Fisher, P. (1968). Phys. Rev. 165, 909.
- Riskaer, S. (1966). Phys. Rev. 152, 845.
- Saravia, L. R., and Brust, D. (1969). Phys. Rev. 178, 1240.
- Schetzina, J. F., and McKelvey, J. P. (1969). Phys. Rev. 181, 1191.
- Schmidt-Tiedemann, K. J. (1962). Proc. Int. Conf. on the Physics of Semiconductors, Exeter, (Ed. A. C. Stickland), p. 191 (The Institute of Physics and the Physical Society: London).
- Smakula, A., and Sils, V. (1955). Phys. Rev. 99, 1744.
- Smith, C. S. (1954). Phys. Rev. 94, 42.
- Soepangkat, H. P., and Fisher, P. (1973). Phys. Rev. B 8, 870.
- Tan, H. S., and Castner, T. G. (1980). Bull. Am. Phys. Soc. 25, 204.
- Tekippe, V. J. (1973). Ph.D. Thesis, Purdue University.
- Tekippe, V. J., Chandrasekhar, H. R., Fisher, P., and Ramdas, A. K. (1972). Phys. Rev. B 6, 2348.

Walton, A. K., Williams, G. P., and Reddy, K. V. K. (1971). *Phys. Status Solidi* (b) 47, K29.
Watkins, G. D., and Ham, F. S. (1970). *Phys. Rev.* B 1, 4071.
Wilson, D. K. (1964). *Phys. Rev.* 134, A265.
Wilson, D. K., and Feher, G. (1961). *Phys. Rev.* 124, 1068.

Manuscript received 16 April 1981, accepted 27 May 1981

