Piezoemission of GaSb: Impurities and Bound Excitons

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The effect of an uniaxial stress on the impurity and exciton lines is studied. The deformation potentials are determined. The analysis of the uniaxial-stress data shows that the residual acceptor in GaSb is a single acceptor and that the two bound excitons β and γ are excitons bound to neutral acceptors. We emphasize the importance of the j-j splitting in the γ complex. The temperature dependence of the photoconductivity signal reveals the thermal ionization of the complexes. The variation of the intensities of the lines with the temperature and the excitation rate gives evidence concerning the processes by which the injected carriers are bound at low temperature.

I. INTRODUCTION

Absorption of excitons and impurities in gallium antimonide was studied by Johnson and Fan[1] at 4.2 °K. Three sharp peaks and a low-absorption tail were observed in the neighborhood of the intrinsic absorption edge. The absorption tail is sensitive to the concentration of impurities and to the sample temperature. It was associated by Johnson and Fan with electronic transitions to the conduction band from impurities near the valence band. In unintentionally doped materials, the residual acceptor level at 0.034 eV from the valence band is responsible for the absorption tail. This level was attributed by Habegger and Fan[2] to the level for a second hole bound by the imperfection center. The level for the first bound hole was situated at 0.07 eV from the valence band. These conclusions came from recombination experiments on p-type samples into which lithium had been diffused and from impurity–valence-band absorption measurements in undoped and compensated samples.

The sharp peaks (α, β, γ) observed in the neighborhood of the absorption edge have been assigned to exciton and exciton-impurity complexes. But it was not possible to correlate the observed peaks with the known concentration of impurities. The effects of an applied magnetic field on the absorption spectrum were investigated and the results were interpreted in terms of spin splitting of the electron. Hopfield[3] studied the quantum chemistry of bound-exciton complexes. His results and the experimental dissociation energies of the observed bound excitons were used by Johnson and Fan to discuss the nature of the impurity involved. Let us review briefly the different possibilities. In GaSb, where $m_e < m_h$, there is a possibility that the exciton can be bound to a ionized donor. We call the binding energy of the system composed of the exciton plus an ionized donor W and the donor ionization energy E_i. The ratio W/E_i must be less than 1.2 (case of the bound molecular ion H_2^*). The observed binding energies are $W \simeq 9$ meV for the β complex and $W \simeq 16$ meV for the γ complex. They would correspond to a ionization energy of the donor much greater ($E_i \geq 7.5$ meV for the β complex and $E_i \geq 13$ meV for the γ complex) than the theoretically expected donor ionization energy $E_i \simeq 3$ meV. The binding of the exciton to a neutral donor must be also ruled out. In this case, the energy difference between the exciton-impurity complex and the free exciton should be some small fraction of the donor ionization energy. The dissociation energies of the complexes ($E_D = 5.1$ meV for the β complex and $E_D = 14.2$ meV for the γ complex) would also correspond to a donor ionization energy much greater than the theoretically expected one. The case of a ionized acceptor has been controversial. According to their calculations, Sharma and Rodriquez[4] conclude that in GaSb, an exciton can be bound to a ionized acceptor. In fact they are wrong, Lévy-Leblond[5] confirms the calculations of Hopfield[3] and shows there is no binding of an electron to a ionized acceptor when the mass ratio m_h/m_e is greater than a critical value $\sigma_c \lesssim 1$. In GaSb, $m_h/m_e \simeq 4.35$: For this material, an exciton cannot be bound to a ionized acceptor. Johnson and Fan[1] have considered the case of a neutral acceptor: The value $E_D = 5.1$ meV for the β complex is 0.14 times the energy of the level (1) (0.034 eV) attributed to the residual acceptor commonly present in undoped GaSb. Although on the basis of a larger m_h/m_e ratio one might have expected a smaller ratio of E_D/E_a in GaSb than in silicon (0.10) instead of the observed value (0.14), Johnson and Fan conclude that the β complex might be a combination of an exciton with the residual acceptor in the neutral state.[6] On the same basis as $E_D/E_a \simeq 0.14$ the large value of E_D for the γ peak (14.2 meV) requires a value $E_a \simeq 0.1$ eV, which is more than any acceptor ionization energy observed in GaSb. Johnson and Fan conclude that the complex γ cannot be an exciton bound to a neutral acceptor. They suppose that the γ complex may correspond

to the binding of the hole of the exciton in an excited state of the acceptor.

We have studied the piezoemission from unintentionally doped samples of GaSb ($p \simeq 2 \times 10^{17}$ cm^{-3}) for the purpose of obtaining further information on the nature of the impurities and exciton-impurity complexes. The variation of the spontaneous emission and photoconductivity signals with temperature were used also to obtain better understanding of the emission processes. We show that the residual acceptor level is not a double acceptor level but a single acceptor level. The interpretation of our piezoemission data gives an experimental support to the conclusion of Johnson and Fan on the nature of the complex β. We show that the complex γ, as the complex β, is an exciton bound to a neutral acceptor. We emphasize the importance of the j-j splitting in the complex γ.

II. EXPERIMENTAL BACKGROUND

The excitation source was either a high-pressure mercury lamp, a GaAs laser operating at 77 °K, a cw ionized-argon laser or an electron beam. The sample was mounted on the cold finger of a metallic Dewar or immersed in pumped liquid helium. To minimize reabsorption, we observed the light emitted from the sample side which was irradiated by the excitation light or the electron beam. The detector was a cooled PbS cell.

The apparatus used for uniaxial experiments is a standard one. The samples were purchased from Cominco Ltd. They were p type with a carrier concentration of $\simeq 2 \times 10^{17}$ cm^{-3} at 77 °K. They were oriented in the [100], [110], and [111] orientations. The sample volume was about $1 \times 1 \times 8$ mm. In the uniaxial stress experiments, the temperature of the sample was about 35 °K. However, for the study of the γ line, the sample was immersed in pumped liquid helium but the applied stress was much weaker. The polarized-light study was made with an H-R Kodak Polaroid.

TABLE I. Emission lines of GaSb. Some of the lines observed at great wavelength may be the phonon replicas of other lines observed at shorter wavelength. For example, the A line may be the phonon replica of the γ line and the F and D lines the phonon replicas of the B line.

Lines	Position of the maximum at $T = 4$ °K or $T = 20$ °K when the line is absent at 4 °K (meV)	Absorption peak (Ref. 1) at $T = 1.4$ °K (meV)	Binding energies of the complexes (meV)	Binding energies of the hole in the acceptor (meV)
α	810 (20 °K)	810	2 (Ref. 8)	
β	803 (20 °K)	805	9	
I_0	800 (20 °K)	800		
γ	796	796	16	
I_1	777.5			34.5
A	765			
I_2	758			54
B	752			
C	730			
D	722			
E	711			
F	694			
G	680			

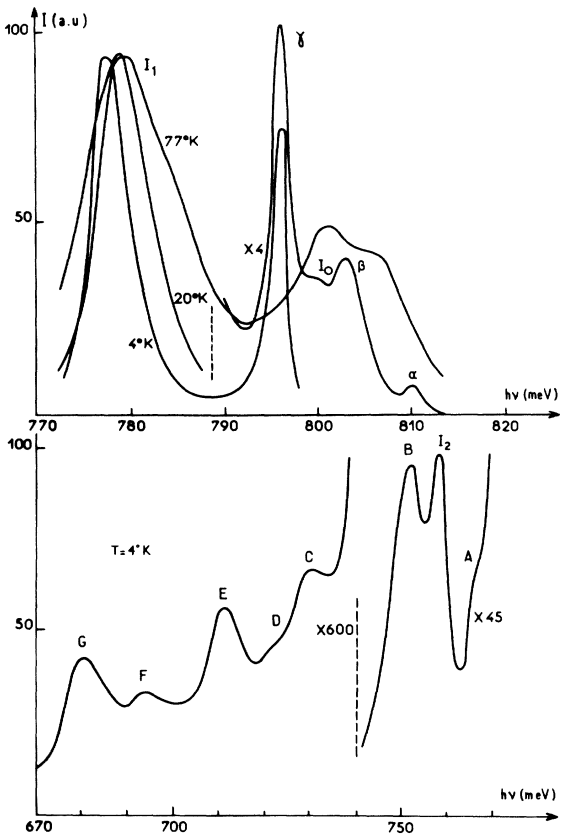

FIG. 1. Emission spectrum of GaSb at low excitation, for different temperatures (a.u. indicates the use of arbitrary units).

III. RESULTS

Recombination emission was studied by Johnson *et al.*[7] at 4.2, 80, and 300 °K for various types of samples. Different bands were observed, corresponding to electron-hole recombination at 80 and 300 °K, recombination of the γ exciton-impurity complex at 4.2 °K, and recombination involving various levels in the energy gap.

We report here spectra at several temperatures. At 20 °K, the emission spectrum shows more lines than in the 4.2 °K spectrum obtained by Johnson *et al.* The observed emission lines and the binding energies of the complexes are listed in Table I. The binding energy of the free exciton is taken from the work of Thanh.[8] The spectrum is shown in Fig. 1.

The I_1 line is due to the recombination on the residual acceptor level (1). The line at 796 meV corresponds to the γ peak seen in absorption and

emission by Johnson.[1,7] The line situated at 803 meV at 20 °K is at a slightly lower energy than that of the absorption peak β. The highest energy line is at the same photon energy $h\nu = 810$ meV as the absorption peak α.

As Fig. 1 shows, a weak line I_0 is seen at 800 meV. The corresponding absorption line has not been reported in the absorption measurements of Johnson and Fan.[1] However, it is possible that the slight bump seen at approximately 800 meV on their presented absorption spectrum corresponds to the I_0 line.

IV. RESIDUAL ACCEPTOR LEVEL

A. Fermi Level in Unintentionally Doped Samples at Low Temperature

The low-energy tail of the absorption spectrum at 4.2 °K in undoped samples was associated by Johnson and Fan[1] with electronic transitions to the conduction band from the residual acceptor level at 0.034 eV from the valence band. However, at low temperature, the photoconductivity spectrum (Fig. 2) does not show any signal at the same photon energy. In contradiction to the explanation given by Johnson and Fan, Habegger and Fan[2] concluded that in unintentionally doped samples at 4 °K, the Fermi level is closer to the valence band than the level (1) of the residual acceptor. We give here a new possible interpretation of the absorption tail. We associate the tail with electronic transitions from the spin-orbit split-off band to the residual acceptor level. The intensity of the absorption at some meV from the edge is about 5–10 cm^{-1}. It is comparable with the intervalence band absorption observed by Kosicki[9] at 300 °K, in GaSb samples ($p \simeq 10^{17}$ cm^{-3}) at high pressure. Furthermore, the value of the spin-orbit splitting energy found by Kosicki at 300 °K is about 0.75 eV. It is known that the spin-orbit splitting energy is not very sensitive to the pressure or the temperature. The value found by Kosicki could correspond to the difference between the edge absorption energy ($E \simeq 765$ meV) and the ionization energy of the acceptor ($E_a \simeq 34$ meV).

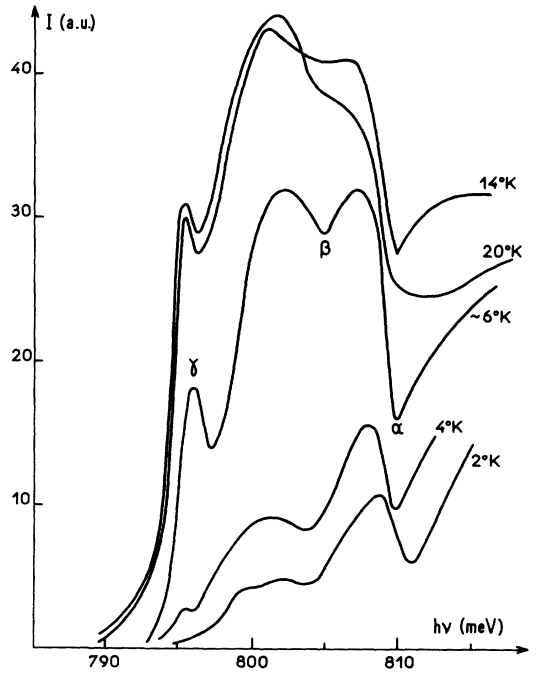

FIG. 2. Photoconductivity spectra of GaSb at different temperatures. The spectra have been reduced to the same vertical scale in order to have the same photoconductivity signal in the intrinsic region of the spectrum at $h\nu = 830$ meV.

The photoconductivity spectrum (Fig. 2) starts at an energy of 795 meV at 2 °K. We attribute the signal to the transition to the conduction band from a partly compensated shallow acceptor level at 12 meV from the valence band. This value is close to the value found theoretically by Thanh[8] ($E_a = 10$ meV). These conclusions agree with the results of Effer and Etter[10] in Hall-effect measurement on similar samples. They fit their data with a model of two energy levels, 11 and 32 meV above the valence band with corresponding acceptor concentrations of 1.0×10^{16} and 1.4×10^{17} cm^{-3} and a donor concentration of 9.0×10^{15} cm^{-3}.

B. Single Acceptor Level

1. Quantum Efficiency and Radiative Lifetime

Quantum efficiency was measured at $T \simeq 5$ °K by comparing the intensities of the fluorescent light and the exciting light reflected by a plane mirror which was substituted to the sample. We find a quantum efficiency

$$\eta = \tau_{NR}/(\tau_R + \tau_{NR}) \simeq 70\%,$$

where τ_{NR} and τ_R are, respectively, the nonradiative and radiative lifetimes of the electrons in the conduction band.

Precision is not easy to evaluate. It is estimated to be ± 20%. The I_1 line and the γ line contribute $\frac{4}{5}$ and $\frac{1}{5}$ to the total emitted light.

From the value of the quantum efficiency ($\eta \simeq 0.5$) of the recombination on the acceptor level and the value of the total lifetime measured by Parsons[11] ($\tau \simeq 6$ nsec), one can derive the value of the radiative lifetime, $\tau_R = 12$ nsec. This value can be compared with the radiative lifetime corresponding to the recombination of an electron in the conduction band on a single acceptor level. From the intrinsic absorption data given by Johnson and Fan,[1] in the frame of the effective-mass theory, one finds $\tau_R = 33$ nsec. In view of the crudeness of our approximations, we conclude that the two determinations of τ_R are roughly in agreement.

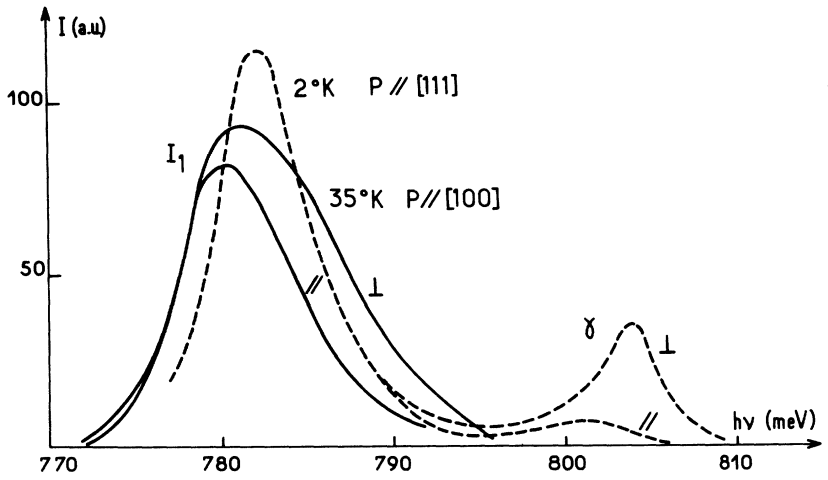

FIG. 3. Spectrum of the I_1 line for two polarization directions when the crystal is stressed along a crystallographic axis: solid line, $T \simeq 35$ °K, $P = 1000$ kg/cm^2 along the [100] direction; dotted line, $T = 2$ °K, $P = 1800$ kg/cm^2 along the [111] direction; the intensity of the spectrum with the polarization direction perpendicular to the stress axis has been multiplied by 3.2 in order to have the same intensity at the maximum for any direction of polarization.

2. Uniaxial Stress

The effect of uniaxial stress has been studied at two temperatures, 35 and 2 °K. At 35 °K, for a direction of polarization of the light perpendicular to the stress axis, one sees a broadening of the line which corresponds to two not-very-well-resolved components and only one component for the parallel direction (Fig. 3). At 2 °K, only one component is observed in any direction of polarization.

In contrast with the case of the β line which will be discussed later, the position of the component at 2 °K agrees with the position of the lower-energy component observed at 35 °K. The selection rules agree very well with theory for a $(\Gamma_6 - \Gamma_8)$ transition, for example a band to band one, when one takes into account the thermalisation of holes in the upper state of the split Γ_8 level. In particular, at 2 °K the ratio of the intensities for parallel and perpendicular polarization directions is found to be equal to 3.2, a value which corresponds roughly to the theoretical value of 4 at low stress in the effective-mass approximation.[12] The deformation potentials b' and d' are determined by the splitting of the line for a stress in the [100] and [111] directions (Fig. 4). The splitting is determined by taking twice the energy difference between the parallel component and the mean position of the components as determined by the average shift of the α line. The rough decomposition of the perpendicular broad line into two components confirms this determination.

The slope of the average position of $\alpha(4.6 \times 10^{-6}$ eV kg^{-1} cm^2) agrees with the previous determinations of the hydrostatic shift of the band gap.[13] One finds $b' = -1.2$ eV, $d' = -3.5$ eV. Good agreement is found for the [110] direction. The sign of the deformation potentials is determined by selection rules: The lower-energy component is allowed and the upper-energy component is forbidden for parallel polarization. From comparison with the deformation potentials b and d for the free-exciton line,[14] one finds $b'/b = 0.6$ and $d'/d = 0.75$. These ratios have the same order of magnitude as the ratios found theoretically in Ge and Si by Bir, Butikov, and Pikus[15] and experimentally in GaAs by Bhargava and Nathan,[16] for single acceptor levels. We conclude that the level (1) is definitively a single acceptor level.

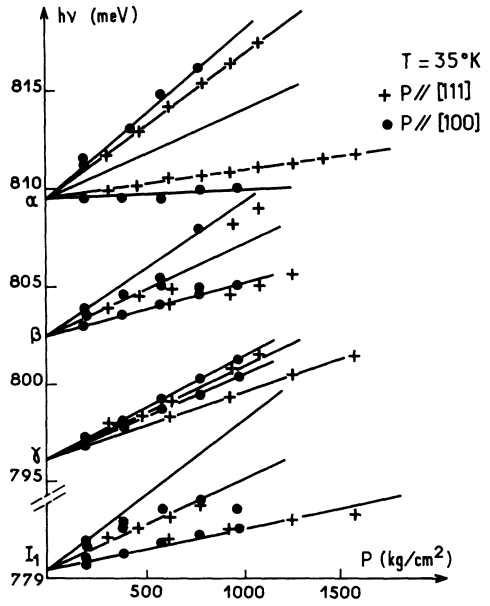

FIG. 4. Shift of the maxima of the emission lines, $T \simeq 35$ °K: plus, $P \parallel [111]$; solid circle, $P \parallel [100]$.

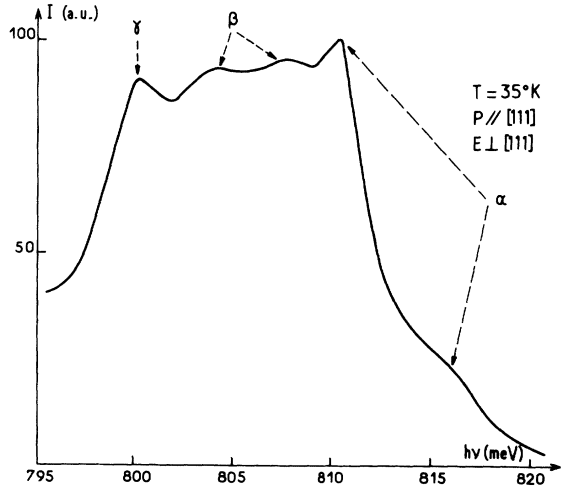

FIG. 5. Emission spectrum of GaSb, $T \simeq 35$ °K; $P = 1000$ kg/cm^2 along the [111] axis. The polarization direction is perpendicular to the stress axis.

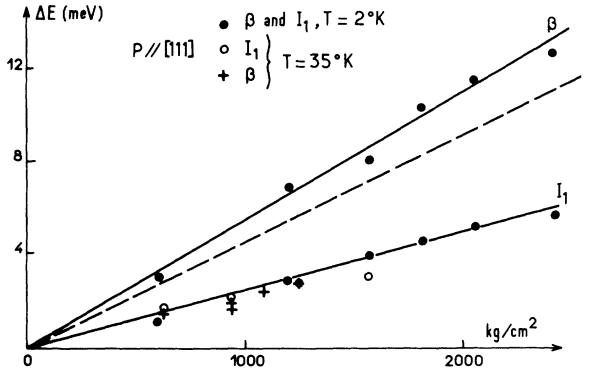

FIG. 7. Shift of the maxima of the β and I_1 lines as a function of the applied stress: $T = 2$ °K, $P \parallel [111]$. The source is a He-Cd laser. The dotted line roughly represents the hydrostatic shift. We have reproduced on the same figure the shift of the low-energy component of the β and I_1 lines at $T \simeq 35$ °K (plus, β line; circle, I_1 line) in order to show the different behavior of the lines at the two temperatures.

V. β COMPLEX

A. Uniaxial Stress

The effect of a uniaxial stress on the β line was studied at 2 and 35 °K. At 35 °K, we see two components of the line in the spectrum (Fig. 5). The lower-energy component is allowed for parallel and perpendicular directions of polarization; the higher-energy component seems to be allowed essentially for a direction of polarization perpendicular to the stress axis. These results are very similar to the case of the I_1 line. But, at 2 °K, only one component is observed in any direction of polarization (Fig. 6), and the position of the component completely disagrees with the position of the lower-energy component observed at 35 °K. The shift of this component with stress applied along the [111] direction is 5.5×10^{-6} eV kg^{-1} cm^2 and the shifts of the two components observed at 35 °K are 2.4×10^{-6} and 6×10^{-6} eV kg^{-1} cm^2 (Fig. 7). These results can be explained if the complex is an exciton bound to a neutral acceptor.

Morgan[17] has done the analysis of the effect of a uniaxial stress on such an exciton. The results are plotted in Fig. 8(b) and Table II for the case where the j-j splitting and the crystal-field splitting of the two-holes state and the electron-hole

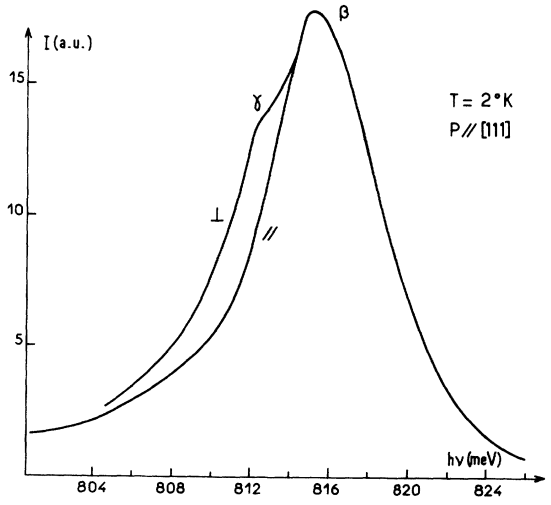

FIG. 6. Spectrum of the β line for two directions of polarization, $T = 2$ °K, $P = 2400$ kg/cm^2 along the [111] axis. The source is a He-Cd laser. The bump on the low-energy side of the line with the perpendicular polarization is due to the γ line.

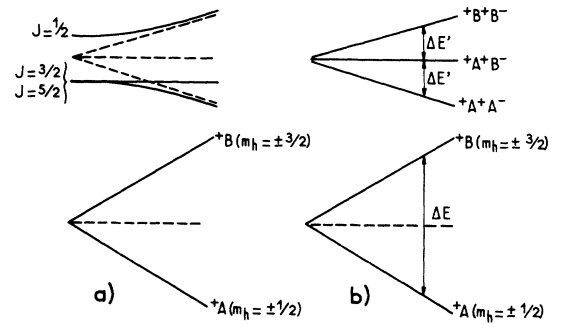

FIG. 8. Excitons bound to neutral acceptors. Splitting of the exciton states and splitting of the final state of the transition. (a) The j-j splitting of the two-hole state is much larger than the strain energy of the exciton states. Electron-hole spin-orbit energy and crystal-field splitting are neglected. (b) The strain energy is much larger than any initial splitting of the exciton states.

TABLE II. Selection rules for the optical decay of excitons bound to neutral acceptors, when the strain energy is much larger than any initial splitting of the exciton states.

Initial state \ Final state	$m_h=\pm\frac{1}{2}$ ($+_A$)			$m_h=\pm\frac{3}{2}$ ($+_B$)		
	π	σ_x	$\Delta(h\nu)$	π	σ_x	$\Delta(h\nu)$
$(+_B+_B-)$	0	0	$\Delta E'+\frac{1}{2}\Delta E$	0	3	$\Delta E'-\frac{1}{2}\Delta E$
$(+_A+_B-)$	0	6	$\frac{1}{2}\Delta E$	8	2	$-\frac{1}{2}\Delta E$
$(+_A+_A-)$	4	1	$-\Delta E'+\frac{1}{2}\Delta E$	0	0	$-\Delta E'-\frac{1}{2}\Delta E$

spin-orbit energy δ are neglected.

In this simple model, the wave function corresponding to any exciton state is the product of the wave functions of two holes taken in any valence band, the wave function of one electron in the conduction band and an envelope function. When the two holes are taken from the same valence band, the product of the holes wave functions is antisymmetrized. The two valence bands $J=\frac{3}{2}$, $m_h=\pm\frac{1}{2}$, and $m_h=\pm\frac{3}{2}$ are called A and B and the corresponding holes, $+_A$ and $+_B$. The sign (−) denotes the electron.

We obtain three exciton states corresponding to the three configurations $+_A+_A-$, $+_A+_B-$, $+_B+_B-$ in the initial state and two one-hole states $+_B$ and $+_A$ in the final state.[18] The separation $\Delta E'$ between two exciton states is determined by the envelope function of the exciton. As pointed out by Bailey,[19] this splitting can be much less than the splitting ΔE of the one-hole state.

In this case, we obtain four lines: one at an energy $(-\Delta E'+\frac{1}{2}\Delta E)$ away from the average position of the components. [This line comes from the lower-energy $(+_A+_A-)$ state and is observed at low temperature]; two lines at $-\frac{1}{2}\Delta E$ and $+\frac{1}{2}\Delta E$ coming from the middle state $(+_A+_B-)$; and one line at $(\Delta E'-\frac{1}{2}\Delta E)$ coming from the upper-energy state $(+_B+_B-)$.

The total number of lines is reduced to two when $\Delta E'\ll\frac{1}{2}\Delta E$. The essential point is that the line observed at *low temperature* is almost at the same position as the *higher-energy component* observed at higher temperature (the difference of energy is only $\Delta E'$). It is exactly what we observe since the shift of the line observed at 2 °K and the shift of the higher-energy component observed at 35 °K are, respectively, 5.5×10^{-6} and 6×10^{-6} eV kg^{-1} cm^2. We conclude that the complex β is definitively an exciton bound to a neutral acceptor. From the difference of energy between the two lines, we deduce the splitting $\Delta E'$ of the exciton state and from the difference of energy between the two components observed at 35 °K, we deduce the splitting ΔE of the bound hole in the final state.

The separation $\Delta E'$ of two exciton states is about $\frac{1}{7}$ the splitting of the final state ΔE. We determine roughly the deformation potentials of the bound hole $b''\simeq-1$ eV, $d''\simeq-3$ eV, and the deformation potential of the bound exciton, $D\simeq-0.5$ eV.

B. Identification of Acceptor Responsible for β Line

The deformation potential b'' and d'' of the bound hole in the final state is not very different from the deformation potential b' and d' obtained for the I_1 line (Fig. 7). Level (1) at 0.034 eV from the valence band is very likely to be the ground state of the transition.

Furthermore, we evaluate the number of absorbing centers for the transition and we compare it with the known number of impurities (1), $N_a=2\times10^{17}$ cm^{-3}. This number of absorbing centers is obtained from absorption data when the oscillator strength is known. We evaluate f from the theory of Rashba and Gurgenishvili.[20] The ratio of the oscillator strengths f_b for one bound exciton to that of a free exciton per unit cell f_f is

$$f_b/f_f=(E_0/E_D)^{3/2}, \tag{1}$$

where $E_0=(2h^2/m)\,(\pi/v)^{2/3}$. v is the volume of the unit cell, m is the equivalent mass, and E_D is the dissociation energy of the bound exciton. This calculation implies that the binding of the exciton is small compared to the internal binding energy of the free exciton which is 2 meV. Although this is not exactly the case, an order of magnitude of the oscillator strength can still be obtained.

From the absorption data of Johnson and Fan,[1] we evaluate $f_f\simeq6\times10^{-6}$ and obtain from Eq. (1) $f_b=0.22$. Hence, the radiative lifetime is found to be $\tau=250$ nsec. This long time is favorable for observing laser effect on the line. The concentration of the absorbing centers may be derived from the Smakula[21] equation

$$Nf=3.55\times10^{16}\int\alpha\,dE, \tag{2}$$

where N is in atoms/cm^3, α is the absorption coefficient in cm^{-1}, and E is in eV. From the absorption data of Johnson and Fan,[1] we find $N=2\times10^{17}$ cm^{-3}.

This number is in good agreement with the concentration of impurities (1) at 0.034 eV from the valence band. This large concentration of centers may be related to the width of the β line and to its broadening with increasing temperature or the rate of excitation. We conclude as Johnson and Fan that the β complex is an exciton bound to the neutral residual acceptor which is a simple acceptor as shown before.

VI. γ COMPLEX

A. Uniaxial Stress

The effect of a uniaxial stress has been studied at 2 °K. We obtain results which are different from those obtained from the I_1 and β lines (see

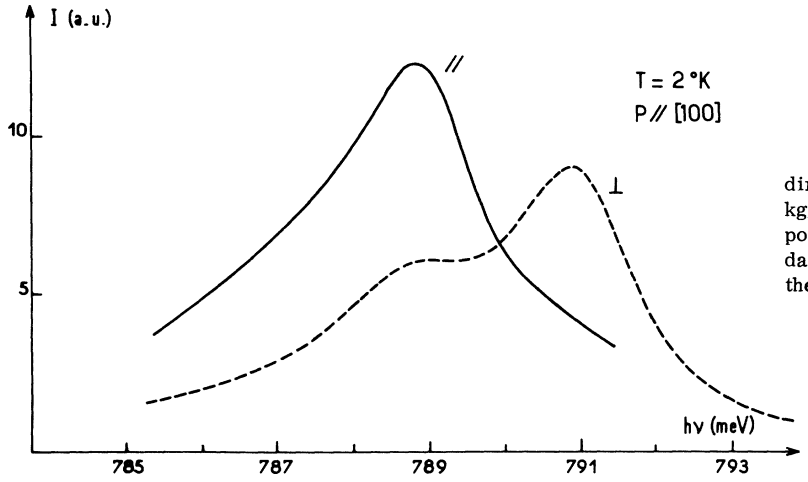

FIG. 9. Spectra of the γ line for the two directions of polarization, $T=2$ °K, $P=1450$ kg/cm^2 along the [100] direction: solid line, polarization parallel to the stress axis; dashed line, polarization perdendicular to the stress axis.

Fig. 9): (a) We observe a splitting of the line into two components. (b) The two components of the line are of the same order of magnitude even for an energy splitting much larger than the thermal energy kT. (c) The observed splitting is much weaker than the splitting of the other lines.

The splitting could be attributed to the orientation degeneracy of noncubic centers being lifted but the selection rules are not in agreement with the selection rules found by Kaplyanski *et al.*[22] for noncubic centers. In addition, and in contrast with the prediction for noncubic centers, these observed selection rules do not change when using a stress applied along the [110] direction, and we are looking at the emission of light from two perpendicular faces of the sample.

Finally, an important dichroism is observed in absorption measurement at 2 °K with stress applied along each direction (Fig. 10). Our conclusion is that the γ line cannot be due to the emission from a noncubic center and that the final state of the transition in emission (initial state in absorption) is split by the stress.[23]

We use the analysis performed by Morgan[17] of the effect of uniaxial stress on an exciton bound to a neutral acceptor when the j-j splitting Δ of the two-hole state is large relative to the strain energy $\Delta E'$ and when the electron-hole spin-orbit energy δ is very small.

The results are presented in Fig. 8(a) and in Table III. At zero stress the upper-energy line is five times less intense than the lower-energy line. Then, the weak bump seen in absorption at 800 meV and the I_0 line seen in emission could correspond to the upper state. With an applied stress, the two levels $J=\frac{3}{2}$ and $J=\frac{5}{2}$ are nearly degenerated. At

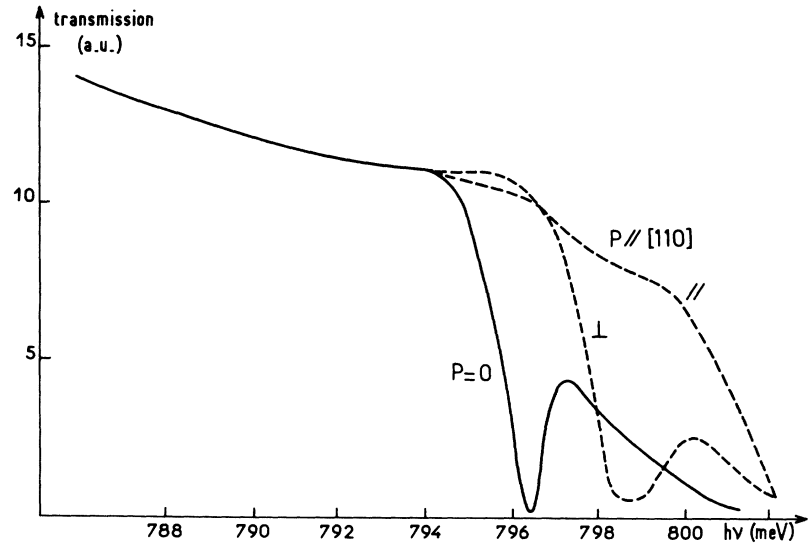

FIG. 10. Transmission spectrum of GaSb, $T=2$ °K; solid line, $P=0$; dashed line, $P=450$ kg/cm^2 along the [110] direction.

TABLE III. Selection rules for the optical decay of excitons bound to neutral acceptors when j-j splitting of the two-hole state is much larger than the strain energy of the exciton state. Electron-hole spin-orbit energy and crystal-field splitting are neglected.

Initial state \ Final state	$m_h = \pm\frac{1}{2}$ $(+_A)$		$m_h = \pm\frac{3}{2}$ $(+_B)$	
	π	σ_x	π	σ_x
$J=\frac{1}{2}$	4	1	0	3
$J=\frac{5}{2}$, $J=\frac{3}{2}$	4	13	16	7

low temperature one observes the transitions from these levels to the bound hole level, Morgan finds a polarization ratio $(I_\sigma/I_\pi)=\frac{13}{4}$ for the higher-energy (final $m_h=\pm\frac{1}{2}$) component of the line split by strain and $(I_\sigma/I_\pi)=\frac{7}{16}$ for the lower-energy (final $m_h=\pm\frac{3}{2}$) component.

These selection rules correspond to our data (though the weak component of the higher-energy component in the π polarization was not observed). We conclude that the complex γ is definitively an exciton bound to a neutral single acceptor.[24]

From the data for the [100] and [111] directions (Fig. 11) we obtain the deformation potentials of the bound hole $b\simeq -0.5$ eV, $d\simeq -1$ eV. The precision of the measurement is poor because some friction exists at low stresses and also because the two components are not very well resolved. The precision is estimated to be about 30%. With this precision, we obtain rough agreement between the values obtained in the [100], [111], and [110] directions for the bound hole. The I_2 line at 758 meV is attributed to the recombination of free electrons on an acceptor level (2) at 0.054 eV from the valence band. Very likely the neutral acceptor to which the exciton is bound to form the γ complex is the same since the splitting of the I_2 line (observed only for a stress applied along the [111] direction) is very nearly the same as the splitting of the γ line. The dissociation energy of the complex γ would then be equal to 0.2–0.25 times the ionization energy of the impurity.

B. Stark Effect from Charged Impurities

At low temperature and weak excitation, the line shape is quite asymmetric, tailing towards the low-energy side of the peak (Fig. 12). We interpret this anomalous spectral shape of bound-exciton emission as being essentially caused by the Stark effect from charged impurities. Owing to this effect, the energy of a bound exciton is lowered. Hanamura[25] theoretically treated this tailing phenomenon by assuming that among charged impurities randomly distributed in the crystal, only the one which is located nearest to a bound exciton contributes to the Stark effect on that bound exciton and that the nearest impurity obeys the Poisson distribution. The spectral line shape of the bound-exciton emission is given as a function of ΔE, which is the shift of the energy of the $1s$ state bound exciton, by the following expression:

$$I(\Delta E) = CA|\Delta E|^{7/4}\exp(-\tfrac{4}{3}A|\Delta E|^{-3/4}),$$

and $A=\pi N a_0^3 (4E_{ex})^{3/4}$, where N is the concentration of charged impurities, a_0 and E_{ex} are the effective Bohr radius and binding energy of intrinsic exciton, and C is a proportionality constant.

As seen in the figure, the fit is quite satisfactory, assuming $N=10^{16}$ cm^{-3}, except for the high-energy side of the line. This result is very similar to that obtained by Kukimoto *et al.* on bound-exciton-emis-

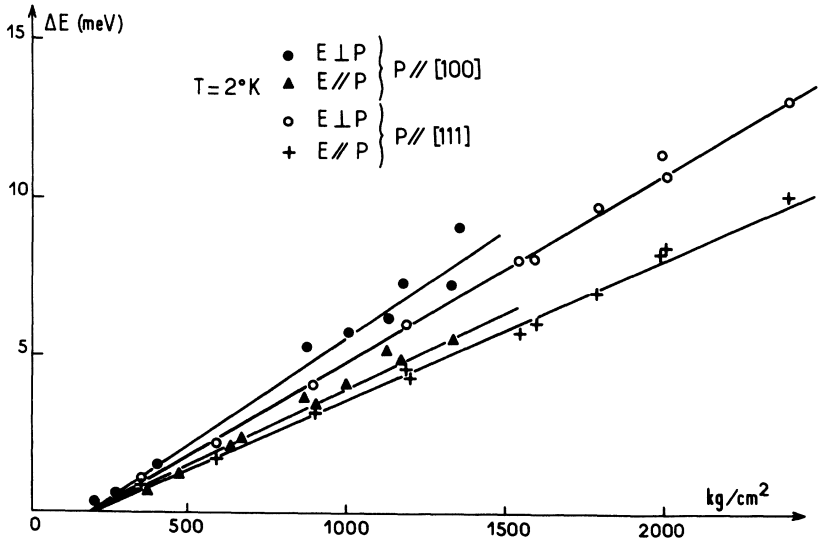

FIG. 11. Shift of the maxima of the γ line as a function of the applied stress at $T=2$ °K: solid circle, $P\parallel[100]$, $E\perp P$; solid triangle, $P\parallel[100]$, $E\parallel P$; open circle, $P\parallel[111]$, $E\perp P$; plus, $P\parallel[111]$, $E\parallel P$.

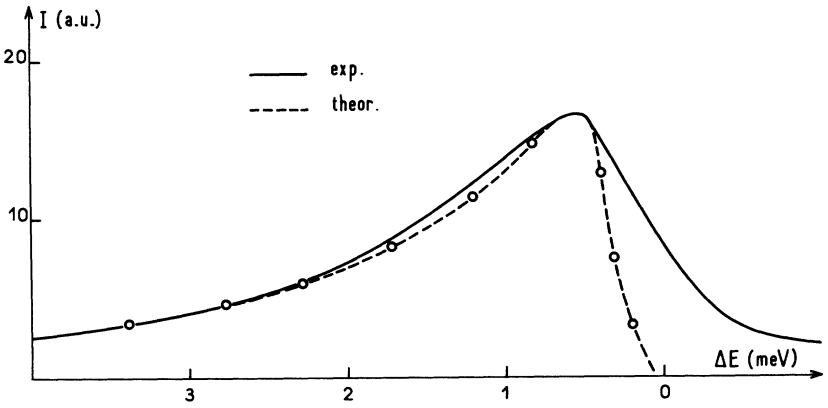

FIG. 12. Spectrum of the γ line, $T = 2\,^{\circ}\mathrm{K}$. The exciting source is a high-pressure mercury lamp. Solid line, experimental data. Dashed line, theoretical curve with $N = 10^{16}\ \mathrm{cm}^{-3}$.

sion lines in CdS.[26]

VII. DEPENDENCE WITH TEMPERATURE OF PROCESSES OF FORMATION AND IONIZATION FOR β AND γ COMPLEXES

A. Ionization of Complexes

In photoconductivity experiments, the peak corresponding to the γ line at a photon energy of 796 meV and the signal corresponding to the β line at a photon energy of 805 meV are growing quickly when the temperature is increasing (Fig. 2). A similar peak at a photon energy of 796 meV is also clearly seen in the excitation spectrum of the I_1 line at $T \simeq 7\,^{\circ}\mathrm{K}$ (Fig. 13). These facts are attributed to the thermal excitation into the conduction band of the electrons which are weakly bound in the β and γ complexes. From the variation with temperature of the ratio (I_γ/I_1) of the two lines intensities (Fig. 14), annihilation of the exciton in the γ complex and recombination on the residual acceptor level, one can estimate the binding energy of the electron in the γ complex to be $\Delta E \simeq 3.5$ meV.

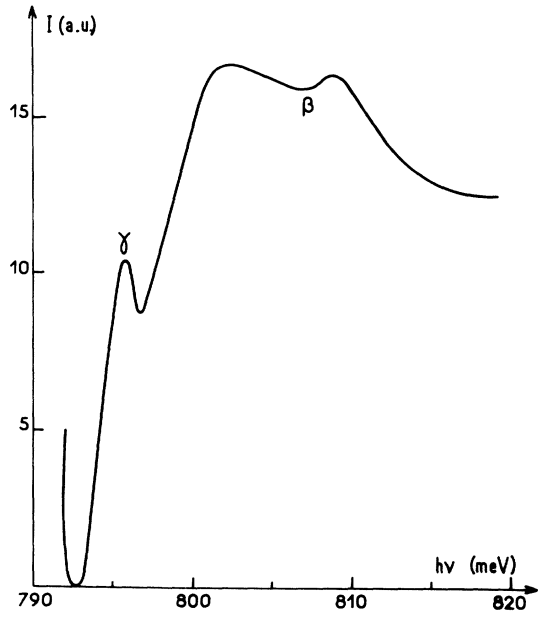

FIG. 13. Exitation spectrum of the I_1 line: $T \simeq 7\,^{\circ}\mathrm{K}$.

B. Formation of Complexes

At any temperature, the ratio of the α- and β-line

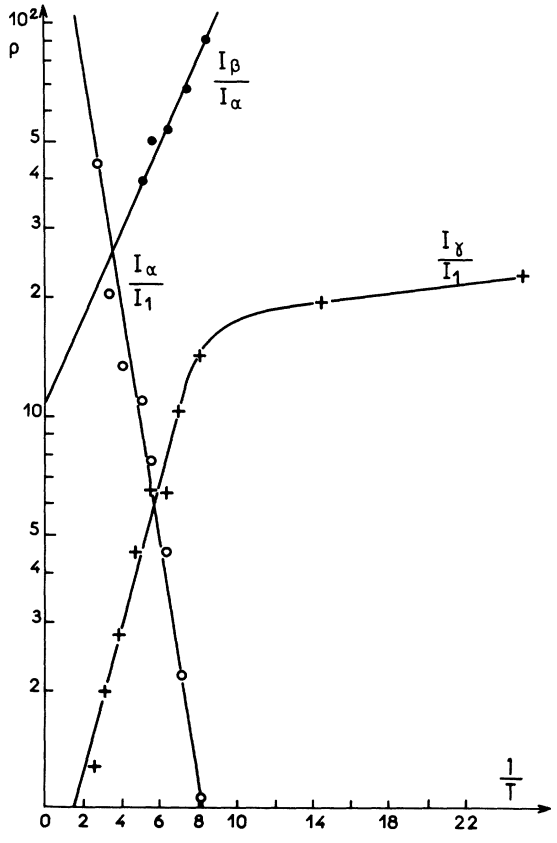

FIG. 14. Plot of the ratios of the intensities of the α line to the I_1 line intensity (open circle), the γ line to the I_1 line intensity (plus), and the β line to the α line intensity (solid circle) as a function of the temperature.

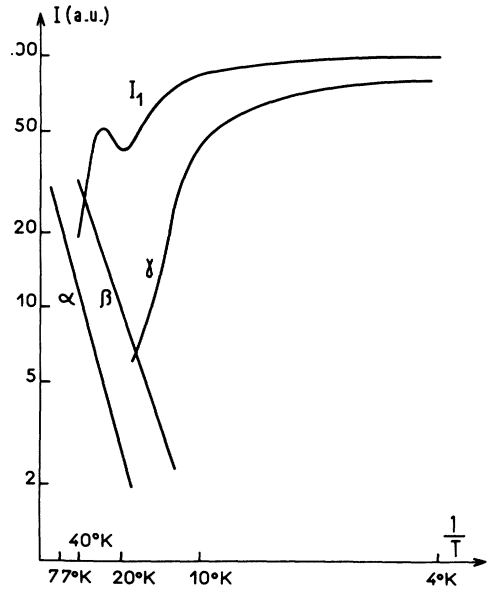

FIG. 15. Variation of the α, β, γ, and I_1 line intensities with temperature.

intensities does not depend on the intensity of the excitation. This is easily understood in the case where there is successively formation of free excitons and binding of these excitons. The increase of these line intensities with temperature (Fig. 15) reflects essentially the increase of the concentration of free holes.

The variation of the α- and β-line intensities is linear or quadratic with the rate of excitation depending upon whether the injected hole concentration is low or high with respect to the concentration of thermally excited holes from the shallow acceptors.

We obtain a quite different behavior of the γ line: (a) The γ line intensity varies linearly (Fig. 16) with the rate of excitation throughout the temperature range where it is studied (except at 2 °K with a very weak excitation). (b) The γ line intensity is important at low temperature and decreases as the temperature increases.

We can explain these facts if we suppose that a part of the acceptor (2) already has bound two holes at equilibrium: This is possible since the Fermi level at helium temperature is near a simple acceptor (ionization energy $\simeq 10$ meV) and a fraction of the corresponding holes can be captured by acceptor (2) in a state at nearly the same energy. Another possibility is the existence of electron traps. The filling of these traps obtained at very low excitation would provide an equal number of holes captured by acceptor (2). Then the linear behavior of γ would reflect the electron density.

The important assumption in this model is that the single acceptor (2) can bind two holes. In the case of the H^- ion, the binding energy of the first electron bound to the proton is about ten times the binding energy of the second one. In our case, we find two binding energies, $E_a \simeq 54$ meV and $E_b \simeq 12.5$ meV (from the energy difference between the binding energy of the complex 16 meV, and the binding energy of the electron in the complex, 3.5 meV).

VIII. CONCLUSIONS

The analysis of our uniaxial-stress experiments has shown that the residual acceptor is a single acceptor. It has permitted the determination of the nature of the bound excitons β and γ: The two excitons are definitively excitons bound to neutral acceptors. But the behavior of the two lines with an applied stress is quite different because of the importance of the j-j splitting of the two-hole state in the γ complex. In both cases the stress-induced splitting of the exciton state (initial state) is much weaker than the stress-induced splitting of the bound hole (final state). The identification of the impurity center responsible for the β and γ complexes is made by a comparison between the splitting of the acceptor level and the splitting of the final state of the transition from the bound-exciton state. We conclude that the β and γ complexes are combinations of an exciton with an acceptor in the neutral state of which the ionization energy is, respectively, 0.034 and 0.054 eV.

A model is tentatively proposed to explain the temperature dependence and excitation intensity

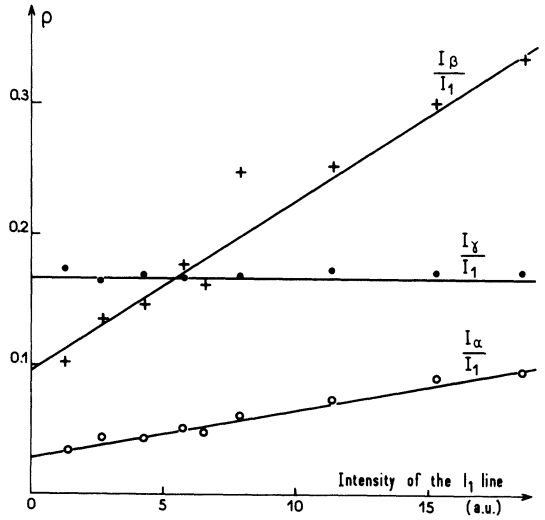

FIG. 16. Plot of the ratios of the intensities of the α, β, and γ lines to the intensity of the I_1 line as a function of the intensity of the I_1 line; $T = 20$ °K; the exciting source is a cw GaAs laser. Open circle, α/I_1; plus, β/I_1; solid circle, γ/I_1.

dependence of the lines intensities. In this model, the acceptor responsible of the γ line binds two holes. It must be pointed that uniaxial-stress experiments can provide some interesting information on the nature of the bound excitons. Magneto-optical studies are good tools to give evidence for the electrons in the complexes, but often cannot reveal the number of holes since the g factor of holes is often very small. On the contrary, uniaxial-stress experiments into which the valence band is split, are sensitive to the number of holes. The two types of experiments complement each other. However, the lines are rather broad and the poor spectral resolution of the principal stress subcomponents prevents us from making definitive assignment.

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[6]This conclusion is not in agreement with the previous conclusion that the residual acceptor is a double acceptor.

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[18]In the paper by P. T. Bailey [Phys. Rev. B 1, 588 (1970)], there seems to be some confusion about the ordering of energy states. For a compressive stress in GaAs, the Γ_6 valence band stays higher in energy than the Γ_7 valence band, but, in the final state of the transition, which is a one-hole state of the transition, one must invert the order of these two levels. Furthermore, the α state $(+_A+_A-)$ which is formed by taking holes in the upper valence band $(+_A)$ must lie at a lower energy than the β state $(+_B+_B-)$. Finally, we do not quite understand how Bailey gets the strengths of the transitions corresponding to the two polarizations. His results do not agree with the strengths which can be calculated from the coupling coefficients in the T_{2d} group.

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[23]The recent article by F. H. Pollak and R. L. Aggarwal [Phys. Rev. B 4, 432 (1971)] confirms our results. In piezoreflectivity, they do not observe any splitting, but from their data, it is evident that there is an important dichroism in reflectivity. The light polarized parallel to the stress axis is less absorbed than the light polarized perpendicularly. This means that the low-energy component which is essentially allowed with the parallel polarization(see Fig. 9), is not seen because of the thermalization of the carrier in the initial state in absorption. Furthermore, the shift of the line observed by Pollak does not exactly correspond to the shift of the center of gravity of the α line. The difference between the two shifts is not equal to half the splitting we have observed in emission. We do not know if this discrepancy is due to the lack of precision in the measurements or if it is due to a shift of the final state in absorption.

[24]Our results could correspond also to the case of an exciton bound to a singly ionized double acceptor. But this complex is unlikely for the common band structure where the electron mass is not sufficiently heavy (see Ref. 3).

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