THE EFFECT OF STRAIN ON THE EXCITON SPECTRUM OF GERMANIUM

by

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### in the department of

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We accept this thesis as conforming to the required standard

### THE UNIVERSITY OF BRITISH COLUMBIA

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# The University of British Columbia FACULTY OF GRADUATE STUDIES

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of

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B.Sc. (Special), University of London, 1961

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ABSTRACT

The intensity of optical absorption, near the absorption edge in germanium, is examined as a function of strain applied to the lattice at 90°K. The results are interpreted in terms of the change of the band structure of the lattice with applied strain. The absorption edge in unstrained germanium shows a single sharp peak due to exciton formation, whereas the edge in the strained specimens shows two exciton The peak positions vary linearly with both peaks. compressional and tensional strain up to the maximum strains applied (0.1% deformation). The exciton binding energies in the strained germanium lattice, calculated within the effective mass approximation, are approximately equal and independent of the magnitude of the strain. The separation of the peaks gives for the shear deformation potentials, the values  $|b| = (2.7 \pm 0.3) eV/unit \langle 100 \rangle$  shear and |d| = $(4.7 \pm 0.5)$ eV/unit  $\langle 111 \rangle$  shear. The positions of the peaks give the shift of the energy gap as - (10.3 + 1)eV/unit dilatation.

Lattice imperfections are found to have no effect on the interpretation of the results. The broad absorption edge observed in evaporated films of germanium is accounted for in terms of internal strains.

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#### CHAPTER I : INTRODUCTION

In the ground state of a semiconductor, all states of the valence band are occupied and all those of the conduction band are empty. The first excited state of the crystal is the creation of an electron hole pair. The coulomb interaction of the pair gives rise to bound states of the electron and hole, with energies below the conduction band (reference 1). These states are called exciton states and the electron-hole pair is often loosely referred to as an exciton. A free electron in the conduction band and a free hole in the valence band, may thus be considered as an ionised state of the exciton. Light is absorbed by exciting the crystal into exciton states.

Direct transitions , involving the interaction of electrons with photons only, must satisfy the momentum conservation rule  $\vec{k}_e + \vec{k}_h = 0$  (where the  $\vec{k}_e$ ,  $\vec{k}_h$  are the electron and hole wave vectors), since the photon momentum is negligible. Thus transitions to bound exciton states give rise to a line spectrum. The onset of continuous absorption occurs when the photon energy is equal to the "forbidden"energy gap between the valence and conduction bands. Studies of this absorption edge have yielded useful information on the band structure of several semiconductors.

In the case of germanium, the valence band maximum is fourfold degenerate ( including spin ) at k=0 of the Brillouin zone. The conduction band minima are at the Brillouin zone boundaries, with an auxiliary minimum at k=0 (reference 2).Thus the creation of excitons of lowest energy are forbidden by momentum considerations unless a phonon is simultaneously created or annihilated (reference 3). Macfarlane et al (reference 4) have shown that absorption of light due to these indirect transitions appears

appears only as a long-wavelength tail to the absorption edge, since these transitions are far less probable than the direct transitions at k = 0.

Using high resolution and thin, freely hanging specimens of high purity germanium, Macfarlane et al (reference 5) observed a sharp absorption peak in the edge at high absorption coefficients, at temperatures below 196°K. They interpreted this as the lowest energy line in the line spectrum due to exciton formation. However, two peaks were observed in the spectrum by Zwerdling, et alia (reference 6) using similar specimens, glued to a glass substrate. The absorption edge was also shifted to shorter wavelengths. Macfarlane et al later showed that the difference in the two spectra was because the specimens of Zwerdling et al. were strained by the substrate on cooling (reference 7).

This led Kleiner and Roth (reference 8) to investigate the effect of strain on the band structure of germanium from a theoretical point of view. They found that when the cubic symmetry of the lattice is removed by a homogenious strain, the valence band degeneracy at k=0 is removed. There is also a change in the energy gap corresponding to the change in the lattice parameters. They then interpreted the two peaks observed by Zwerdling et al (and later by Macfarlane) as the exciton spectra associated with the two pairs of bands. Owing to the lack of data, Kleiner and Roth were unable to evaluate the deformation potentials of the germanium lattice explicitly, from their theory. A more complete theory on the effect of strainon the hole energy spectrum of germanium has been given by Picus and Bir (reference 9).

Deformation potentials are important parameters in all theories associated with lattice deformation. They were first introduced by Bardeen and Shockley who used them in the theory of electron and hole scattering.(reference 10). They are also important in the theory of the effect of internal and externally applied strains on the band structure of a crystal. Thus it is desirable to have accurate values of these parameters.

Studying the exciton spectrum as a function of strain provides a check of the agreement between experiment and the theory of Kleiner and Roth, and is a particularly convenient method of determining the deformation potentials of the pure germanium lattice explicitly. In this investigation the spectrum is studied as a function of both compressional and tensional strain. The exciton binding energies in germanium are calculated within the effective mass approximation, using the formalism of Dresselhaus (reference 2) in order that the positions of the band edges may be obtained from the experimental data. In view of the possibility that this information may be obtained directly from the experimental data, the theory of Elliott (reference 11) on the optical absorption near the edge, for two simple spherical bands, was extended to the case of germanium, where the bands have a more complicated shape.

Finally, the effect of lattice imperfections on the absorption edge of the germanium specimens is studied in some detail, in order to ensure that the observed effects were properties of the perfect germanium lattice. The absorption spectrum of evaporated films of intrinsic germanium in the wavelength range  $0.5\mu$  to  $1.0\mu$  ( $1\mu = 10^{-4}$  cm) is accounted for in the light of this discussion.

### CHAPTER II : EXPERIMENTAL METHODS AND PROCEDURE.

Experimentally, observing the effect of strain on the exciton spectrum of germanium, involved the following problems: a) In order to minimise the effect of lattice imperfections, single crystals of high purity and low dislocation density, had to be prepared. Since the elastic moduli of germanium depend on the choice of crystal axes, the crystal orientation had to be known.

b) The fine structure due to direct exciton absorption occurs at high absorption coefficients ( $\sim 3500 \text{ cm}^{-1}$ ), (reference 5). Thus it was necessary to prepare thin wafers of germanium from these single crystals.

c) For the examination of the exciton spectrum of both strained and unstrained germanium specimens, a high resolution monochromator was required, with an arrangement to cool the specimens to about 77°K. (reference 5).

A. CRYSTAL GROWTH.

Crystals of pure germanium were pulled from the melt by the Czochralski tecnique: Zone refined germanium of high purity was melted in a graphite in a graphite crucible by resistance heating and germanium seed crystals of  $\langle 100 \rangle$ ,  $\langle 110 \rangle$ ,  $\langle 111 \rangle$ , orientations were used to pull the crystals from the melt. The crystal growth was performed in an argon atmosphere to avoid contamination of the germanium by reactive materials. The germanium ingots were then sliced into discs, of about 1mm. in thickness, with a diamond impregnated saw, so that the plane of the discs was perpendicular to the growth axis.

PURITY : The purity of the discs was checked by measuring their

resistances at 23°C with a four-probe machine. The resistivity of all discs was found to be about 60 ohm-cm,(except at the two extreme ends of the ingot,which were discarded), indicating that theimpurity content was less than 10<sup>18</sup> impurities/cc. TWINNING : A check was made for twinning of the crystal during growth, by boiling freshly lapped discs in a 30% hydrogen peroxide etching solution. Since there was no change in the reflectivity of the discs across their surfaces, they were assumed to be single crystal.

DISLOCATION DENSITY : The method of Pfann (reference 12) was used to determine the dislocation density. The germanium discs were lapped with 800 mesh (#800) Alumina and etched for about 90 seconds in fast CP4 (25cc nitric acid, 15cc hydrofluoric acid, 15cc acetic acid). The etch pits were clearly visible under a magnification of 100 x , for the discs in the [100] and [111] planes only. If it is assumed that the etch pits are located at the intersection of the dislocation lines with the crystal surface (reference 12), then the etch pit counts indicated dislocation densities of about 5000 lines/cm<sup>2</sup> for both crystals.

CRYSTAL ORIENTATION : The crystal orientation was clearly indicated by the symmetry of the ingots about the growth axis; however an independent check was afforded by examining the shapes of the etch pits and comparing them with those described by Ellis (reference 13). The agreement indicated that the planes of the discs were within 3 degrees of the nominal planes. In the  $\langle 100 \rangle$ oriented discs, terraces in the etch pits, corresponding to jogs of the dislocation, could be seen.

#### B. SPECIMEN PREPARATION.

The exciton absorption peak in germanium occurs at a photon energy where the absorption coefficient is about 3500 cm<sup>-1</sup> (reference 5). At higher energies the absorption coefficient increases. It is shown later that the transmission T of a specimen of thickness <u>d</u> is related to the absorption coefficient by  $T \propto exp - \propto d$ . The optimum condition for the observation of the exciton peak is  $\frac{dT}{dx}$  is a maximum at  $\propto = 3500$  cm<sup>-1</sup>. Thus the optimum specimen thickness is about  $3\mu$ .

Three possible methods of specimen preparation were investigated : Chemical etching, electroetching, and mechanical polishing. The first two methods proved unsuccessful, and it is worthwhile to outline the reasons for failure.

a) CHEMICAL ETCHING :

The germanium discs were ground to a thickness of about 50 and etched in slow CP4 (10 cc nitric acid, 10cc hydrofluoric acid, 20cc acetic acid). It was found that the edges of the wafers dissolved in the etch very rapidly, while there was only little change in thickness. Masking the edges with epoxy did not retard the effect as the epoxy was undermined by the etch. Further, the polishing was uneven, and holes developed through the wafer.

### b) ELECTROETCHING

The germanium wafer was used as the anode in a KOH electrolyte, and platinum as the cathode. The procedure followed was that described by Uhlir (reference 14). It was found that etching occurred, but it was localised at the parts of the wafer nearest to the metal contact with the germanium. The primary anodic process in germanium is carried out by holes (reference 13), so this

result could be accounted for if the hole density were greatest near the metal contact. Hole injection may take place at a metal-germanium contact, so this is the probable explanation of the above effect. Shining light on the wafer, or increasing the temperature did increase the anodic current density, but uneven etching still occurred. Making large area contacts or using a moving pressure contact would be technically difficult for very thin wafers, so electroetching was abandoned.

c) MECHANICAL POLISHING.

This method was tried last of all because it has been reported (reference 14) that abrasion damage penetrates over 20µ below the crystal surface, even when a lapped surface is subsequently highly polished. Photomagnetoelectric measurements on the surface recombination velocity (reference 15), on the other hand, reveal that the abrasion damage extends, on the average, to a depth comparable to the abrasive particle size only.

Specimens down to 5µ thick were successfully prepared by mechanical polishing. Although this was greater than the optimum thickness, it was found that thicknesses up to 20µ were adequate for the oservation of the exciton spectrum.

The sequence of abrasives and laps used was extensively studied with a view to the quality of the polish and the speed of specimen preparation. The following procedure gave best results: Several wafers (usually four) were shaped in cross section so that they fitted together in a mosaic form, without any appreciable gaps between them. They were glued to a plate of glass with rosin wax, and chips of germanium were glued around the wafers on the glass so that all edges of a wafer were in contact with another piece of germanium. The chips prevented the edges of the wafers

from rounding during polishing. The complete mosaic was ground flat with #450 Silicon Carbide (SiC) on glass ( abrasive particle size ~22 $\mu$ ). Subsequent abrasives used in order were: #600 SiC on a glass plate (abrasive particle size ~15 $\mu$ ), 50 $\mu$  removed #800 Al<sub>2</sub>O<sub>3</sub> on glass (abrasive particle size ~10 $\mu$ ), 50 $\mu$  removed. The mosaic was finely ground at this stage. It was mounted in an automatic jig fitted to a mechanical polishing wheel, and the polishing sequence was:

#600 SiC on astromet cloth\*(see footnote), with the wheel rotating at 600 revolutions per minute until all the pits due to lapping were removed and the surface was well polished.

# Linde B Al<sub>2</sub>O<sub>3</sub> (abrasive particle size ~0.2 $\mu$ ) on astromet cloth with the wheel rotating at 600 revs/min. After one hour with this abrasive, all scratches from the previous abrasive were removed and the surface was highly polished.

The polished surfaces were flat over 90% of the surface and only a very slight curvature was seen right at the wafer edges. The wafers were still at least 300 $\mu$  thick. They were removed from the glass plate by melting the wax, washed in alcohol and glued to another plate with the polished surface downwards. For the specimens which were to be removed subsequently from the glass the glue used was Dennison type A14<sup>†</sup>(see footnote). The specimens which were not to be removed from the substrate, were glued with an epoxy, especially prepared for the purpose of obtaining thin

\*Astromet cloth is a Precision Scientific Instruments product. It is a durable cloth with a very short nap, for polishing flat surfaces. †Dennison Type Al4 was sent to me by Raytheon Co. for the purpose of obtaining very thin layers of cement.It has a very low melting point, low viscosity just above the melting point, has little tendency to form bubbles, and is readily soluble in alcohol. It is very hard at room temperature. layers of glue. The epoxy had a low viscosity and high bond strength; it was cured for 48 hours at room temperature.

A micrometer was used to measure the specimen thicknesses since the substrate thickness was known from a previous measurement. It was found from repeated experiments that the glue formed a very thin parallel layer.

The wafer was lapped by hand with #600 SiC on glass until the thickness was about 100µ, and then with #800 Al<sub>2</sub>O<sub>3</sub> on glass until the thickness was about  $25\mu$ . This point was the most critical in the specimen preparation and it was essential that only a very small, even pressure be applied evenly to the wafer while lapping. The wafer thickness was constantly checked to ensure uniformity. The wafer and substrate were then mounted in the jig and polished on astromet cloth with #600 SiC, with the wheel rotating at 300 revs/min., until all lapping pits were removed and the wafer was reduced to the required thickness. Since no masking of the wafer edges was used for this side of the specimen an estimate of the wafer thickness could be made, and its uniformity, by looking at the condition of the extreme edges of the wafer. Only a slight reduction in the area of the wafer occurred before it was about 10µ thick. A high final polish was obtained with Linde B abrasive on astromet cloth.

The specimens mounted on glass with epoxy were ready for use in the monochromator at this stage, but those mounted with Dennison Type Al4 were placed in alcohol until all the cement had dissolved. The unsupported germanium specimens were slightly flexible, though they did not curl on removal from the substrate if both surfaces were equally well polished. The specimens were

washed in alcohol and placed between two sapphire windows to avoid handling them further.

This method of specimen preparation proved very fast and successful. Since only the centre section of the specimens were used for optical measurements, the rounding of the edges did not matter. Interference fringes were observed in the transmission spectra of the specimens, indicating that they were nearly uniform in thickness. The optical properties of the specimens were essentially unaffected by the polishing rate or the presence of a few pits or scratches.

C. THE MONOCHROMATOR.

A high resolution infra red Ebert monochromator was used in this investigation. The optical arrangement is shown in Fig 1. The entrance and exit slits, curved to minimise aberrations, are placed in the focal plane of the converging spherical mirror  $M_i$ . The diffraction grating G is a Bausch and Lomb reflexion grating of 300 lines/mm., blazed at 1.5 in the second order. The fnumber of the system, limited by the grating, is fl2.5. The whole system is mounted inside a tank, which can be evacuated.

The monochromator was operated at a resolution A of 6000 to 15000 at 1.4  $\mu$  in the second order, corresponding to mechanical slit widths of 0.4 and 0.18mm respectively. FORE-DISPERSING OPTICS :

In order to prevent different orders of reflexion, from overlapping at the exit slit  $S_2$ , fore-dispersing optics were added to the monochromator. This allowed a determined band width of radiation to enter  $S_1$ . To obtain only one wavelength  $\lambda$  in the second order from the monochromator, the maximum bandwidth to enter  $S_1$  must be  $2\lambda$  to  $\frac{2\lambda}{3}$ . The Ebert system could not be used in





Fig. 1

(to follow page 10)

Fig 2

Plan view of the fore-dispersing optics, showing the light path.



the fore-optics because of mechanical limitations, but since the selected bandwidths were large, small aberrations were unimportant. The optical system is shown in Fig 2. The entrance slit S<sub>3</sub> is curved so that the image of S<sub>3</sub> in the spherical mirror M<sub>3</sub> is co-linear with S<sub>1</sub> . M<sub>3</sub> is about 5 degrees off axis. The system has unit magnification so S<sub>3</sub> and S<sub>1</sub> were both in the focal plane of M<sub>3</sub>. The fore-dispersing prism is calcium fluoride, aluminised on one face. The dispersion and refractive index of CaF<sub>2</sub> are respectively 0.005 and 1.42 at about 1.4 $\mu$ , giving a linear dispersion at S<sub>1</sub> of 0.19 cm/ $\mu$ .

The bandwidth of radiation could be varied by changing the slit width of S<sub>3</sub> . If S<sub>3</sub> was very narrow - effectively a line source - only those wavelengths for which the image of S<sub>3</sub> a) fell directly on S, entered the main ΙĪ Δλ monochromator. The expected intensity distribution of radiation passing through S, is illustrated in Fig 3a. This was the b) ΙI minimum band width for a given slit width of  $S_1$ . For  $S_1 = 0.4mm$ , the bandwidth  $\Delta \lambda = 0.2 \mu$ . Using an extended Fig. 3 source slit S<sub>3</sub>, images of S<sub>2</sub> for different wavelengths overlapped at S<sub>1</sub> so that the bandwidth of radiation entering S, was increased. The intensity distribution for this case is shown in Fig 3b. If  $S_3 = 0.7$ mm and  $S_1 = 0.4$ mm then  $\Delta \lambda = 0.6\mu$ .

The predicted behavior of the fore-optics was borne out in practice. This eliminated the necessity of filters in the system, and maximum intensity was maintained and scattered radiation reaching the exit slit  $S_2$  was kept to a minimum. The fore-optics

chamber was evacuated with the main monochromator, and the foredipersing prism could be rotated from outside the vacuum system for selection of the wavelength bands.

SOURCE :

The source used was a Sylvania Sun Gun tungsten filament lamp with a colour temperature of  $3400^{\circ}$ K when run at 120 volts a.c.. This source was particularly useful because of its very small size and small helical filament ( $\frac{1}{2}$  inch long), so that the filament could be placed very close to S<sub>3</sub>, the only focussing optics being a cylindrical mirror behind the source. This gave the maximum intensity possible from the source and the small optical path in air minimised atmospheric absorption. The intensity -wavelength curve was a good approximation to black body radiation which peaks at about 1.2 $\mu$  at 3400°K.

The light beam was modulated at 870 cycles/second by a disc chopper placed between  $S_3$  and the source. DETECTOR SYSTEM :

In order to measure large absorption coefficients it was necessary to keep the signal-to-noise ratio as high as possible, and the drift of the source and detector system as low as possible.

The exit optics consisted of an image distorter which focussed a distorted image of about  $\frac{1}{2}$ cm<sup>2</sup> of the slit S<sub>2</sub> onto the specimen, and the light transmitted through the specimen was focussed onto a lead sulphide detector. Since the signal/noise ratio of a PbS detector is proportional to (sensitive area)<sup>- $\frac{1}{2}$ </sup>, a very short focal length mirror and a detector of  $\frac{1}{2}$  mm<sup>2</sup> area were used. Preliminary experiments on various PbS detectors showed that the Infratron B-J-SA19 was the most suitable . This detector had a reponse time of 200µseconds at 300<sup>°</sup>K and a dark resistance of



Block diagram of the detector electronics.



l megohm. A transistor preamplifier was mounted directly behind the detector and mirror, inside the vacuum system to avoid noise pickup. The output signal of the preamplifier was fed into a narrow band amplifier tuned to 870 cycles/second. The effective noise input of the amplifier was less than the shot noise of the detector. With a monochromator slit width of 0.4mm, maximum light intensity, and no specimen in the light path, the signalto-noise ratio was about 500. The source and detector system drifts were negligible. The complete electronics is shown diagrammatically in Fig 4.

The exit optics was evacuated separately from the main monochromator to a pressure of about  $10^{-5}$  mm Hg. EXPERIMENTAL PROCEDURE

The specimens and mount were clamped on the dewar block as shown in Fig 5. The copper plate was screwed down, sufficiently tightly to just hold the specimen in place, so as not to strain the specimen by the contraction of the retaining screws on cooling. The copper radiation shield, cooled to the same temperature as the dewar block, minimised heat exchange between the specimen and the surrounding walls. The exit optical system was evacuated with the dewar in place and the specimen was cooled by conduction through the copper block



specimen retainer plate

Fig 5 : The dewar and specimen holder

when the refrigerant was introduced into the dewar.

The germanium wafers were strained by the differential contraction of the germanium and substrate on cooling. The degree of strain could be varied by a suitable choice of substrate. Since the expansion coefficients of germanium and the substrates were isotropic, the applied strains were uniform in the plane of the wafer. The choice of substrate and glue was limited by the requirements that both had to be transparent in the wavelength range  $1.3 \pm 0.2.9 \mu$ , both had to be hard enough to withstand the mechanical stresses during polishing and had to be unaffected by water. The substrates used in these experiments are tabulated with their expansion coefficients in table I. The glue had not to crack when cooled to 77°K and had to be in a layer, thin enough that its contraction did not influence the strain on the specimens (see Appendix A). The epoxy used satisfied all these requirements.

The temperature of the specimens could be determined by comparing the spectrum of the strained specimens with an unstrained specimen mounted in a similar manner, and using the data of Macfarlane et al (reference 5)\*(see footnote). The specimen temperature was found to be about 10°K higher than that of the refrigerant, but was reproducible from specimen to specimen within 2°K.

The transmission T of the specimen and substrate (and glue) was recorded on a strip chart recorder while the monochromator grating was rotated. A run without the specimen in the light path was made with the dewar lowered so that the beam from the

\* Macfarlane et al used a dewar in which the unstrained specimens were in direct contact with the exchange gas of the refrigerant which accurately determined the temperature.

### TABLE I

The expansion coefficients of germanium and various substrates.

	· · ·		
	Expansion coeff 300°K to 600K	Expansion coeff 70°K to 300°K	Expansion coeff relative to Ge 70°K to 300°K
Germanium*		$45 \times 10^{-7} / ^{\circ} C$ .	
#0080	92 x $10^{-7}/^{\circ}$ C.	65	20 x 10 <sup>-7</sup> /°C.
#8410	71		•
#7056	51	39.5	<del>-</del> 5.5
<i>‡</i> 7740	32.5	25.5	-19.5
<b>#</b> 7900	8	4	-41.0
Sapphire (⊥r c-axis)	50		

# indicates Corning glass no. \* S.I.Novikova (reference 16)

The  $300^{\circ}$ K to  $600^{\circ}$ K. expansion coefficients are tabulated for comparison of sapphire and #8410 with the other glasses.

monochromator passed directly to the detector, through the upper port in the dewar block. The relation between T and the absorption coefficient  $\propto$  of a specimen of thickness d may be written

$$T = \frac{\text{Transmitted beam intensity}}{\text{Incident beam intensity}} = f(R_I) \frac{(1-R_I)(1-R_2)\exp{-\alpha d}}{1-R_IR_2\exp{-2\alpha d}}$$

where  $R_1, R_2$ , are the reflectivities of the first and second specimen surfaces and  $f(R_i)$  is a function of the reflectivities of all the other interfaces traversed by the beam. In this equation the  $R_i$  have been assumed to be small. The denominator takes into account the light transmitted after an even number of reflexions inside the specimen. The phase factors of the light beam have been omitted because the observed fringes were very weak and were easily averaged. The above equation for T is the averaged transmission. The reflectivity at the interface of two media of refractive indices  $n_1$ ,  $n_2$ , is

$$R = \frac{(n_{i} - n_{1})^{2}}{(n_{i} + n_{2})^{2}}$$

The variation of <u>n</u> with  $\propto$  in these experiments is negligible since in the energy region examined the absorption coefficient of germanium is less than 5000cm<sup>-1</sup>. All the substrate materials were transparent in this energy region and for this small range the variation of <u>n</u> with photon energy was negligible for all materials used.

For the unstrained specimens both surfaces were in contact with sapphire,(n=1.7), so that at the germanium-sapphire interfaces (n=4, for ge.) R = 0.16. Thus the denominator in the equation for T could contribute at most 2.5% to T and f(R<sub>i</sub>) is approximately unity. For the strained specimens, one surface was in contact with sapphire and the other with epoxy, the refractive index of which was not known. It is also unlikely that all surfaces made perfect optical contact. To avoid detailed correction factors, the transmission data were normalised so that  $T_n = 1$  in the region of the spectrum where the specimens were transparent and the expression used to calculate  $\prec$  was

$$T_n = exp - \propto d$$

with an estimated maximum error of 5% in exp-qd.

The apparent transmission of a specimen at high photon energies where the specimens should have been opaque ,was 0.4%. This signal was due to scattered radiation reaching the detector, in spite of the baffles placed in the monochromator. For the measurement of small transmission ratios this effect became significant since the baseline of transmission was shifted by the background radiation. This shift was accounted for to some extent by taking the true baseline as the asymptote of the transmission curve at high photon energies.

Finally, to obtain absorption coefficients from the transmission data, the specimen thickness <u>d</u> had to be known. For many of the specimens used, interference fringes were seen in the part of the spectrum where the specimens were transparent, and these fringes gave an average value of the specimen thickness. The fringes were usually quite faint, indicating that the specimens were not perfectly uniform in thickness. For the evaluation of  $\propto$ , the value of <u>d</u> required was approximately the minimum thickness since  $T_n = \exp{-\alpha d}$ , and not the average thickness so some error arose here.

With the above approximations, the estimated maximum error in the absorption coefficients is 10%. The reproducibility of measurements was within this range. The measurement of high absorption coeffients ( 5000cm<sup>-1</sup>) was limited by noise in the detector system and scattered radiation.

The monochromator wavedrive was calibrated, using the 1.4425µ and the 1.4119µ water vapour absorption lines (reference 17). Air was let into the main monochromator tank and a brief run over this wavelength range was made.

#### E : RESULTS OF ABSORPTION MEASUREMENTS

Typical absorption spectra of the (110) oriented specimens mounted on various substrates at 90°K are shown in figures 6 to 9. The spectrum of unstrained germanium was the same for all crystal orientations and similar to the spectrum described by Macfarlane et al (reference 5). The single peak observed in the absorption edge at an absorption coefficient of about 3500cm<sup>-1</sup>, was identified by Macfarlane as exciton absorption. The position of the peak  $E_{ex}^{o}$ could be located within the resolution of the monochromator and was conveniently used as the zero of photon energy for all other measurements at the same temperature. The spectrum of unstrained germanium at 300°K is shown for comparison in Fig 6. It was found to be a little broader than the edge at 90°K and the exciton absorption appears only as a knee in the edge, in agreement with Macfarlane et al. At 300°K  $E_{ex}^{O} = 0.8040 \pm 0.0006$  eV and with liquid nitrogen refrigerant  $E_{ex}^{o} = 0.8790 \pm 0.0003 eV$ . The latter was reproducible within 0.0006eV, and indicates a specimen temperature of 90 ± 2°K. All specimens showed identical absorption spectra at room temperature. The specimens mounted on #0080 glass were under

compression when cooled to  $90^{\circ}$ K (see table I). The absorption edge of these specimens was found to be shifted to higher photon energies relative to the unstrained specimens, and a second, well defined absorption peak appeared on the absorption edge. This second peak has also been associated with exciton absorption (reference7,8). The spectrum was qualitatively similar for all specimens and the positions of the two peaks are tabulated in table II. The spectrum of the specimen on #8410 glass was also qualitatively similar to fig 7, but the shift of the absorption edge and the separation of the two peaks was smaller. The results in table II are the mean values of results from five specimens of each orientation on #0080 glass and just one specimen on #8410 glass. Three runs at 90°K were done for each specimen. The errors quoted are the estimated maximum errors, and all specimens were reproducible within this range. The reproducibility was limited by the reproducibility of specimen temperature, since for a change of 2°K the absorption edge shifted through about 0.9 milli-eV. The peak separation was relatively insensitive to temperature variations and the errors in these values are smaller.

It was found that if vacuum grease was used to provide good thermal contact between the dewar block and the specimens that the results were irreproducible and the separation of the absorption peaks was considerably greater than without grease. The cause for this must be that on cooling, the grease forms a firm bond between the specimen and the block which strains the specimen to a greater extent than the substrate. The specimens were thus mounted without grease.

The specimens mounted on #7740 and #7900 glass were under

tension when cooled to 90°K, and the absorption edge was shifted to lower photon energies. The spectrum of specimens on #7740 showed one peak at absorption coefficients of about 3500cm<sup>-1</sup> and a definite knee in the edge at 1500cm<sup>-1</sup>. This knee could be analysed as a second absorption peak and its position could be quite well located. The spectrum of specimens on #7900 showed no fine structure in the absorption edge. One very broad knee was apparent at absorption coefficients of 1100cm<sup>-/</sup> and another at about3500cm<sup>-1</sup>. This absorption could be accounted for by assuming that the two absorption peaks were broadened with a broadening half width of about 1.5 milli eV. A rough estimate of the peak positions could then be obtained. Only one or two specimens of each orientation were prepared on #7740 and #7900 glass, since the peaks could not be located with sufficient accuracy to clearly indicate the differences between different specimen orientations.

Slight variations in the optical absorption edge were seen from specimen to specimen on similar substrates. The absorption peak heights varied in magnitude, and the edge appeared slightly broader in some specimens. In particular, the low energy peak of specimens mounted on #7740 glass was less well defined in some cases than in others. Possible explanations of these effects will be discussed in chapter IV.

The variation of the absorption peak positions with strain are plotted in figures 10,11,12. The error flags are again the estimated maximum error. Since each point is the mean result of five to fifteen readings, the probable error in each point is smaller than this. The uncertainty in the thermal expansion of germanium is included in the error of the point for unstrained germanium. For all orientations the graphs are linear within the errors, and the intersection of the two lines is at  $E_{ex}^{O}$  (approx).

The results of the peak positions in the specimens mounted on #8410 and sapphire are fitted to the graph for the  $\langle 111 \rangle$ oriented specimens. They are consistent with the other results, and their expansion coefficients (90°K to 300°K) may be deduced from the graphs as :

Sapphire : 29 x  $10^{-7}$ /°C. #8410 : 47 x  $10^{-7}$ /°C. Since no broadening of the absorption edge on the low energy side was seen in the spectra of the "unstrained" germanium, this result indicates that the specimens were truly unstrained by the sapphire windows.

The spectra of the specimens were also examined at 196°K, but because of the small strains applied, the difficulty in maintaining a constant temperature and the broadening of the absorption peaks at this temperature, the data only served to show consistency with the above results.

#### F : PLASTIC FLOW.

The calculation of the strains on the specimens at 90°K (see appendix A) assumes that the specimens did not deform plastically. A check for plastic flow was made for two specimens mounted on #7900 glass since these specimens were under tension and experienced the largest strains at 90°K. The specimens were cooled to 90°K and warmed up to 300°K a few times, and each time the spectra at both temperatures were unaltered. If plastic flow were taking place, frozen in stresses would be expected after the first cycle and the absorption spectra would be altered. Figure 6









(to follow page 21)




## Table II

The positions of the absorption peaks in the edge of the strained germanium spectra at 90°K measured relative to the mean position of the peak in unstrained germanium at 90°K.

Substrate	Specimen orientation	Strain on specimen	Absorpti mi	lon peak 1111-eV	posit	ions	Peak se mill	eparation li-eV
<b>#0</b> 080	<111> <110> <100>	-0.00042 "	5.7 4.6 4.5	8.8 8.0 8.5	± 0.9 ± 0.9 ± 0.9		3.1 3.4 4.0	± 0.3 ± 0.3 ± 0.4
<i>‡</i> 8410	< 111>		0.3	1.1 :	± 0.9		0.8	± 0.3
#7056	· <111>	0.00012	-1.2	-	± 0.9			• <b></b> .
<b>#7740</b>	< 111 > < 110 > < 100 >	0.00041 "	-4.7 -5.1 -3.6	-7.0 -7.8 -6.4	± 0.9 ± 0.9 ± 0.9		2.3 2.7 2.8	± 0.4 ± 0.4 ± 0.4
<b>#7900</b>	< 111 > < 110 > < 100 >	0.00086 "	-11 -11 -9	-17 -17 -15	± 1.5 ± 1.5 ± 1.5		6 6 6	± 2 ± 2 ± 2
sapphire	< 111>		-4.4	-5.9	± 0.9		1.5	± 0.4
effect of grease	< 111 >		8.2	14.8			6.6	

Fig 10



Diagram showing the variation of the exciton peak positions with strain on the specimens when the applied stress is in the [111] plane.

## Fig 11

Diagram showing the variation of exciton peak positions with strain when the stress is applied in the [100] plane



(to follow page 22)

Fig 12



(to follow page 22)

CHAPTER III : THEORETICAL BACKGROUND AND ANALYSIS OF RESULTS.

In the last chapter it was seen how strain affects the absorption edge of germanium. It is the purpose of this chapter to show how the results were interpreted.

Kleiner and Roth (reference 8) have shown how the exciton absorption peak positions in the spectrum of strained germanium may be used to evaluate the deformation potentials. Their analysis had in it the implicit assumptions that the excitons arising from the two pairs of bands had binding energies which were equal and invariant under strain. It is evident from the description by Picus and Bir (reference 9) of the band structure of the strained germanium lattice, that these assumptions may not be valid.

In order to check the validity of these assumptions, the band structure of unstrained germanium will be briefly reviewed in section (a) and the effect of the strain applied in this experiment on the band structure of the specimens, will be discussed. Then in section (b) the exciton states in both strained and unstrained germanium will be described within the effective mass approximation.

In view of the possibility that the exciton binding energies may be obtained directly from experimental data, (reference 11), the intensity of optical absorption near the band edge will be discussed in section (c). Elliott (reference 11) has treated the case of two simple spherical bands and shown how analysis of the absorption edge of such a semiconductor may yield the values of the band gap and exciton binding energy. In section (c) this treatment will be briefly extended to the case of strained and unstrained germanium.

In section (d) the experimental data of chapter II will be interpreted in terms of the effect of strain on the valence and conduction bands of germanium and the deformation potentials will be evaluated.

a) THE BAND STRUCTURE OF GERMANIUM.

i. The unstrained lattice.

The band structure of unstrained germanium has been described by Dresselhaus (reference 2). The conduction band minima are at the edges of the Brillouin zone where  $\vec{k} = \frac{\Pi}{\Omega}(\pm 1, \pm 1, \pm 1)$ , (<u>a</u> being the length of the side of the unit cubic cell



The band structure of unstrained germanium.

of the germanium lattice). At k=0 there is an auxiliary minimum, 0.16eV above the zone boundary minima; this minimum transforms according to the  $\Gamma_2$  irreducible representation of the  $T_d$  x I point group. This minimum is two-fold degenerate (including spin) and approximately spherical so that it may be described by a single effective electron mass. Other conduction bands are split off to higher energies by at least 0.5 eV.

The only valence band maximum is at k=0 of the Brillouin zone and transforms according to the  $\Gamma_8^+$  irreducible representation of the  $T_d' \times I$  point group. This maximum is fourfold degenerate, in unstrained germanium, at k=0, but the degeneracy is partly removed away from k=0 into two two-fold degenerate bands. A twofold degenerate band is split off 0.3 eV (at k=0) from the valence band maximum, by spin-orbit coupling. The two upper valence bands are warped spheres near k=0and may be described by

 $E_{1,2} = Ak^2 \pm (B^2k^4 + C^2 [k_1^2k_2^2 + k_2^2k_3^2 + k_3^2k_1^2) = E_{1,2}(\bar{k}, 0) \dots 1$ where E is the hole energy for zero strain. Each root occurs twice as each band is doubly degenerate. The positive sign is maintained for the lower "light" hole band and the negative sign for the upper "heavy" hole band. Since the warping is small, the bands may be described approximately by two spherically symmetric effective hole masses  $m_{heavy} = 0.34m_0$ ,  $m_{light} = 0.043m_0$ .

The valence bands may be conveniently labelled by the usual atomic orbital symbols as shown on the diagram. These labels have real significance only in the tight binding approximation. ii. The strained lattice.

When a strain  $\tilde{\varepsilon}$  is applied to a germanium crystal, the lattice, in general, no longer has cubic symmetry and the fourdimensional irreducible representation  $\Gamma_{\mathfrak{g}}$  breaks down into two two-fold representations. Because of the presence of a centre of inversion in the crystal, the degeneracy is not entirely removed (referencel8). The conduction band degeneracy at k = 0 is unaffected by the strain, though the degeneracy of the zone boundary minima is partially removed. The entire conduction band is shifted through an energy  $a'\Delta$  where  $\Delta$  is the lattice dilation  $\Delta = \mathcal{E}_n + \mathcal{E}_{22} + \mathcal{E}_{33}$ . Thus the electron energy

 $E_e(\vec{k}, \tilde{\epsilon}) = E_e(k, 0) + a'\Delta$  ..... 2

When the degeneracy at k = 0 of the valence band is removed by the strain  $\tilde{\epsilon}$  applied to the crystal, the hole energy spectrum is considerably altered. Picus and Bir (reference 9) have shown that the bands in the strained lattice may be described by

 $E_{1/2}(\vec{k},\vec{\epsilon}) = a\Delta \pm \sqrt{\xi_{k} + \xi_{\epsilon k} + \xi_{\epsilon}} + Ak^{2}....3$ 

where 
$$\mathcal{E}_{k} = B^{2}k^{4} + C^{2}(k_{1}^{2}k_{2}^{2} + k_{2}^{2}k_{3}^{2} + k_{3}^{2}k_{1}^{2})$$
  
 $\mathcal{E}_{\varepsilon} = \frac{1}{2}b^{2}[(\varepsilon_{11} - \varepsilon_{22})^{2} + (\varepsilon_{22} - \varepsilon_{33})^{2} + (\varepsilon_{33} - \varepsilon_{11})^{2}] + d^{2}(\varepsilon_{12}^{2} + \varepsilon_{23}^{2} + \varepsilon_{31}^{2})$   
 $\mathcal{E}_{\varepsilon k} = Bb[3(k_{1}^{2}\varepsilon_{11} + k_{2}^{2}\varepsilon_{22} + k_{3}^{2}\varepsilon_{33}) - k^{2}\Delta]$   
 $+ 2Dd(k_{1}k_{2}\varepsilon_{12} + k_{2}k_{2}\varepsilon_{22} + k_{3}k_{1}\varepsilon_{21})$ 

The constants are deformation potential constants and D is the cyclotron resonance parameter  $D = (C^2 + 3B^2)^{\frac{1}{2}}$ .  $E_{1,2}(\vec{k}, \tilde{\xi})$  is the hole energy, measured from the band edge in unstrained germanium, the subscripts referring to the plus and minus signs.

At k = 0 we see from equations 2 and 3

 $E_e(0,\tilde{\epsilon}) = E_e(0,0) + a'\Delta$  and  $E_{1,2}(0,\tilde{\epsilon}) = a\Delta \pm \sqrt{\tilde{\epsilon}_{\epsilon}}$ Writing  $\overline{E}_h = \frac{1}{2} \left[ E_1(0,\tilde{\epsilon}) + E_2(0,\tilde{\epsilon}) \right]$  for the mean shift of the valence band edge, we find the variation of the forbidden energy gap with lattice dilatation

 $\left[E_e(0,\tilde{\epsilon}) + \overline{E}_h(0,\epsilon)\right] - E_e(0,0) = (a' + a) \Delta$  ..... 4 - and the splitting of the bands at k = 0 is  $2\sqrt{\xi_{\epsilon}}$  .....5 The same expression is arrived at by diagonalising the hamiltonian of Kleiner and Roth (reference 8). Their notation is obtained by putting

 $b = -\frac{2}{3}D_{u}$ ,  $d = -\frac{2}{\sqrt{3}}D_{u}'$ ,  $a = -D_{d}'$ ,  $a' = D_{d}'$ 

For the two cases  $\mathcal{E}_{\kappa} > \mathcal{E}_{\varepsilon \kappa} > \mathcal{E}_{\varepsilon}$  and  $\mathcal{E}_{\kappa} < \mathcal{E}_{\varepsilon \kappa} < \mathcal{E}_{\varepsilon}$  equation 3 may be written in a simple form in a coordinate system associated with the principal axes of the strain tensor

 $\tilde{\varepsilon}' = \begin{cases} \varepsilon_{ij}' = \varepsilon_{ij} & i = j \\ \varepsilon_{ij}' = p \varepsilon_{ij} & i \neq j \end{cases} \text{ where } p = \frac{Dd}{3Bb}$ 

<u>Case 1</u>.  $\mathcal{E}_{k} > \mathcal{E}_{\varepsilon k} > \mathcal{E}_{\varepsilon}$ 

For large k equation 3 becomes

$$E_{1,2}(\vec{k}, \vec{\epsilon}) = a \Delta + E_{1,2}(\vec{k}, 0) \pm \frac{Bb}{2} \sum_{i} \frac{3k_{i}^{2} - k^{2}}{\sqrt{\epsilon_{k}}} \epsilon_{ii}''$$

where the  $\mathcal{E}_{ii}^{''}$  are components of  $\mathcal{E}_{ij}^{'}$  along its principal axes.

The larger k, the less important is the last term and the bands go to their shapes in the unstrained lattice. They are approximately spherical and can be described by the single effective masses  $m_{iight}$ ,  $m_{heavy}$ , having the same values as in the unstrained lattice. The requirement  $\mathcal{E}_k > \mathcal{E}_{\epsilon k} > \mathcal{E}_{\epsilon}$  implies energy differences  $E_i(\vec{k},0) - E_2(\vec{k},0)$  large compared with the splitting of the bands  $E_i(0,\tilde{\epsilon}) - E_2(0,\tilde{\epsilon})$ . In the case of germanium this certainly means that  $E_i(\vec{k},\tilde{\epsilon})$ , where  $E_i > E_2$ , is greater than twice the splitting of the bands at k = 0. (see figure 14)

Case 2.

For small k equation 3 becomes

$$E_{1,2}(\vec{k},\tilde{\epsilon}) = a \Delta \pm \sqrt{\mathcal{E}_{\epsilon}} + \frac{\hbar^2}{2} \sum_{i} \frac{k_{i}^2}{m_{i}^*}$$

Thus when the degeneracy is removed the valence bands near k = 0 become ellipsoidal and are described by effective masses

The shape of the bands near k = 0 is independent of the magnitude of the strain and depends only on its orientation.

In both the above cases the effective mass tensor is diagonal. In the region where  $E_1(\vec{k},0) - E_2(\vec{k},0)$  is of the order of  $E_1(0,\tilde{\epsilon}) - E_2(0,\tilde{\epsilon})$ , the bands cannot be described simply. Off diagonal terms appear in the effective mass tensor and all the elements are functions of  $\vec{k}$ .

The valence band structure described by equation 3 is plotted in figure 14 for a strain  $\tilde{\xi} = T \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -\lambda \end{pmatrix}$  in the [100]

crystal plane.





For curves 1,2,  $\mathbf{k}_i = \mathbf{k}_i$  or  $\mathbf{k}_2$ ; for curves 3,4,  $\mathbf{k}_i = \mathbf{k}_3$ .  $\mathbf{k}'$  is the value of  $\mathbf{k}_i$  for which  $\mathbf{E}_i(\vec{k},0) - \mathbf{E}_2(\vec{k},0) = \mathbf{E}_i(0,\tilde{\mathbf{E}}) - \mathbf{E}_2(0,\tilde{\mathbf{E}})$ .

From appendix B it can be seen that the principal axes of  $\tilde{\mathcal{E}}$ and  $\hat{\epsilon}'$  coincide for the strains applied in the [100], [110] and [111] crystal planes. Thus the inverse effective masses  $\frac{1}{m} \star$ may be calculated from equation 6.

i) Stress in a [100] plane.

$$\widetilde{\xi}' = \widetilde{\xi}'' = T \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 - \lambda \end{pmatrix} \qquad \text{Thus} \qquad \frac{\tilde{h}^2}{2m_{t\pm}^*} = \frac{\tilde{h}^2}{2m_{2\pm}^*} = A \pm \frac{1}{2}B$$
  
and 
$$\frac{h}{2m_{3\pm}^*} = A \mp B$$

ii) Stress in a [111] plane.

It has been shown in appendix B that for the strains applied in a [111] plane in this experiment

$$\widetilde{\mathcal{E}} = \frac{T}{3} \begin{pmatrix} 2-\lambda & -1-\lambda & 1+\lambda \\ -1-\lambda & 2-\lambda & 1+\lambda \\ 1+\lambda & 1+\lambda & 2-\lambda \end{pmatrix} \quad \text{and} \quad \widetilde{\mathcal{E}}'' = \widetilde{\alpha}^{-1} \widetilde{\alpha}^{-1} \widetilde{\mathcal{E}}'$$

$$\frac{\tilde{n}^2}{2m_{1\pm}^*} = \frac{\tilde{n}^2}{2m_{2\pm}^*} = A \pm \frac{D}{2\sqrt{3}} \quad \text{and} \quad \frac{\tilde{n}^2}{2m_{1\pm}^*} = A \mp \frac{D}{\sqrt{3}}$$

 $2m_{1\pm}^* = 2m_{2\pm}^* = A - 2\sqrt{3}$ iii) Stress applied in a [100] plane.

Again from appendix B we have

$$\widetilde{\mathcal{E}} = \frac{T}{2} \begin{pmatrix} 1-\lambda & 0 & 1+\lambda \\ 0 & 2 & 0 \\ 1+\lambda & 0 & 1-\lambda \end{pmatrix} \quad \text{and} \quad \widetilde{\mathcal{E}}'' = \widetilde{\alpha'} \widetilde{\alpha'} \widetilde{\mathcal{E}}'$$

$$\frac{\hbar^2}{2m_{1\pm}^*} = A \pm \frac{D - (b/d)B}{2[1+(b/d)^2]'/2} \qquad \frac{\hbar^2}{2m_{2\pm}^*} = A \pm \frac{B(b/d)}{[1+(b/d)^2]'/2}$$

$$\frac{\hbar^2}{2m_{3\pm}^*} = A \mp \frac{D + (b/d)B}{2[1+(b/d)^2]'/2}$$

Hence

Hence

and

Using the cyclotron resonance parameters of Levinger and Frankl (reference 31) the effective masses were calculated and tabulated in table III. Only the effective hole masses in specimens of [100] and [111] orientations may be tabulated without prior knowledge of the deformation potentials. The last two columns were completed using the values of  $\underline{b}$  and  $\underline{d}$  obtained later.

#### TABLE III

The effective hole masses in strained germanium specimens

	[100]		[111]		[ 110 ]*		
	+ "light hole"	"heavy hole"	+	-	+	-	
m,*	0.057 <sub>M</sub>	0.111 m.	0.053 M.	0.130 м.	0.051 m.	0.143 m.	
m2*	0.057	0.111	0.053	0.130	0.057	0.111	
m <b>*</b>	0.213	0.046	0.476	0.041	0.370	0.042	
3/m*m2m3*	0.089	0.083	0.113	0.089	0.102	0.087	
μ,	0.020	0.024	0.020	0.025	0.019	0.025	
M2	0.020	0.024	0.020	0.025	0.020	0.024	
$\mu_3$	0.027	0.018	0.029	0.018	0.029	0.018	
3/ Ju, M2/43	0.022	0.022	0.022	0.022	0.022	0.022	

A = 13.3 B = 8.6 C = 12.4 hence D = 19.4 (reference 30). \* Using b/d = 0.57 from the final results. The  $\mu_i$  are the reduced effective exciton masses  $\frac{1}{\mu_i} = \left(\frac{1}{m_i} + \frac{1}{m_e}\right)$ .  $m_e^* = electron effective mass = 0.031 m_e$ 

The effect of spin-orbit split off valence band has been neglected in these calculations since in all cases the band splitting by strain was very much less than 0.3 eV.

It is seen in table III that the "density of states" hole mass  $\sqrt[3]{m_1^*m_2^*m_3^*}$  is approximately the same for both bands, so we may lable the bands by "light" and "heavy" holes only because of their behaviour at large k.

# b) DESCRIPTION OF THE EXCITON STATES IN THE EFFECTIVE MASS APPROXIMATION.

It has been shown (reference 2) that in media of high dielectric constant that the description of the exciton state may be carried out in the effective mass approximation. In this section the description of the exciton will be directed to the particular cases of the strained and unstrained germanium lattice.

In the effective mass approximation the hamiltonian of an electron-hole pair, is

$$H = H_{p} + H_{h} + V(\hat{r}) \qquad \dots \qquad 7$$

where  $H_e$ ,  $H_h$ , are the hamiltonians of the electron in the conduction band and hole in the valence band respectively and  $V(\bar{r})$  is the coulomb interaction of the electron and hole.

$$V(\vec{r}) = \frac{e}{\kappa |\vec{r}|}$$

The use of the effective mass approximation is limited by the condition that  $V(\vec{r})$  be slowly varying over the lattice spacing.  $\times$  describes the modification of the coulomb field of the electron and hole by the polarisation of the lattice, and in germanium is taken to be the static dielectric constant. In germanium  $\chi$  is large so the interaction is weak and the effective mass approximation is expected to be good.

 $\vec{K} = \vec{k}_e + \vec{k}_h$ 

When a crystal is illuminated, the probability of creation of an exciton in the n<sup>th</sup> state  $|\vec{K}, \vec{r}_n\rangle_{jj}$ , per unit time, for a direct transition is

 $|H_{0,k}|^2 = \frac{e^2 \hbar^2 A_0^2}{4m^2} |\langle 0| \vec{\xi} (\exp i\vec{\eta} \cdot \vec{r}) V_e| \vec{K}, \vec{r}_n \rangle_{jj'}|^2 \delta(h\nu = E_e + E_h)$ where  $|0\rangle$  is the crystal ground state,  $\frac{\hbar}{i} V_e$  is a momentum operator acting on electron states,  $E_e$  and  $E_h$  are the hole and electron energies and  $A_o$ ,  $\nu$ ,  $\vec{\xi}$ ,  $\vec{\eta}$  are the amplitude, frequency, polarisation vector and propagation vector of the incident radiation. For the linear combination 8, of electron-hole pair states,  $|H_{ok}|^2$  vanishes unless  $\vec{k}_e - \vec{k}_h = \vec{\eta} \sim 0$ This is a statement of conservation of crystal momentum. The photon momentum is small compared with the electron and hole momenta.

For germanium, value of  $(E_e - E_h) = \Delta E$ , for which  $\vec{k}_e - \vec{k}_h = 0$ occurs at the centre of the Brillouin zone, so that the onset of direct band to band transitions occurs when  $h\nu = \Delta E_{\vec{k}=o}$ . At the band edge, the hole part of the hamiltonian may be written in Shockley representation  $H_h = \begin{pmatrix} H_{hl} & H_{l2} \\ H_{l2}^{\dagger} & H_{h2} \end{pmatrix}$ 

after the usual separation of the spin-orbit split off band terms. The labels 1,2, refer to the two  $p_{\frac{3}{2}}$  valence bands and  $H_{\frac{12}{2}}$ is an exchange term.

Thus the exciton hamiltonian is

$$H = \begin{pmatrix} H_{e} + H_{h1} + V(r) & H_{12} \\ H_{12}^{\dagger} & H_{e} + H_{h2} + V(r) \end{pmatrix} \dots 9$$

Kane (reference 19) has found that exchange terms from other bands in the germanium lattice appear to be small and will be neglected here.(see footnote).

It was seen in the last section that the electron and hole effective mass tensors in unstrained germanium are diagonal, and also in strained germanium, except for the hole energy region where  $E_1(\vec{k},0) - E_2(\vec{k},0) \sim E_1(0,\tilde{\epsilon}) - E_2(0,\tilde{\epsilon})$ . Since this energy region is not important in the analysis of the experimental results it will be disregarded in the following analysis, and only diagonal effective mass tensors will be considered.

Now  $H_e = -\frac{\hbar}{2m_e^*} \nabla_e^*$  and  $H_{h_{1,2}} = -\sum_i \frac{\hbar}{2m_{i,\pm}^*} \nabla_i^2$  (i = 1, 2, 3) First of all it will be assumed that  $H_{12}$  is small and may be neglected. Later the effect of  $H_{12}$  will be discussed. Thus for each pair of bands, the Schrodinger equation has the form

$$\left(-\frac{h}{2m_e^*}\nabla_e^2 - \sum_i \frac{\hbar^2}{2m_i^*}\nabla_i^2 - \frac{e^2}{\chi_i r_i}\right)|\vec{k}, \vec{r}_n\rangle = E_n |\vec{k}, \vec{r}_n\rangle \dots 10$$
  
where  $|\vec{k}, \vec{r}_n\rangle$  is the n<sup>th</sup> exciton state associated with one pair

The effective mass formalism would be unaltered if exchange terms were included, but the effective masses used would not be the cyclotron resonance masses. of bands. In the expansion 8 of the state the sum over the bands j,j', may be omitted since only a small range of Bloch functions is important in the sum. (This is analogous to neglecting  $H_{12}$ ).

Making the "centre of mass transformation"

$$X_{i} = \frac{m_{e}^{*} x_{ei} + m_{i}^{*} x_{hi}}{m_{e}^{*} + m_{i}^{*}} \qquad x_{i}' = x_{ei} - x_{hi}$$

where  $x_{ei}$ ,  $x_{hi}$  are the electron and hole coordinates, the equation 8 becomes

This equation can only be solved exactly for the case of two spherical bands  $\mu_1 = \mu_2 = \mu_3$ . For ellipsoidal bands, variational methods may in principle be used to solve equation 11.

Three cases will be separately considered: i) Spherical, non-degenerate bands. This is approximately the case in strained germanium when the hole energy is greater than twice the splitting of the  $p_{3_{2}}$  bands at k = 0, (case 1 of last section), and in unstrained germanium when  $E_{h}(\vec{k},0) > 0$ . ii) Spheroidal, non-degenerate valence bands. This is the case in strained germanium near k = 0 of the Brillouin zone (see table III).

iii) Spherical degenerate bands. This is approximately the case in unstrained germanium at k = 0.

#### i) <u>Simple spherical bands</u>.

Equation 11 has been solved by Elliott (reference 11) for two spherical non-degenerate bands. The perturbation V(r) gives rise to a band of states below the conduction band. With the optical selection rule  $\vec{k}_e + \vec{k}_h = 0$  a line spectrum appears from the K = 0 states of the exciton bands;

$$E'_n = \Delta E_o = \frac{G}{n^2}$$
 for  $h\nu < \Delta E_o$ 

and a continuum of states for  $h\nu > \Delta E_c$ . The ground state binding energy  $G = \frac{e^4 \mu}{2 \hbar^2 \kappa^2} = \frac{e^2}{2\kappa a}$  where <u>a</u> is the ground state "Bohr radius".

The eigenfunctions  $F^{n}(\vec{r})$  for the bound states are hydrogen atom functions with  $\mu$  and  $\frac{e^{i}}{\chi}$  in place of m<sub>o</sub> and e<sup>i</sup>. For the ionised states  $F^{n}(\vec{r})$  is a coulomb function.

Thus in germanium the exciton states in the continuum, arising from the two spherical bands, will be coulomb functions of this type.

# ii) <u>Simple spheroidal bands</u> M. M.

In this case the equation 11 is similar to the equation for donor impurities in germanium. This equation has been solved approximately for  $\mu_1 < \mu_3$  (reference 20) by using the variational function  $F'(\vec{r}) = \frac{1}{(\pi a^2 b)} \frac{1}{y_2} \exp \left(\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2}\right)^{1/2}$ for the ground state solution. For other exciton states other

functions  $F^{n}(\vec{r})$  were used. So to obtain a complete description of the exciton spectrum is very tedious.

In germanium, the reduced effective masses  $\mu_i$  are determined primarily by the small electron mass (see table III) so that the  $\mu_i$  are approximately equal for all strains applied. Using the above function  $F'(\vec{r})$  it is found that the ground state binding energy is approximately the same as that for an exciton formed from two spherical bands with  $\mu = \sqrt[3]{\mu_1 \mu_2}$ , in this case. If the same is true when  $\mu_2 > \mu_1$  then the exciton binding energies in strained germanium are both ~1.2 milli-eV. (The validity of the variational functions has not been tested for  $\mu_1 > \mu_1$ )

iii) Degenerate spherical bands.

In equation 11 the exchange term  $H_{12}$  was neglected. When the two valence bands are degenerate,  $H_{12}$  will be of the same order of magnitude as  $H_{h1}$  and  $H_{h2}$  so that equation does not describe the exciton states at k = 0 of unstrained germanium. For degenerate bands an exact solution cannot be obtained, however, it may be expected that a minimum and maximum estimate of the exciton binding energies may be obtained by using the light and heavy hole masses in the expression for G.

 $0.9 \leq G \leq 1.4$  milli-eV.

The effect of exchange,

The separation of the  $p_{3/2}$  valence bands in germanium is afunction of strain applied to the crystal. Thus the effect of  $H_{1/2}$  on the exciton state will also be a function of strain. Price (reference 21) has discussed the strain dependence of acceptor binding energy by including  $H_{1/2}$  in the hamiltonian. Because  $H_e$ appears in the exciton hamiltonian, the effect of  $H_{1/2}$  on the exciton binding energy would be much smaller than on the acceptor binding energy, so that it may be neglected. This supports the conclusion of part (iii).

c) THE INTENSITY OF OPTICAL ABSORPTION NEAR THE ABSORPTION EDGE.

The intensity of optical absorption associated with exciton creation is described by an absorption coefficient

 $\gamma_{j}(\omega) \propto \frac{\kappa_{\omega}}{\rho(\omega)} |H_{0,\kappa}|_{jj'}^2 N(\varepsilon)$ where two bands j,j' only are considered.  $\rho(\omega)$  is the energy density of incident radiation of frequency  $\omega$  and N(E) is the density of exciton states  $|\vec{K},\vec{r}\rangle$  per unit energy range at E, associated with the bands j,j'.

Because of the optical selection rule  $\vec{k}_e + \vec{k}_h = 0$ . the density of exciton states in k-space is the same as that of the electron states; i.e.  $\frac{i}{8\pi^3}$  per unit volume. Thus the density of exciton states per unit energy range at E is the surface integral in k-space:

$$N(E) = \frac{1}{8\pi^3} \int_{S} |\nabla_{k}(E)|^{-1} dS$$

..... 12

In the continuum of states the exciton kinetic energy is

 $\hbar^2 k_a^2 \sim \hbar^2 k_{\perp}^2$ 

$$E_{KE} = \frac{1}{2m_e^*} + \frac{1}{2} \frac{1}{2m_i^*} = \frac{1}{2\mu_i} \frac{1}{2\mu_i}$$
To evaluate equation 12 the substitution  $K_i^{\prime} = \left(\frac{m_o}{\mu_i}\right)^{l_2} K_i$  is made,  
yielding  $N(E) = \frac{\left(2\mu_i\mu_2\mu_3\right)^{l_2}E_{KE}^{l_2}}{2\pi^2\hbar^3}$ 
Remembering  $\rho(\omega) \propto \omega^2 A_o^2$  we have  $\gamma(\omega) \propto \frac{(\mu_i\mu_i\mu_3)^{l_2}(h\nu-\Delta E_o)}{\omega}|\langle o|\bar{\xi}e^{i\bar{\eta}\cdot\bar{\tau}}\bar{\eta}_e|\bar{K},\bar{\tau}\rangle_i$ ,  $|l_i^{\prime}$ 

 $r \hbar^2 K^2$ 

Following Elliott (reference 11), we have, using the expansion 8

$$|\langle 0|\overline{\xi}e^{i\overline{\eta}.\overline{r}}\nabla_{e}|\overline{k},\overline{r}\rangle|^{2} = |\sum_{ke,k_{h}}\Psi_{ke,k_{h},j,j'}^{Kn}\langle\overline{k}e,j'|e^{i\overline{\eta}.\overline{r}}\overline{\xi},\nabla_{e}|-k_{h,j}\rangle|^{2}$$

where again the sum over j, j' has been neglected. Since only a small range of  $\vec{k}_e$ ,  $\vec{k}_h$  is important in this sum, it may be assumed that the integrals are independent of  $\vec{k}_e$ ,  $\vec{k}_h$ . Thus

$$|\langle 0|\vec{\xi} e^{i\vec{\eta}\cdot\vec{r}} \nabla_e |\vec{\kappa},\vec{r}\rangle|^2 = |\langle 0,j'|e^{i\vec{\eta}\cdot\vec{r}} \vec{\xi} \nabla_e |0,j\rangle|^2 |\sum_{k} \Psi_{\kappa,-\kappa}|^2 = |\langle 0,j'|e^{i\vec{\eta}\cdot\vec{r}} \vec{\xi} \nabla_e |0,j\rangle|^2 |F^*(0)|^2$$

where the fourier transform of  $\Psi_{\mathbf{x},\mathbf{x}}^{o_n}$  has been used. For convenience  $p_{jj'}$  will be written for  $|\langle o,j'|e^{i\vec{\eta}\cdot\vec{r}}\ \vec{\xi}\ \nabla_e|o,j\rangle|$ . In the last section it was shown how the  $\mathbf{F}^{\mathbf{n}}(\vec{\mathbf{r}})$  may be found for the case of germanium, so the  $\alpha_{(\omega)}(\omega)$  can in principle be evaluated.

i) <u>Simple spherical bands</u>.

 $\propto(\omega)$  has been evaluated by Elliott (reference 11) for the case of two simple spherical bands. For transitions into the bound exciton states  $\propto(\omega) \propto \omega \mu^2 \rho_{jj}^2$ , and for transitions into the continuum of states

$$\begin{array}{l} \alpha(\omega) \propto \ \omega \mu^2 p_{jj}^2 \, \frac{\exp x}{\sinh x} & \text{where } x = \left(\frac{\pi^2 G}{h \nu - \Delta E_o}\right)^{\prime 2} \end{array}$$

For unstrained germanium, when k > 0, the absorption due to band to band transitions is ( $\omega$  is slowly varying)  $\alpha(\omega) = \alpha_{j_1}(\omega) + \alpha_{j_2}(\omega) \propto \mu_{+}^2 p_{j_1}^2 \frac{\exp x_1}{\sinh x_1} + \mu_{-}^2 p_{j_2}^2 \frac{\exp x_2}{\sinh x_2} \dots 13$ For the strained germanium when  $(h\nu - \Delta E) > 4\sqrt{\mathcal{E}}_{\epsilon}$  the absorption components  $\alpha_{j_1}(\omega)$  and  $\alpha_{j_2}(\omega)$  are the same as in the unstrained crystal, but they are displaced relative to eachother along the energy axis through  $Bb \sum_{l} \frac{3k_l^2 - k^2}{\sqrt{\mathcal{E}}_k} \mathcal{E}_{*}^{**}$  (see section <u>a</u>) and shifted together through (a' + a) $\Delta$ . (see equation 4).

In the above cases,  $G_1$ ,  $G_2$ , are not the exciton binding energies, but numbers calculated from the reduced effective exciton masses ( since  $\mu$  is different at k = 0). ii) Simple spheroidal valence bands

 $\chi(\omega)$  may be calculated using the variational functions given by Kohn and Luttinger (reference 20).  $F^{n}(0)$  is nonzero only for s-states where  $|F^{n}(0)|^{2} = (\pi a^{2} b n^{3})^{-1}$ . The variational parameters a, b must be minim ised w.r.t. energy and the product  $a^{2}b$  will be of the same order for both bands in the specimens used. As in the case of spherical bands, a series of lines is predicted from the K = 0 states of the exciton bands, with intensity falling off as  $n^{-3}$ . The absorption coeff-icient for transitions into the bound states is

 $\alpha(\omega) = \alpha \qquad \omega \left( \mu_1^2 \mu_2 \right)^{2/3} \mathbf{p}_{jj}^2,$ 

Since the factor  $(\mu_{1}^{*}\mu_{2})$  is approximately the same for the the two pairs of bands at k = 0 for the strained specimens used, the ratio of intensities of the two exciton absorption peaks is  $\frac{\gamma_{1}(\omega)}{\alpha_{1}(\omega)} \sim \frac{p_{11}^{2}}{p_{12}^{2}} \qquad \dots 14$ 

#### iii) Degenerate valence bands

In this case the sum over j' must be included in the expansion of  $|\vec{K},\vec{r}\rangle$  and evaluation of the intensity of absorption associated with exciton bound states in unstrained germanium becomes very complicated.

From the above considerations, it is evident that the exciton binding energies may not be obtained by the analysis of absorption curves of germanium. However, the ratio  $\frac{p_{j_1}^2}{p_{j_2}^2}$  may be estimated using equation 14, and then the reduced exciton effective masses in equation 13 may be obtained, using the empirical values of  $\prec(\omega)$ .

d) ANALYSIS OF EXPERIMENTAL RESULTS.

i) Absorption peaks.

In the absorption spectrum of unstrained germanium (figure 6) only one exciton peak is seen, whereas in the spectra of strained germanium (figures 7,8,9) two exciton peaks (or knees) are seen. The ratio of intensities  $\alpha_{ju}(\omega) : \gamma_{iv}(\omega)$  (u, v = 1or 2) of the two peaks is seen to be about 3. Since  $\alpha_{jv}(\omega) \propto \frac{1}{n^3}$  for the bound exciton states, this ratio indicates that the observed peaks are ground state exciton peaks associated with the two pairs of bands. From equation 14 it is seen that  $p_{j_i}$ and  $p_{j_2}$  are of comparable magnitude when  $\frac{\gamma_{j_2}(\omega)}{\omega_{j_1}(\omega)} \sim 3$ . (The labels  $\dot{u}, \dot{v}$  are used instead of 1,2 since the bands were not identified) ii) Continuum.

An attempt to fit equation 13 to the experimental results was made as follows: The value of  $\alpha(\omega_i)$  at a point where  $(\hbar\omega_i - \Delta E) \sim 3x$ (exciton peak separation) was found. This was then equated to  $\alpha_{j_i}(\omega_i) + \alpha_{j_2}(\omega_i)$  in equation 13. Since the separation of the exciton peaks was small, no correction was made for the relative shift of  $\alpha_{j_i}(\omega)$  and  $\alpha_{j_k}(\omega)$ . Then the four parameters  $p_{j_1}$ ,  $p_{j_2}$ ,  $\mu_+$ ,  $\mu_-$  were varied so that equation 13 gave a good fit to the experimental curves for all  $\omega > \omega_i$ .

It was found that the fit was not unique. A good fit of the data could be obtained by assuming  $p_{j_2} = 0$  and  $\mu_{+} = 0.024m_{\circ}$ in agreement with Macfarlane et al (reference 5) who considered only one contribution to  $\alpha(\omega)$  in unstrained germanium. However, this is not suggested by equation 14 and the observed spectra. By taking values of  $\mu_{+}, \mu_{-}$  calculated from the electron and hole cyclotron resonance masses, it was found that a good fit of the curves was obtained by taking  $p_{j_1} = p_{j_2}$ . With other choice of the parameters equally good fits could be obtained.

Though experimental results were consistent with the theory no conclusive information on the exciton effective masses was obtained from the data.

#### iii) Values of deformation potentials

Since the exciton binding energies are approximately equal and invariant under strain (see section b), the exciton

TABLE IV

The deformation potentials of germanium.

Plane of specimen	[100]	[111]	[110]
Ĕ	$ \begin{pmatrix} \mathbf{T} \\ \mathbf{T} \\ -\lambda \mathbf{T} \\ \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \\ \mathbf{O} \end{pmatrix} $	$\frac{\mathrm{T}}{\mathrm{3}} \begin{pmatrix} 2-\lambda\\ 2-\lambda\\ 2-\lambda\\ 1+\lambda\\ 1+\lambda\\ 1-\lambda \end{pmatrix}$	$\frac{\mathrm{T}}{2} \begin{pmatrix} 1 - \lambda \\ 2 \\ 1 - \lambda \\ 0 \\ 1 + \lambda \\ 0 \end{pmatrix}$
λ <sup>(*)</sup>	$\frac{2c_{12}}{c_{11}}=0.748$	$\frac{2(c_{11} + 2c_{12} - 2c_{44})}{c_{11} + 2c_{12} + 4c_{44}} = .363$	$\frac{c_{11} + 3c_{12} - 2c_{44}}{c_{11} + c_{12} + 2c_{44}} = 0.443$
(a' + a)	$\frac{\overline{E} - E_{o}}{T} \frac{1}{2-\lambda}$	$\frac{\overline{E} - E}{T} \circ \frac{1}{2 - \lambda}$	$\frac{\overline{E} - E_o}{T} \frac{1}{2-\lambda}$
	= -(11.3 ± 1)eV	= -(9.7 ± 1 )eV	= -(10.0 ± 1)eV
shear deformation	$ b  = \frac{\delta}{ T } \cdot \frac{1}{2(1+\lambda)}$	$ d  = \frac{\delta \sqrt{3}}{ T } \frac{1}{2(1+\lambda)}$	$\int b^2 + d^2 = \frac{\delta}{ T } \frac{1}{(1+\lambda)}$
potentials	$= (2.7 \pm 0.3) \mathrm{eV}$	$= (4.7 \pm 0.5) eV$	$= (5.6 \pm 0.6) eV$

\*The elastic constants data are taken from the data of Fine (reference 21)

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 $\overline{E} = E_e(0, \widehat{E}) + \overline{E}_h(0, \widehat{E}) , \quad E_\sigma = E_e(0, 0)$ 

<del>4</del>0

peak separation is equal to the splitting of the  $p_{3/2}$  valence bands, and the change in the mean exciton position with strain is equal to the change in the forbidden energy gap with strain. In figures 10,11,12, it is seen that for all specimen orientations the exciton peak positions shift linearly with the strain applied to the crystal. Thus the valence band splitting and the change of the band gap are linear with strain. This behaviour was theoretically predicted by Picus and Bir and Kleiner and Roth (references 8,9). Using equations 3,4 the deformation potentials were calculated from the experimental results and are tabulated in table IV. The value of  $\frac{E - E_o}{T}$ was obtained from figures 10,11,12 and the values of /bl and /dl were calculated using the results of specimens mounted on #0080 glass only, since these readings were much more reliable than the others. The strains  $\tilde{\epsilon}$  applied to the specimens, referred to the principal crystal axes are evaluated in appendix B. e) DISCUSSION OF RESULTS.

It is seen from table IV that the mean value of (a' + a)is  $-(10.3 \pm 1)$  eV per unit dilatation of the lattice. The error has been estimated as the maximum probable error. This deformation potential may be written as a pressure coefficient of  $-(13.7 \pm 1.5) \times 10^{-12} \text{ eV cm}^2/\text{dyne}$ . This value is in excellent agreement with other workers on the pressure variation of the band gap. Cardona and Paul (reference 23) found (a' + a) was -(13.3  $\pm$  1.5) x 10<sup>-/2</sup> eVcm<sup>2</sup>/dyne using thin specimens and low resolution. Fan (reference21) only examined the absorption edge up to absorption coefficients of about 400 cm<sup>-1</sup>, however the shift at this coefficient was  $-14.1 \times 10^{-12} \text{ eVcm}^2/\text{dyne}$ .

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Electrical and optical measurements of the pressure variation of the indirect band gap (reference 24) show that the shift of the zone boundary minima of the conduction band is much smaller than at the centre of the Brillouin zone. Thus the entire band does not shift uniformly with pure lattice dilatation.

The shear deformation potentials, |b| and |d| were found to be  $(2.7 \pm 0.3) \text{ eV}$  and  $(4.7 \pm 0.5) \text{ eV}$  per unit shear. The value of  $\sqrt{b^2 + d^2}$  is in excellent agreement with these values and affords a check as to the consistency of the method. Good agreement between |b| and |d| found in this work and those quoted recently by Hall (reference 25) is obtained. Hall studied the effect of strain on the acceptor binding energy, and found b = -(2.4 \pm 0.4) \text{eV} and d= -(6.0 ± 1.5) eV per unit shear.

In this work the signs of  $\underline{b}$  and  $\underline{d}$  could not be determined since the exciton peaks could not be identified with the valence bands with which they were associated.

#### CHAPTER IV : THE EFFECT OF LATTICE DEFECTS ON THE OPTICAL

### ABSORPTION SPECTRUM OF GERMANIUM.

In order to draw conclusions about the pure germanium lattice from the optical absorption spectrum, it is necessary to eliminate the effect of lattice defects in the specimens used. Probable defects in the single crystal germanium lattice are phonons, impurities and vacancies, surface states and dislocations. In this chapter, the effect of these defects on the absorption edge of the specimens will be discussed.

a) PHONONS.

In the foregoing experiments the lowest specimen temperature was about 90°K, so the effect of phonons will be of importance. Two major effects will be separately considered. i. Violation of the optical selection rule  $\vec{k}_e + \vec{k}_h = 0$  results, when phonons are simultaneously emmitted or absorbed during an electronic transition. The selection rule for such "indirect" transitions is  $\vec{k}_e + \vec{k}_h \pm \vec{k}_p = 0$  where  $\vec{k}_p$  is the wave-vector of the absorbed or emmitted phonon (reference 3). In germanium, the conduction band minima are at the Brillouin zone boundary at an energy  $\Delta E'$ from the valence band maximum ( $\Delta E' < \Delta E_o$ ), so that the onset of band to band transitions is by these indirect transitions when  $h\nu = \Delta E'$  and  $\overline{k}_{\rho} = \frac{\pi}{a} (\pm 1, \pm 1, \pm 1)$ . These transitions are much less probable than the direct transitions when  $h \lor > \Delta E$ , and Macfarlane et al (reference 4) have shown that they do not contribute more than 10% of the total absorption. For  $\Delta E' < h \vee < \Delta E_{\circ}$  a longwavelength tail to the absorption edge is seen with absorption  $coefficients \propto < 200 cm^{-1}$ .

ii. The change of lattice vibrations with temperature produces a change in the mean potential of an electron in the lattice. The

# <u>TABLE V</u> Comparison of the theoretical value of $\left(\frac{\partial(\Delta E)}{\partial T}\right)_{r}$ with experiment.

Т°К	∝ x10 <sup>6</sup> cm/°C	ð(a' + a) milli-eV/℃	$\left(\frac{d(\Delta E)}{dT}\right)_{P}$	$\left(\frac{d(\Delta E)}{dT}\right)_{p} = \delta(a'+a)$	$\left(\frac{\partial \Delta E}{\partial T}\right)_{V}$
	Novikova reference 16	this work	Macfarlane reference 5		Antončik reference 25
4	0	0	0.01 meV/2	0.01 <i>meV/</i> %	0.01 meV/%
40	0	0	0.08	0.08	0.09
80	1.3	0.04	0.18	0.14	0.11
100	2.3	0.07	0.23	0.16	0.13
200	4.8	0.15	0.37	0.22	0.14
300	5.8	0.18	0.42	0.24	0.16

 $\propto$  is the linear expansion coefficient and  $\forall \, \text{is the volume coefficient.}$ 

effect causes a shift of the entire absorption edge with temperature. The magnitude of the shift in germanium has been theoretically evaluated by Antončik (reference 25). It is interesting to compare the results of Antončik with the experimental results of this work and the results of Macfarlane et al (reference 5) on the temperature shift of the absorption  $\left(\frac{\mathrm{d}(\Delta \mathrm{E})}{\mathrm{d} \mathrm{T}}\right)_{\mathrm{p}} = \left(\frac{\partial(\Delta \mathrm{E})}{\partial \mathrm{T}}\right)_{\mathrm{v}} + \left(\frac{\partial(\Delta \mathrm{E})}{\partial \mathrm{V}}\right)_{\mathrm{T}} \left(\frac{\mathrm{d} \mathrm{V}}{\mathrm{d} \mathrm{T}}\right)_{\mathrm{p}}$ edge. Now Since  $\left(\frac{\partial (\Delta E)}{\partial V}\right)$  is the deformation potential (a' + a) and  $\left(\frac{dV}{dT}\right)_p$  is the volume expansion coefficient  $\delta$ , we have  $\left(\frac{\partial(\Delta E)}{\partial T}\right)_{v} = \left(\frac{d(\Delta E)}{dT}\right)_{p} - \delta(a' + a)$ Macfarlane et al measured  $\left(\frac{\partial(\Delta \dot{E})}{\partial T}\right)$  from 4°K to 300°K. The results are tabulated in table V. It is seen that there is quite good agreement between theory and experiment at all temperatures, if it is assumed that (a' + a) is not temperature dependent. b) IMPURITIES AND VACANCIES.

The resistivity of the germanium crystals at 23°C. before specimen preparation was about 60 ohm-cm. The resistivity increased by a factor of about 100 when the crystal was cooled to 90°K. This indicated that the impurity and vacancy content was less than 10<sup>12</sup> defects/cc. ( It is expected that the effect of vacancies would be similar to the effect of acceptor impurities). It is unlikely that any impurities were introduced into the crystals during specimen preparation, since at no time during the preparation was the crystal temperature raised above 80°C. Copper is the only common element that would diffuse into germanium below 80°C. (even this process is slow) so care was taken that the specimens did not come into contact with copper. It is also unlikely that the vacancy concentration increased appreciably during specimen preparation and during the straining of the specimen at these low temperatures.

The absorption cross-section of impurities in germanium is typically  $10^{-14}$  to  $10^{-16}$  cm<sup>2</sup> (reference 26). If the same cross-section is taken for vacancies then with only  $10^{-12}$  defects/cc the impurity and vacancy absorption would be negligible, even if it were in the spectral region examined. The spectra of three unstrained specimens from three different crystals were all identical, so the fine structure in the edge was not a property of one crystal only. One specimen was prepared from 2 ohm-cm N-type germanium  $(10^{15}$  impurities/cc). The absorption edge was somewhat broader, but the exciton peak was still visible at the same photon energy as in the purer material, though less intense. The broadening may be attributed to the decrease in lifetime of the exciton in the impure lattice.

#### c) SURFACE STATES

At the surface of a crystal the periodic lattice is terminated and band theory is no longer valid. The surface may be regarded as a plane of atoms with unpaired bonds into which an electron may be excited. If an absorption cross-section  $\sigma$  is assigned to a surface state then for N states/cm<sup>2</sup> the total absorption at the surface is  $\sigma$ N. Since there are only two surfaces of the crystal traversed by the light beam, the normalised transmission through a specimen is

$$T_n = (1 - \sigma N)^2 \exp{-\alpha d}$$

Clearly  $\sigma N < 1$ . It is apparent that the factor  $(1 - \sigma N)^2$  which takes into account the surface states, is independent of the specimen thickness.

When  $\propto = 0$  in the bulk of the specimen, the transmission is a function of  $\sigma$ -only. It has been shown by Dexter (reference 27) that such unpaired bonds lead to a long-wavelength tail to the absorption edge\*.

The value of  $\sigma$  would not be significantly affected by strain so that no change in the "surface state spectrum" would be expected on straining the specimens. Thus it appears from figures 6 to 9 that surface states did not affect the optical absorption of the specimens. Thus  $\sigma N \ll 1$ . It is for this reason that the surface states have not noticably affected previous absorption measurements.

d) DISLOCATIONS.

Initially, the bulk germanium crystals had a dislocation density of about 5000 lines/cm<sup>2</sup>. During the specimen preparation it is possible that dislocations may have been introduced into the crystal as a result of abrasion damage. A few of the specimens were etched by placing them face-downwards in a bubble of fast CP4 on a polyethylene sheet. This avoided etching the glass substrates. The specimens could only be etched for about 20 seconds before they were completely dissolved. These conditions were not adequate for the observation of etch pits, but even with this brief etch,dots appeared randomly on the specimen at a density of about  $10^{5}$  to  $10^{6}$  per cm<sup>2</sup>(when viewed with a microscope of 500x magnification) It is possible that these marks were an indication of the dislocation density.

The effect of dislocations is two-fold. (i) dislocations act \* Dexter appears to interpret the magnitude of the absorption associated with surface states incorrectly. It seems that he considers the volume concentration of surface states and assigns to them an absorption coefficient. The absorption by these states will thus depend on specimen thickness.

as acceptors since along a dislocation line there is a line of atoms with unpaired bonds. Dexter (reference 27) has made an estimate of the absorption by electrons excited into these bonds. The absorption appears as a long-wavelength tail to the edge, with a maximum absorption coefficient of  $100 \text{cm}^{-1}$  for a dislocation density of  $10^{12} \text{lines/cm}^2$ . For lower dislocation densities, this effect would be negligible in the spectral region examined in this experiment.

(ii) The second effect of dislocations is due to the distortion of the crystal lattice around a dislocation. This effect will be discussed in detail in the following section: INTERNAL STRAINS.

The distortion of a crystal lattice associated with a dislocation consists of severe atomic misfit around the dislocation (bad material) and elastic strains in the surrounding good material.

In the germanium specimens internal strains will be frozen in as a result of dislocations introduced during crystal growth and specimen preparation. At any point in the crystal there will be an internal strain  $\tilde{\mathcal{E}}_i$  in addition to the external applied strain, with which there is associated a shift in the absorption edge and a splitting of the valence bands. In this section an order of magnitude estimate will be made of the effect of the internal strains on the absorption edge of a specimen.

The normalised transmission of light of photon energy hy through an area A of specimen of thickness d is

$$T_{n} = \frac{1}{A} \int_{A}^{d} dA \exp - \left[ \int_{0}^{d} \alpha_{xyz}(h\nu) dz \right]$$

where  $\alpha_{xyz}$  is the absorption coefficient at a point (xyz) in the crystal.

The effect of  $\widetilde{\mathcal{E}}_i$  is to shift the two absorption edges, corresponding to transitions from the two  $p_{\frac{3}{2}}$  valence bands to the conduction band, through energies  $\Delta E_{\pm}$  given by (see chapter III)

 $\Delta E_{\pm} = a \sum_{i} \mathcal{E}_{ii} \pm \frac{1}{2} \left[ b^{2} \sum_{ij} (\mathcal{E}_{ii} - \mathcal{E}_{jj})^{2} + 2d^{2} \sum_{i,j}^{i+j} \mathcal{E}_{ij}^{2} \right]^{1/2}$ where (a' + a) has been abbreviated to <u>a</u> and the  $\mathcal{E}_{ij}$  are internal strain components.

The displacement  $u_i$  of a point in an isotropic crystal at a distance r from the dislocation has been calculated by Read (reference 28). From these equations the strains were readily calculated. For an estimate of the effect of  $\mathcal{E}_i$  on the absorption edge of germanium these equations are used and b<sup>2</sup> is set equal to  $\frac{1}{3} d^2$ .(see table IV). It was found that

$$\Delta E_{\pm}(r,\theta) = \frac{13}{2\pi r} \left[ af_1(\theta) \pm bf_2(\theta) \right]$$

where  $f_1(\theta) = \frac{2\lambda^2}{1-\lambda} \sin\theta$  $f_2(\theta) = \frac{1}{1-\lambda} \left[ 19\cos^6\theta - 21\cos^4\theta + 3\cos^2\theta + 4\lambda\cos^2\theta - \frac{1}{2}\right]$ and

and eta is the burghers vector of the dislocation, heta is the angle between  $\vec{r}$  and the slip plane of the dislocation.

The absorption edges associated with the two pairs of bands will be represented by step functions:

for  $h\nu < E_o - \Delta E_+$   $\alpha = \alpha$ , for  $h\nu > E_o - \Delta E_+$  $\alpha = 0$ for  $h\nu < E_{\circ} - \Delta E_{-} \qquad \checkmark = \varkappa_{2}$  for  $h\nu > E_{\circ} - \Delta E_{-}$ and  $\alpha = 0$  $E_o$  is the forbidden energy gap in unstrained germanium at k=0 $(E_o = E_e(0,0))$ .

The two cases of low and high dislocation densities in the thin germanium specimens will be treated separately.

i) Low dislocation density.  $(<10^{6} \text{ lines/cm}^2)$ .

For low dislocation densities the number of dislocations in the plane of the specimens is small, for specimens 10 µ thick. The model assumed for this calculation is a regular lattice of straight dislocations with equal numbers of positive and negative edge dislocations perpendicular to the plane of the specimen, each being separated from its nearest neighbour by a distance <u>h</u>. With this model there is no variation of strain through the specimen thickness so  $T_n = \frac{1}{A} \int_A^{\rho} r d\theta dr \exp{-\alpha_{r\theta}(h\nu)} d$ The crystal is treated as an elastic continuum, rather than discrete lattice points so that sums over elemental volumes may be replaced by integrals.

When  $(E_{\circ} - h\nu) > 0$  absorption will only occur in the fractional volume of the crystal where (treating the absorption contributions from the two bands separately): ...equations 1, 2.

 $\begin{array}{ll} (E_{\circ} - h\nu) < \frac{\beta}{2\pi r_{i}} \left[ af_{1}(\theta) + bf_{2}(\theta) \right] & \text{then } exp - \alpha_{r\theta}(h\nu) d = exp - \alpha_{i}d \\ (E_{\circ} - h\nu) < \frac{\beta}{2\pi r_{2}} \left[ af_{1}(\theta) - bf_{2}(\theta) \right] & \text{then } exp - \alpha_{r\theta}(h\nu) d = exp - \alpha_{2}d \\ \text{For both contributions, when } (E_{\circ} - h\nu) > \frac{\beta}{2\pi r_{i}} \left[ af_{1}(\theta) \pm bf_{2}(\theta) \right] \\ \text{then } exp - \alpha_{r\theta}(h\nu) d = 1 & \text{Thus the transmission of the specimen is} \\ T_{n} = \int_{\circ}^{2\pi} d\theta \left[ \frac{N}{2} exp - (\alpha_{1} + \alpha_{2}) d \int_{r_{b}}^{r_{2}} rdr + \frac{N}{2} exp - \alpha_{i}d \int_{r_{2}}^{r_{i}} rdr + \frac{N}{2} \int_{r_{2}}^{r_{i}} rdr \\ & + N \int_{r_{1}}^{r_{a}} rdr + N \int_{\circ}^{r_{b}} rdr exp - \alpha_{b}d \end{array} \right]$ 

where  $r_1, r_2$ , are defined by equations 1 and 2 above,  $r_a$  is defined by the requirement that  $N\pi r_a^2 = 1$ ,  $r_b$  is the radius of bad material around a dislocation and  $\approx_b$  is the absorption coefficient associated with the bad material. The factor  $\frac{1}{2}$  appears in the first three integrals since for only one half of the crosssectional area of the specimens is the product  $\beta[af_1(\theta) \pm bf_2(\theta)]$ positive. The choice  $r_1 > r_2$ , has been made arbitrarily.

For low dislocation densities  $r_b \ll r_a$ , so we can let  $r_b \rightarrow 0$ . Now  $\int_{0}^{2\pi} d\theta \int_{0}^{r_2} r dr = \frac{\beta^2}{8\pi^2 (E_0 - h\nu)^2} \int_{0}^{2\pi} \left[ af_1(\theta) - bf_2(\theta) \right]^2 d\theta$ Using  $\lambda = 0.6$  this integral gives approximately

$$\frac{\beta^2}{8\pi^2(E_0 - h\nu)^2} \left[ \frac{\pi}{4}a^2 - 0.3ab + \frac{9\pi}{2}b^2 \right]$$

For germanium  $a \sim 10 \text{ eV}$ ,  $b \sim 3 \text{ eV}$  so the term in ab is small compared with the other terms, thus  $\int_{0}^{2\pi} d\theta \int_{0}^{r_{1}} r dr \simeq \int_{0}^{2\pi} d\theta \int_{0}^{r_{2}} r dr$ and  $T_{n} = \left[1 - \frac{N\beta^{2}(a^{2} + 18b^{2})}{64\pi(E_{0} - h\gamma)^{2}}\left[1 - \exp(\alpha_{1} + \alpha_{2})d\right]\right]$ 

The procedure for  $(h\nu - E_o) > 0$  is similar. In this case absorption occurs in the whole crystal except that for which  $(h\nu - E_o) < |\Delta E_{\pm}|$ . It is found that

$$T_{n} = \left[ \exp \left(\alpha_{1} + \alpha_{2}\right) d + \frac{N\beta\left(a^{2} + 18b^{2}\right)}{64\left(E_{0} - h\nu\right)^{2}} \left[1 - \exp \left(\alpha_{1} + \alpha_{2}\right) d\right] \right]$$

This function is not defined near  $(E_{\circ} - h\nu) = 0$  since in this treatment there is no region of the crystal unaffected by dislocations. Because of the symmetry of the function about  $E_{\circ}$ ,

for continuity at E<sub>o</sub> ,  $T_n = \frac{1}{2} \begin{bmatrix} 1 - \exp((\alpha_1 + \alpha_2) d \end{bmatrix}$ For  $h\nu \gg E_o$  ,  $T_n \rightarrow \exp((\alpha_1 + \alpha_2) d$  and for  $h\nu \ll E_o$  ,  $T_n \rightarrow 1$  as expected. The effect of dislocations is to broaden the absorption edge with no nett shift of the edge. A half-width of the broadening may be defined by the value of ( $E_o - h\nu$ ) when  $T_n = \frac{1}{4}$ 

i.e.  $(E_0 - h\nu)_{\frac{1}{2} - \text{width}} \sim 5 \times 10^{-8} \text{ N}^{\frac{1}{2}}$ where we have used  $d = 10\mu$ ,  $(\alpha_1 + \alpha_2) = 4000 \text{ cm}^{-1}$ ,  $\beta = \langle 100 \rangle$  lattice vector = 4 Å.

To obtain a broadening half width equal to the monochromator resolution of 0.2 milli-eV, the specimens would need a dislocation density of  $\sim 10^7$  lines/cm<sup>2</sup>. (This is outside the limit of the model). It is possible that the observed variation in peak height was due to this broadening mechanism. The position of the exciton peak in the absorption spectrum of the specimens would not be affected by these internal strains.
ii. High dislocation density ( >  $10^{8}$  lines/cm<sup>2</sup>).

With a high dislocation density there will be a considerable variation of strain through the specimen thickness. A random distribution of straight dislocations will be assumed, no other restrictions being placed on the model. Dexter (reference 27) has shown how dislocations may account for a long wavelength tail, or apparent shift of the absorption edge, using this model, and his treatment will be extended for the case of germanium.

For a random distribution of dislocations, the absorption of a crystal may be described by a single absorption coefficient, equal to the mean absorption coefficient of the crystal, averaged over the volume.  $T_n = \frac{1}{A} \int_A dA \exp \left[ \int \alpha'_{xyz} (h\nu) dz \right] = \exp \left[ -\overline{\alpha'_{xyz}} dV \right]$  where  $\overline{\alpha'_{xyz}} = \frac{1}{V} \int_V \alpha'_{xyz} dV$ 

When  $(E_{o} - h\nu) > 0$  absorption will only occur in the fractional volume of the crystal for which  $(E_{o} - h\nu) < \triangle E_{\pm}$  - again the two bands being considered separately. Now we have

 $\overline{\alpha}_{xy_2} = \frac{1}{2} N_{\mathbf{y}} \alpha_1 \int_0^{2\pi} d\theta \int_{r_b}^{r_b} r dr + \frac{1}{2} N_{\mathbf{y}} \alpha_2 \int_0^{2\pi} d\theta \int_{r_b}^{r_2} r dr + N \int_0^{2\pi} d\theta \int_0^{r_b} \alpha_b r dr$ where  $N_{\mathbf{y}} = 3N$  is the dislocation density in lines/unit volume, and  $r_1, r_2$ , were defined by equations 1 and 2 above. The integrals have already been evaluated and it is found that

 $\overline{\alpha}_{xyz} = \frac{3N\beta^2}{64\pi(E_o - h\nu)^2} (a^2 + 18b^2)(\alpha_1 + \alpha_2) - N\left[\frac{\pi}{2}r_b^2(\alpha_1 + \alpha_2) - \int_0^{2\pi} d\theta \int_0^{r_b} \alpha_b r dr\right]$ Similarly for  $(h\nu - E_o) > 0$  $\overline{\alpha}_{xyz} = (\alpha_1 + \alpha_2) \left[1 - \frac{3N\beta^2}{64\pi(E_o - h\nu)^2} (a^2 + 18b^2) + N\int_0^{2\pi} d\theta \int_0^{r_b} \alpha_b^{\prime} r dr\right]$ 

The last terms have been included here since the effect of bad material is not known. For very high dislocation densities the volume of bad material may not be negligible compared with the good material. For a solid to exhibit crystalline character - lattice periodicity,- then  $2r_b$  must be less than  $r_a$ . For  $r_b \sim 10$  Å

this requirement is  $N < 10^{'^3}$  lines/cm<sup>2</sup>.

For an estimate of  $\overline{\alpha}_{xy2}$  the last terms in the above equations, involving the bad material will be neglected. Again it is clear that the equations are not defined at  $E_0 \simeq h \vee$ , but for continuity at  $E_0$ ,  $\overline{\alpha}_{xy2} = \frac{1}{2}(\alpha_1 + \alpha_2)$  at  $E_0$ . This is expected since half the crystal is under strain  $+\widetilde{\mathcal{E}}$  and the other half under strain  $-\widetilde{\mathcal{E}}$ .

Again it is clear that the effect of the dislocations is to broaden the absorption edge. A half-width of the broadening may be defined as the value of  $(E_0 - h\nu)$  when  $\overline{\alpha}_{xyz} = \frac{1}{4}(\alpha_1 + \alpha_2)$ .

i.e.  $(E_o - h\nu)_{\frac{1}{2}-width} \sim 10^{-7} N^{\frac{1}{2}}$ using the same constants as before. When  $T_n = \frac{1}{4}$ ,  $(E_o - h\nu) \sim 10^{-7} N^{\frac{1}{2}}$ which is approximately the same result as with the previous model.

From this analysis it is seen that the absorption spectra of the specimens used in these experiments were not affected by dislocations since no measureable broadening of the edge was obtained. In order to observe the effect of dislocations experimentally, it would be necessary to introduce more than 10<sup>8</sup> lines/cm<sup>2</sup> into the crystal. The easiest way of producing high dislocation densities is to evaporate germanium films onto a substrate in a polycrystalline state. The grain boundaries may be represented by dislocations (reference 28).

e) EVAPORATED FILMS OF GERMANIUM

Three specimens of germanium were prepared by evaporating intrinsic germanium from a small graphite boat, heated by joule heating with a heavy current. The bell-jar was evacuated to a pressure of about  $10^{-5}$  mm Hg. The glass substrates were cleaned, prior to evaporation, by ion bombardment. Two specimens 5.1µ and 9.1µ thick were evaporated onto cold substrates and one specimen 6.4µ thick was evaporated onto a substrate, heated from the back with a heating coil. "Thick" films were prepared in order to make comparison with the single crystal specimens.

The transmission of the films was examined from 0.5eV to 1.0eV. A very broad absorption edge was seen in all the specimens, indicating that the films were crystalline, but no fine structure was seen. The film thicknesses were found by by measuring the interference fringes where the films were transparent, and using the refactive index data of Brattain and Briggs (reference 29). The fringes were averaged for the evaluation of the absorption data. The two specimens prepared on cold substrates showed identical absorption, yet the specimen prepared on a hot substrate was noticably different, as seen in Fig 15. The single crystal absorption edge is shown for comparison. The two absorption curves of the evaporated specimens intersect the single crystal edge at about 1800cm<sup>-1</sup>.

The observations are in excellent qualitative agreement with the theory of crystals with a high dislocation density. Using the value  $N_v = 9 \times 10^{11}$  lines/cm<sup>3</sup>, the curve of  $\overline{\propto_{x_{12}}}$  vs (E<sub>o</sub> - h<sub>v</sub>) predicted in the last section is also plotted in fig 15. On the high energy side of E<sub>o</sub> the experimental curves are steeper than predicted as would be expected since the theory assumed a step function absorption edge for the unstrained crystal.

It was noticed that apart from the broad absorption edge, the evaporated films had the same optical properties as the single crystals. The reflectivity was the same, the refractive index increased 2% from 300°K to 90°K (deduced from the phase shift of the interference fringes) and the shift of the absorption edge between these temperatures was the same as the single crystal.



Thus it appears that the absorption edge can give an indication of the quality of an evaporated film. From the curves of figure 15, it is seen that the film prepared on a hot substrate was less strained than the others as might be expected. f) DISCUSSION.

From the discussions of this chapter it is seen that the lattice defects in the specimens did not significantly affect the absorption spectra. The small variations in the exciton peak heights may be accounted for by lattice imperfections, yet the large broadening of the absorption peaks in the specimens mounted on #7900 glass could not be accounted for.

## CHAPTER V : CONCLUSIONS.

The study of the effect of strain on the exciton spectrum of germanium afforded a very direct method of obtaining the deformation potentials of germanium:

 $|b| = (2.7 \pm 0.3) \text{ eV/unit (100) shear,}$ 

 $|d| = (4.7 \pm 0.5) \text{ eV/unit (111) shear,}$ 

 $(a' - a) = -(10.3 \pm 1.0)$  eV/unit dilatation of the lattice. The experiment is inherently quite accurate because of the sharpness of the exciton absorption peaks and the fact that the exciton binding energy is determined primarily by the small electron mass.

An experimental check of the exciton binding energies in strained and unstrained germanium could in principle be made by investigating the Stark effect of the exciton spectrum. The Stark effect depends only on the exciton radius, which in turn depends only on the reduced effective exciton mass.

The study of the effect of lattice defects on the absorption spectrum indicated that the experimental results of this work were properties of the perfect germanium lattice, and were not affected by the lattice imperfections. On the other hand the broad absorption edge observed in evaporated films of germanium could be accounted for in terms of internal strains due to dislocations. Measurements of the absorption edge could prove a useful tool in investigating the structure of films. Further experiments, correlating internal strains with the crystallite size of the films are clearly necessary.

It is also interesting that the theory of Antončik on the change of the energy gap with temperature is in agreement with experimental results. APPENDIX A: CALCULATION OF STRAINS ON THE SPECIMENS Basic elasticity theory.

To avoid confusion with notation, arising from the difference between conventional elasticity theory and the tensor formulation, the basis of the theory will first be outlined.\* Cartesian axes are used throughout the discussion.

When a force F; is applied to a solid, the stresses in the solid are defined by

$$T_{ij} = \Delta A_j \rightarrow 0 \quad \Delta \overline{A}_i \qquad \dots \dots A1$$

where  $\Delta F_i$  is the force acting over elemental area  $\Delta A_j$  of the solid. The T<sub>ii</sub> are compressional (-ve) or tensile (+ve) stresses and the T<sub>ii</sub> are shear stresses.

If a point P of position vector  $\vec{x}$  in the solid is displaced through a distance  $\vec{u}$  under the action of a stress, to the position  $\vec{x}' = \vec{x} + \vec{u}$ , then the deformation of the solid may be described by strains  $\mathcal{E}_{kl} = \frac{1}{2} \left( \frac{\partial u_k}{\partial \vec{x}_l} + -\frac{u_l}{\vec{x}_k} \right) \qquad \dots \qquad A2$ 

Hooke's law is that for small deformations of a solid, the stress is directly proportional to the strain

The  $C_{ijkl}$  are elastic constants and  $\widetilde{C}$  may be treated as a tensor of the fourth order.

Under a general rotation of axes  $T_{ij}$ ,  $\mathcal{E}_{kl}$  and  $C_{ijkl}$  will change. If the rotation operator is  $\tilde{\prec}$  the the strain tensor transforms as  $\mathcal{E}'_{k'l'} = \ll_{kk'} \ll_{il'} \mathcal{E}_{kl}$  or  $\mathcal{E}_{kl} = \ll_{kk'} \ll_{il'} \mathcal{E}'_{k'l'} \dots$  A3 and the elastic constants tensor transforms as

$$C_{ijkl} = C_{ijkl} \propto_{ii} \propto_{jj'} \propto_{kk'} \propto_{il'} \qquad A4$$

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\* See, for example, H.B.Huntingdon: Solid State Physics vol.7 p.213 McGraw Hill publication, edited by Seitz and Turnbull.

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Since  $\tilde{T}$  is symmetrical w.r.t. interchange of i and j and  $\tilde{\varepsilon}$  is symmetrical w.r.t. interchange of k and l, there are only six independent components of each of  $\tilde{\varepsilon}$  and  $\tilde{T}$ .  $\tilde{C}$  is symmetric w.r.t. interchange of i and j, k and l, ij and kl, so that there are are only 21 independent components of  $\tilde{C}$ . Thus  $\tilde{T}$  and  $\tilde{\varepsilon}$  may be written as six-vectors and  $\tilde{C}$  as a 6x6 matrix in accordance with conventional theory, and relable the double subscript with a single subscript: 11 + 1, 22 + 2, 33 + 3, 23 + 4, 31 + 5, 12 + 6. The  $\varepsilon_v$  obtained by this relabling procedure are not the same as the conventional strains  $\varepsilon_v$ . In fact  $\varepsilon_v = \varepsilon_v$  for v = 1, 2, 3, and  $\varepsilon_v = \frac{1}{2}\varepsilon_v$  for v = 4, 5, 6.

Conventional elasticity theory has the disadvantage that the e, and c, are not tensors and transformation of these quantities requires an involved treatment. CALCULATION OF STRAINS ON SPECIMENS.

Consider a specimen of thickness  $\underline{d}$ , area A = a<sup>1</sup> as shown in Fig A(i), and choose cartesian axes so that the plane ABGH is the z = 0 plane. Suppose a stress  $\widetilde{T}$ is applied to the surface ABGH so that the displacement of a point in the plane is  $\vec{u}_{o} = (u_{i}^{o}, u_{2}^{o}, 0)$ . A point on the opposite face of the specimen CDEF, will in general be displaced through  $\vec{u}_{d} = (u_{i}^{d}, u_{2}^{d}, u_{3}^{d})$ where the  $u_{i}^{d}$  may be written in terms of the  $u_{i}^{o}$  by a Taylor expansion

 $u_i^d = u_i^o + (\nabla_z u_i)_o^d + \dots$  ... A5 The specimen will be deformed in crosssection as shown in Fig A(ii). For very



Fig. A

thin specimens the terms in  $d^2$  and higher may be neglected. Thus the strain at z = d in terms of the strain at z = 0 is, from equations A1 and A5

$$\mathcal{E}_{i}^{d} = \mathcal{E}_{i}^{\circ} + (\nabla_{z} \mathcal{E}_{ij})_{o}^{d} \qquad \dots A \mathcal{E}_{ij}$$

This implies that B'C' and A'D' are straight lines.

In this section it will be shown that the strain in the thin specimens is uniform to a good approximation. i.e.  $\mathcal{E}_{ij}^{d} = \mathcal{E}_{ij}^{\circ}$ In approximation A6 this implies  $(\nabla_{\mathbf{z}} \mathcal{E}_{ij})_{o} d \ll \mathcal{E}_{ij}^{\circ}$  ....A7

For convenience the plane of the specimen will be taken as a [100] crystal plane. This choice will not affect the final result. In this coordinate frame  $\tilde{C} = /c_n c_n c_n$ 

In this work the strain is uniform in the z = 0 plane  $\mathcal{E}_{i1} = \mathcal{E}_{12}$ ,  $\mathcal{E}_{i2} = 0$ The condition that  $T_{33} = 0$  is  $\mathcal{E}_{13} = -\frac{2c_{12}}{c_{11}}\mathcal{E}_{11}$ so we have  $T_{11} = T_{22} = \left[c_{11} + c_{12} - \frac{2c_{12}^{22}}{c_{11}}\right]\mathcal{E}_{11}$ Now  $\nabla_{z} \mathcal{E}_{11} \leq 2\nabla_{z} \mathcal{E}_{13} = \frac{4\mathcal{E}_{13}}{a}$  (neglecting higher orders)  $\nabla_{z} \mathcal{E}_{23} = \nabla_{z} \mathcal{E}_{31} = 0$ 

Thus  $\mathcal{E}_{ij}^{\circ} = \mathcal{E}_{ij} \begin{pmatrix} 1 \\ 1 \\ -2c_{ij}/c_{ij} \\ \varepsilon_{zz}/\mathcal{E}_{ij} \\ \varepsilon_{zz}/\mathcal{E}_{ij} \end{pmatrix}$  and  $(\nabla_{z} \mathcal{E}_{ij})_{O} d \leq d \frac{4\mathcal{E}_{ij}}{a} \begin{pmatrix} 1 \\ 1 \\ -2c_{ij}/c_{ij} \\ \varepsilon_{zz}/\mathcal{E}_{ij} \\ \varepsilon_{zz}/\mathcal{E}_{ij} \\ 0 \end{pmatrix}$ 

Now since  $\underline{d} \sim 10^{-3}$  cm and  $\underline{a} \sim 1$  cm the condition A7 is satisfied if  $\varepsilon_{,1} \gg 4 \times 10^{-3} \varepsilon_{,3}$ .  $\varepsilon_{,3}$  will not be greater than  $\varepsilon_{,1}$  so this inequality is satisfied and the strain is uniform through the specimen. The shear stress  $T_{23} = \frac{2F}{A}$  where F is the force applied along OB'. Since  $\varepsilon_{,1}$  is uniform through the specimen  $T_{,1} = \frac{2F}{ad}$ Thus  $\varepsilon_{,3} = \frac{ad}{A} (c_{,1} + c_{,2} - \frac{2c_{,2}^{L}}{c_{,1}}) \frac{\varepsilon_{,1}}{c_{,4}} = \frac{ad}{A} \frac{K}{4c_{,4}} \varepsilon_{,1} \sim 2 \times 10^{-3} \varepsilon_{,1}$  for

germanium. For convenience K has been substituted for  $c_{11} + c_{12} - \frac{2c_{12}^2}{c_{11}}$ 

So we have  $(\nabla_z \varepsilon_{ij})_o d \sim 10^{-5} \varepsilon_{ij}$  and  $\varepsilon_{ij} = \varepsilon_{ij} \begin{pmatrix} 1 \\ 1 \\ -2c_{i2}/c_{ij} \\ 0 \end{pmatrix}$ 

Now suppose that the specimen is rigidly attached to a thick isotropic substrate, and the specimen is strained by the differential contraction on cooling. The angular deformation of the substrate at the interface is  $\frac{T_{23}}{c_{44}}$  since  $T_{23}$  is continuous across the interface.  $c_{44}^{+}$  is an elastic modulus of the substrate material. Now  $\frac{T_{23}}{c_{44}} = \frac{ad}{A} \frac{K}{c_{44}} \varepsilon_{\parallel}$  which is a very small deformation. Thus the substrate is not appreciably affected by the deformation of the germanium specimen.

In practice the problem is a three layer problem: a thick substrate, a thin layer of epoxy and the germanium specimen. By reasoning similar to that above, the strain  $\mathcal{E}_{\mu}$  of the specimen is unaffected by the epoxy and is uniform through the specimen, if the epoxy obeys the relation  $\frac{1}{a}\left(\frac{K}{c}\right)_{epoxy} T_{23}^{\prime} \ll T_{\mu}^{\prime}$ 

where  $T'_{23}$  is now given by the relation

$$\Gamma'_{23} = \frac{a^2}{A} \left[ (\mathcal{E}_{11} K d)_{\text{specimen}} + (\mathcal{E}_{11} K d)_{\text{epoxy}} \right]$$

For specimens and epoxy layers of 10 $\mu$  thickness, and since  $\epsilon_{\mu}$  will be of the same order for both materials, then this condition implies  $\left(\frac{K}{C_{44}}\right)_{epoxy} \left[1 + \frac{Kge}{Kepoxy}\right] \ll 10^5$ 

The epoxy used was hard - especially at reduced temperatures so it is probable that this condition was obeyed. The following experiments were performed to determine whether the inequality holds: a) The germanium specimen was glued to the substrate with different glue thicknesses ( < 25,...). b) Specimens of different thicknesses were prepared (<18µ).</li>
c) Specimens were mounted with both surfaces glued to the same substrate material.

In none of these experiments was the absorption spectrum of a specimen different from the others. The exciton peak positions were reproducible. The sharpness of the exciton peaks ( for specimens under tension) was an indication that the strain was uniform through the specimens. The experiments a,b,c, thus indicate that the above inequality holds.

Since the substrate was negligibly deformed by the specimen, the strain in the germanium was  $\mathcal{E}_{u} = \mathcal{E}_{u} = (\simeq \alpha_{substrate} - \alpha_{ge}) \Delta T$ where  $\Delta T$  was the temperature change on cooling the specimen, and the  $\propto$ s are expansion coefficients (linear).

## APPENDIX B : TRANSFORMATION OF ELASTIC CONSTANTS UNDER ROTATION OF AXES

For all the germanium specimens used in the experiment, it is necessary to know the strains applied to the crystal in the co-ordinate system associated with the principal crystal axes.

We can take the plane of the specimen to be the x-y plane in all cases. The z-direction is then normal to the applied stress. These axes are the principal axes of the strain tensor (see Appendix A). The strain in the x-y plane is given by  $\varepsilon_{n} = \varepsilon_{12} = T$ and in the z direction is  $\varepsilon_{33} = -\lambda T$  where  $\lambda$  is found from the condition that normal stress  $T_{33}$  vanishes.

There three cases to consider: When the x-y plane is a [001] plane, the x'-y' plane is a [110] plane, and when the x"-y" plane is a [111] plane. Since all {111} planes are elastically equivalent any convenient plane may be chosen for the calculation. Similarly for the {110} planes.

a) x,y,z, axes are the  $\langle 100 \rangle$ ,  $\langle 010 \rangle$ ,  $\langle 001 \rangle$ , crystallographic axes.  $\widetilde{C}$  has cubic symmetry in these axes:  $(c_{11}, c_{12}, c_{12})$ 

€ =	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0	
	0	$\begin{array}{ccc} c_{44} & 0 & 0 \\ 0 & c_{4q} & 0 \\ 0 & 0 & c_{44} \end{array}$	

Then the  $\mathcal{E}_{kl}$  are directly  $\mathcal{E}_{ll} = \mathcal{E}_{22} = T$ ,  $\mathcal{E}_{33} = -\lambda T$ ,  $\mathcal{E}_{23} = \mathcal{E}_{31} = \mathcal{E}_{12} = 0$ Using Hookes Law we find  $\lambda = \frac{2c_{12}}{c_{11}}$ b) x', y', z', axes are  $\langle 101 \rangle$ ,  $\langle 010 \rangle$ ,  $\langle T01 \rangle$ , crystal axes.

The plane considered is [10T]. Transformation from the x,y,z, axes to the x',y',z', axes is a rotation through -  $\frac{\pi}{4}$ about the y axis. Thus



$$\widetilde{\alpha} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & 1 \\ 0 & \sqrt{2} & 0 \\ -1 & 0 & 1 \end{pmatrix} \quad \text{and} \quad \widetilde{\alpha}^{-\prime} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 0 & -1 \\ 0 & \sqrt{2} & 0 \\ 1 & 0 & 1 \end{pmatrix}$$
  
e have  $\widetilde{\varepsilon}' = \begin{pmatrix} T \\ T \\ -\lambda T \\ 0 \\ 0 \end{pmatrix} \quad \text{so from equation A3,} \quad \widetilde{\varepsilon} = \begin{pmatrix} 1 - \lambda \\ 2 \\ 1 - \lambda \\ 0 \\ 1 + \lambda \\ 0 \end{pmatrix}$ 

In order to find  $\lambda$ ,  $\tilde{C}'$  must be known. For  $T_{33} = 0$  we require (from Hooke's Law):  $(C'_{3311} + C'_{3322} - \lambda C'_{3333})T = 0$  ....Bl So the complete tensor  $\tilde{C}'$  need not be evaluated. From equation A4 it is found that

 $C'_{3311} = \frac{1}{2}(2C_{11} + 2C_{12} - 4C_{44}), \quad C'_{3333} = \frac{1}{2}(C_{11} + C_{12} + 2C_{44})$  $C'_{3322} = C_{12}$ 

Thus

W

c) x", y", z", axes are the  $\langle 101 \rangle$ ,  $\langle T21 \rangle$ ,  $\langle TT1 \rangle$ , crystal axes. Transformation from the x, y, z, axes to the x", y", z", axes is a rotation of  $-\frac{\pi}{4}$  about the y-axis followed by a rotation of  $-\tan^{-1}\frac{1}{\sqrt{2}}$  about the x' axis. Here we have  $\widetilde{\alpha} = \frac{1}{\sqrt{6}} \begin{pmatrix} \sqrt{3} & 0 & \sqrt{3} \\ -1 & 2 & 1 \\ \sqrt{6} & -\frac{1}{\sqrt{2}} & \sqrt{2} \end{pmatrix}$  and  $\widetilde{\alpha}^{-1} = \frac{1}{\sqrt{6}} \begin{pmatrix} \sqrt{3} & -1 & -\sqrt{2} \\ 0 & 2 & -\sqrt{2} \\ \sqrt{3} & 1 & \sqrt{2} \end{pmatrix}$ 

 $\lambda = \frac{C_{11} + 3C_{12} - 2C_{44}}{C_{11} + C_{12} + 2C_{44}}$ 



As before, from equation A3 it is found that 
$$\hat{\mathcal{E}} = \frac{J}{3} \begin{pmatrix} 2-\lambda \\ 2-\lambda \\ 2-\lambda \\ 1+\lambda \\ 1+\lambda \\ 1+\lambda \end{pmatrix}$$

And to find  $\lambda$  we use equations B1 and A4

$$\lambda = \frac{2(C_{11} + 2C_{12} - 2C_{44})}{(C_{11} + 2C_{12} + 4C_{44})}$$

BIBLIOGRAPHY

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Reference no	۰.
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.

1.	G.Wannier, Phys. Rev., <u>52</u> , 191, (1937).
2.	G.Dresselhaus, J.Phys. Chem. Solids, $\underline{1}$ , 14, (1956).
3.	L.H.Hall, J.Bardeen,F.J.Blatt, Phys. Rev. <u>95</u> , 559,
4.	G.G.Macfarlane, T.P.McLean, J.E.Quarrington and V.Roberts, Phys. Rev. <u>108</u> , 1377, (1957).
5.	G.G.Macfarlane, T.P.McLean, J.E.Quarrington and V.Roberts, Proc Phys. Soc. (London), <u>71</u> , 863, (1958).
6.	S.Zwerdling, B.Lax, L.M.Roth and K.J.Button, Phys. Rev. <u>114</u> , 80, (1959).
7。	G.G.Macfarlane, T.P.MacLean, J.E.Quarrington, and V.Roberts, Phys. Rev. Letters, <u>2</u> , 252, (1959).
8.	W.H.Kleiner and L.M.Roth, Phys. Rev. Letters, 2, 334,
9.	G.E.Picus and G.L.Bir, Sov. Phys. Solid State, 1,
10.	J.Bardeen and W.Shockley, Phys.Rev. <u>80</u> , 72, (1950).
11.	R.J.Elliott, Phys.Rev. <u>108</u> , 1384, (19 <b>57</b> ).
12.	W.G.Pfann and F.L.Vogel (Jr), Acta Met. <u>5</u> ,377, (1957).
13.	S.G.Ellis, Transistors I, publication of the R.C.A. laboratories, Princeton N.J.
14.	A.Uhlir (Jr), Transistor Technology, Bell Laboratory series, <u>3</u> 133,(1958), edited by F.J. Biondi.
15.	J.M.Buck and F.S.McKim, J.Electrochem. Soc. $\frac{103}{(1956)}$
16.	S.I.Novikova, Sov. Phys. Solid State, $2,37,(1960)$ .
17.	E.K.Plyler, N.M.Gailar and T.A.Wiggins, J.Res.Nat.Bur. Stand. <u>48</u> , 221, (1952).
18.	R.J.Elliott, Phys. Rev. <u>96</u> , 280, (1954).
19.	E.O.Kane, J.Phys.Chem. Solids, <u>6</u> , 236 , (1958).
20.	W.Kohn and J.M.Luttinger, Phys. Rev. <u>98</u> ,915, (1957).
21.	P.J.Price, Phys. Rev. <u>124</u> , 713, (1961).
22.	M.E.Fine, J.App1. Phys. <u>24</u> , 338, (1953).

## Reference no.

- M. Cardona and W Paul, J.Phys. Chem. Solids <u>17</u>, 138, (1960).
   H.Y.Fan, M.L.Sheppard and W.Spitzer, Proceedings of the Atlantic City Photoconductivity Conference 1954.\*
- 24. For instance, W.Paul and D.M.Warschauer, J.Phys. Chem. Solids, 8 196, (1959).
- 25. J.J.Hall, Phys.Rev. 128, 68, (1962).
- 26. E.Antoncik, Czech. J.Phys. 5, 449, (1955).
- 27. For instance, E.Burstein, G.Picus and N.Sclar, Proceedings of the Atlantic City Photoconductivity Conference 1954.\*
- 28. D.L.Dexter, Proceedings of the Atlantic City Photoconductivity Conference 1954.\*
- 29. W.Read, Dislocations in crystals, McGraw Hill publication.
- 30. W.H.Brattain and H.B.Briggs, Phys. Rev. 75, 1705,(1949).
- 31. B.W.Levinger and D.R.Frankl, J.Phys. Chem. Solids, 20, 281, (1961).
- \* Proceedings of the Atlantic City Photoconductivity conference1954, edited by R.G.Breckenridge et al published by J.Wiley and sons Inc N.Y. 1955.