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III-4. Interband Piezo-Absorption in GaP

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The fine structure induced by uniaxial stress of the indirect optical absorption edge in GaP has been investigated at 80°K in the stress range 0–50 kg/mm². An observed splitting of a threshold at 5310Å lead to the determination of deformation potential constants associated with valence and conduction band. The effect of stress on an absorption peak at 5420Å indicated that this was due to transitions from the valence band to a zero wave vector impurity state.

§ 1. Introduction

The electronic band structure in GaP[1] is characterized by three equivalent conduction band valleys along the $\langle 001 \rangle$ k-directions and a degenerate valence band extremum at $k=0$ (In connection with this work we shall neglect the small linear terms in the valence band structure at $k=0$). In the presence of shear strain the conduction band valleys in general become non-equivalent in energy and the valence band splits up into two sublevels. To first order in strain these effects can be described by the deformation potentials Ξ_u, Ξ_d, a, b, and d introduced for Si and Ge by Herring and Vogt[2] and by Pikus and Bir[3]. A quantitative determination of the splitting in GaP is possible through a stress-optical investigation of the indirect absorption edge, a method which has been applied previously to Si and Ge[4]. For strain-free GaP, Gershenzon *et al.*[5] found that this edge as in Si and Ge[6] consists of a series of humps each corresponding to creation of an indirect exciton (with binding energy E_{ex}) with simultaneous emission of a phonon (with energy E_p). The absorption for a particular phonon component is characterized by a square root rise above the threshold energy given by:[6]

$$E_t = E_c - E_v - E_{ex} + E_p \,, \qquad (1)$$

where E_c and E_v are extremum energies for conduction and valence band, respectively. For photon energies $\hbar\omega < E_t + E_{ex}$ an additional 3/2 power absorption is present.

Neglecting shifts with strain of E_{ex} and E_p we have

$$\frac{dE_t^{ij}}{dX} = \frac{dE_c^{i}}{dX} - \frac{dE_v^{j}}{dX} \,, \qquad (2)$$

where X is the uniaxial (tensile) stress and i and j ($i=1, 2, 3$ and $j=1, 2$) specify the band pair. These quantities are given in Table I for four stress directions in the $[1\bar{1}0]$ plane. Here, it is seen that [111] stress yields two different values of E_t (for a particular phonon component) whereas the other directions of stress lead to a split-

Table I. Energy shifts with uniaxial tensile stress X of conduction and valence band, expressed by the deformation potentials Ξ_u, Ξ_d, a, b, and d and the compliance coefficients S_{11}, S_{12}, and S_{44}.

Stress direction	dE_c^i/dX		dE_v^j/dX	
	Conduction band valley		Valence band level	
	[100], [010]	[001]	upper	lower
[001]	$-p/3+q$	$2p/3+q$	$r+t$	$-r+t$
[111]	q	q	$s+t$	$-s+t$
[110] [112]	$\pm p/6+q$	$\mp p/3+q$	$(r^2/4+3s^2/4)^{1/2}+t$	$-(r^2/4+3s^2/4)^{1/2}+t$

$p=\Xi_u(S_{11}-S_{12})$; $q=(\Xi_d+\Xi_u/3)(S_{11}+2S_{12})$;
$r=|b|(S_{11}-S_{12})$; $s=|d|S_{44}/2\sqrt{3}$; $t=a(S_{11}+2S_{12})$;

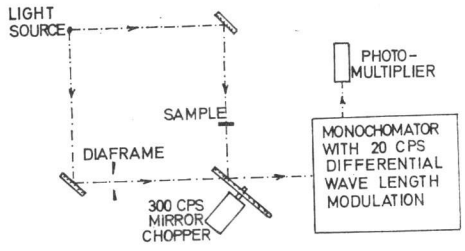

Fig. 1. Optical set-up.

ting into four levels.

§ 2. The Experimental Procedure

The experimental set-up used is shown in Fig. 1. Without wave length modulation the signal detected can be decomposed into two components, a DC-signal equal to $(c+T(\lambda))S_0(\lambda)/2$ where $T(\lambda)$ is the transmission of the sample for the wave length λ, c is the transmission of the diaframe, and $S_0(\lambda)$ is the signal for $c=T(\lambda)=1$, and a 300 cps square signal of $(c-T(\lambda))\,S_0(\lambda)$ peak-to-peak. Then, a signal $S(\lambda)$ proportional to the ratio

$$S(\lambda)=\frac{c-T(\lambda)}{c+T(\lambda)}\,, \qquad (3)$$

was electronically produced. Applying a 20 cps differential wave length modulation (by means of a harmonic motion of a mirror in the monochromator) one obtains a modulation $\Delta S(\lambda)$ of the ratio signal $S(\lambda)$. Hence,

$$\Delta S(\lambda)=\Delta\lambda\frac{dS(\lambda)}{d\lambda}=-\Delta\lambda\frac{2c}{(c+T(\lambda))^2}\frac{dT(\lambda)}{d\lambda}\,. \qquad (4)$$

The Te doped (1.8×10^{18} cm^{-3}) GaP single crystals were cut into bars with dimensions of $1\times1\times10$ mm^3 and a compressive force of 0–50 kg was applied in the longitudinal direction. The strain apparatus used is described elsewhere.[4]

§ 3. The Experimental Results

With c of eq. (3) equal to $T(\lambda)$ in the transparent region of GaP ($\lambda>5500$Å) the measurements of $S(\lambda)$ lead to a zero stress absorption coefficient (80°K) as shown in Fig. 2. Apart from a factor of two in the absorption level the spectral behaviour for $\lambda<5300$Å is in agreement with the results of Gershenzon *et al.*[5] whose assignment of the thresholds with respect to phonons being emitted is adopted here. The absorption peak at 5420Å has an integrated intensity of 20 meV·cm^{-1}.

The detailed structure of the thresholds was revealed by recording $\Delta S(\lambda)$ with wave length

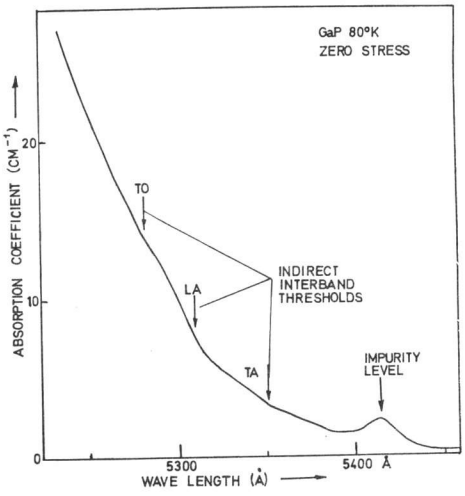

Fig. 2. Zero stress absorption coefficient versus wave length for GaP at 80°K.

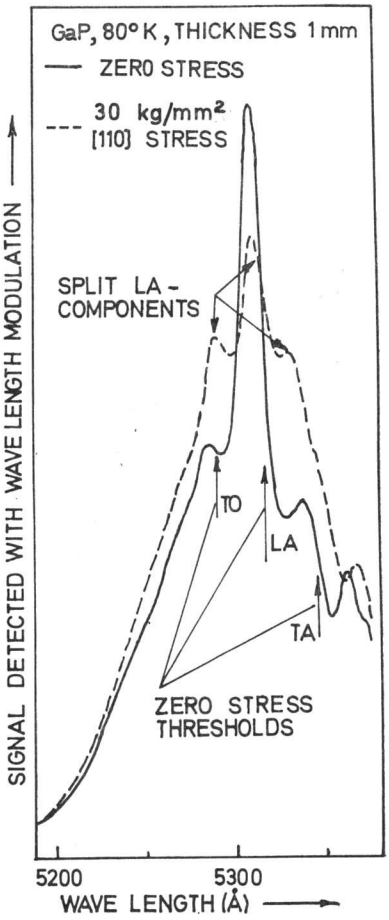

Fig. 3. Signal $\Delta S(\lambda)$ (cf. eq. (4)) for unstrained and strained GaP at 80°K.

modulation (see Fig. 3). In this case the square root absorption rise of each component appears as a peak (cf. eq. (4)) whose low energy half point is the threshold energy E_t. The influence of a stress $X||[110]$ (Fig. 3) is seen to be a splitting into three components of the pronounced peak from the LA (longitudinal acoustic) phonon. Further splitting of the middle component was observed by using linearly polarized light in which case the relative strengths of the split components depend on the polarization direction e with respect to the stress axis X. A plot of the observed threshold energies versus compressive [110] stress is shown in Fig. 4.

A splitting into four components of the LA peak was evident from the measurements whereas only two components from a similar splitting of the weaker TA peak were resolved. The components denoted by "α_2" and "α_4" in Fig. 4

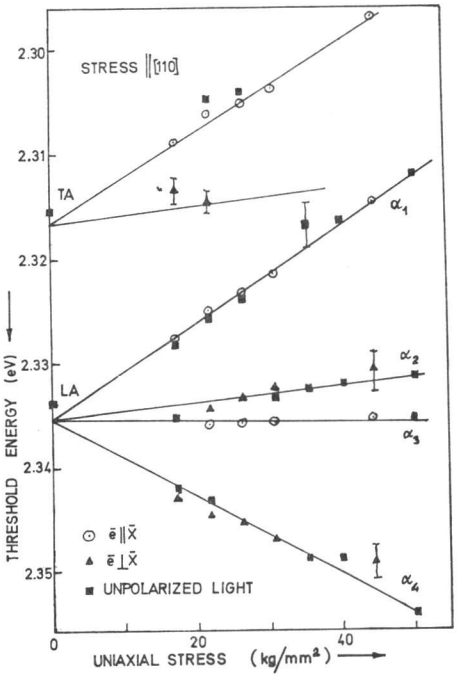

Fig. 4. Threshold energies versus stress parallel to the [110] direction for the LA and the TA components.

Table II. Slopes dE_t/dX in units of meV·mm²/kg observed for the splitting of the LA phonon component in GaP.

Stress || [110]:	0.47,	0.09,	0.02	and	−0.35
Stress || [112]:	0.61,	0.26,	0.21	and	−0.14
Stress || [111]:	0.32	and	−0.03		

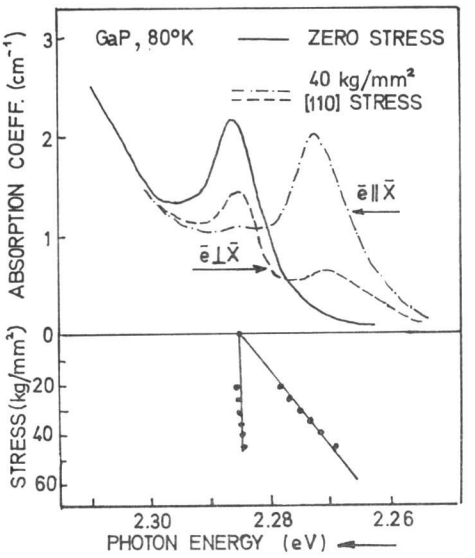

Fig. 5. Splitting for [110] stress of the absorption peak at 5420Å. Spectra with and without stress are shown above and the dependence on stress of the maxima is shown below.

were absent for $e||X$ while no component vanished for $e\perp X$. Spectra for $X||[112]$ were similar to those of [110] stress although the slopes of the splitting lines were altered. For $X||[111]$ the number of LA components was two and the peak with highest energy vanished for $e||X$. The slopes associated with the three stress directions investigated are listed in Table II.

The absorption coefficient for [110] stress near the peak at 5420Å is shown in Fig. 5. It is seen here that the peak splits up into two components of which one is absent for $e||X$. The slopes of the splitting lines are 0.35 and 0 meV·mm²/kg. The number of components, their relative strengths versus polarization direction, and the slopes were found to be independent of the direction of the uniaxial stress.

§ 4. Interpretation

The observed number of components into which the LA component splits up with stress is consistent with the results in Table I. Here, the 4

Table III. Deformation potential constants in eV for GaP derived from the splitting of the LA component. The estimated compliance coefficients $(S_{11}, S_{12}, S_{44})=(1.05, -0.34, 1.55)\times10^{-6}$cm²/kg are used.

Ξ_u	6.2±0.6	b	−1.3±0.15
$\Xi_d+\Xi_u/3-a$	3.7±0.6	d	−4.0±0.5

constants p, $|r|$, $|s|$, and $q-t$ can be determined from the 10 slope values of Table II. A consistent set of constants lead to the deformation potentials in Table III. In the absence of available elastic constants of GaP we have used compliance coefficients 10% lower than those of GaAs.[7] This is estimated on basis of an empirical dependence of elastic constants of the III–V compounds on the lattice constants.

An interesting feature of the experimental results is that the valence band splitting (0.35–0.38 meV·mm^2/kg) is almost stress isotropic. According to Hasegawa[8] this implies that M_J in the JM_J representation of the valence band states is a good quantum number for any direction of stress (M_J quantized along the stress axis). Thus, selection rules based on the M_J classification are valid for any direction of stress. If we assume that the dominating intermediate state in the indirect process is the conduction band at $\boldsymbol{k}=0$ (as in Ge) it can be shown[4] that transitions from the $M_J=3/2$ band is forbidden for $\boldsymbol{e}\|\boldsymbol{X}$. Then, from the observed dependence on polarization of the split components we can conclude that the $M_J=3/2$ band moves down for compressive stress. According to the conventions[3] for the signs of b and d this implies that both quantities are negative in GaP.

For any of the stress directions investigated the extrapolation to zero stress of the splitting lines yielded an energy 1–2 meV above the true zero stress threshold energy (see Fig. 4). Such behaviour was also observed in Ge and Si[4] and can be explained by a (stress independent) high stress binding energy E_{ex} of the exciton different from the zero stress value.

The absorption peak at 5420Å is probably due to the Te dopant. The characteristic features of the splitting of this peak are that the number of components, the dependence of their relative strengths on polarization, and the slopes of the splitting lines are stress isotropic. These phenomena and the fact that the separation is equal to that found for the valence band sublevels indicate that we are dealing with transitions from the valence band into a zero wave vector impurity state with symmetry similar to that of the conduction band at $\boldsymbol{k}=0$.

§ 5. Discussion

The signs as well as the magnitudes of the deformation potentials found here for GaP are very similar to those of Si. Thus, Ξ_u and $\Xi_d+\Xi_u/3-a$ differ by less than 20% from the data of Si[4]. This may be a consequence of the similarity with regard to positions in the reduced zone of the conduction band valleys. The magnitudes of the shear deformation potentials b and d of the valence band are somewhat lower than in Si, but they are very close to the results[4] of Ge: $b=-1.8\pm0.4$ eV and $d=-3.7\pm0.4$ eV.

Our results are equivalent with a shift of the indirect band gap with hydrostatic pressure equal to $(-4.5\pm1.5)\times10^{-6}$ eV/atm (80°K) while a value of -1.1×10^{-6} eV/atm is reported[9] for 300°K.

Our interpretation of the absorption peak at 5420Å is entirely consistent with that given by Thomas and Gershenzon[10] of a similar peak in the flourescence spectrum of sulphur doped GaP. The peak denoted by A in ref. 10) (5360Å at 77°K) was assumed to be due to creation of zero wave vector excitons bound to neutral donors. In connection with our results this model implies that a strain induced splitting of the valence band leads to an equal splitting of the peak associated with this exciton. Since the exciton is derived from the $\boldsymbol{k}=0$ conduction and valence band states the selection rules are similar to those of the direct interband transitions at $\boldsymbol{k}=0$.

Acknowledgements

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DISCUSSION

Paul, W.: I should like to make three comments:

1) It should be said that your hydrostatic pressure coefficients for Si and GaP are about a factor of two larger than those determined directly from hydrostatic pressure measurements. These latter coefficients are among the best we have, and have been deduced from different types of experiment in several laboratories. I cannot see in your fine experiments where the trouble might lie, but I do think both your experimental operation and interpretation should be searched in order to find out what the true coefficient is.

2) I should like to suggest a modification of your ideas on the absorption you associate with impurity levels described by (000) band function, which you compare to the zero wave vector excitons bound to neutral donors of Thomas *et al.*. It is possible in both cases the electron wave function concerned has some component of (000) band function involved, and it is this that gives the finite matrix element for the transition. Nevertheless the energy eigenvalue may be determined by the off-axis (100) minima. I realize one would then expect to see splittings of your line into more components, however. Nevertheless if your suggestion here is correct, it would be quite in line with several pieces of recent evidence establishing the existence of impurity levels in the energy gap which are described predominantly or exclusively by high-energy extrema.

3) Finally, I should like to emphasize the isotropy with stress of your splittings. This is consistent with similar observations from resonance experiments in Ge and Si, and exciton line splittings found by Thomas in CdTe. I think it is the same phenomenon as the empirical rule for pressure coefficients in the whole Ge family, which says that the hydrostatic pressure coefficients are the same for the same transitions, and not necessarily the strain coefficients. The argument for the greater relevance of the stress variable is an experimental one. Explanations which try to relate low compressibilities or compliance coefficients to high deformation potential are obviously troubled by the fact that the deformation potentials describe isolated groups of electrons, whereas the mechanical coefficients relate to the change in energy of all of the electrons.

Thomas, D. G.: There may be a simplification of the splitting of excitons when they are bound to an impurity, because the singlet valley orbit electron states will probably be the states involved in the transition, and these will not have such a complex splitting pattern as will the free electron. Perhaps this is relevant to the simpler splitting of the impurity transition reported in this paper.

Fisher, P.: In your table showing the various values of the deformation potential constants for GaP, Ge and Si,* I noticed that the value which you obtain for the shear deformation potential constant for conduction electrons in germanium was 16.2 eV. Fritzsche has obtained a value of 19.2 eV for this quantity from piezo-resistance measurements, while from Wilson and Feher's piezo-spin resonance values of the ratio of this quantity to the chemical splitting, using our values for the latter, we obtain 19.2 eV for this quantity, also. Have you any explanation for the discrepancy between your value and those of other workers?

Balslev, I.: No, I have no explanation for this disagreement. But I find that the method described in this paper is the most direct in determining the shear deformation potentials.

Meyer, N. I.: In connection with the question concerning the value of Ξ_u in germanium, I should like to mention that piezo-birefringence measurements in our laboratory have yielded values of about 17 eV. Also some Russian workers have obtained such low values from an analysis of the absolute value of the acoustic phonon dominated mobility in Ge.

Hensel, J. C.: I would like to supplement the comments by W. Paul and P. Fisher by remarking that there also exist serious discrepancies between the valence band deformation potentials in germanium and silicon determined by cyclotron resonance with those quoted in the present paper and ref. 4) determined optically.

Ramdas, A. K.: I would like to draw attention to another type of experiment which

* Results from this paper and of ref. 4).

seems to indicate that the $p_{3/2}$ valence band of silicon shows the same splitting (for the same stress) for different directions of uniaxial stress viz. the splitting of the excitation line $2p^1$ of neutral group III acceptors in Si associated with the transition for which the ground state is associated with the $p_{3/2}$ valence band and the excited state associated with the $p_{1/2}$ valence band. These results are discussed in our paper (VI-3) presented in this conference.