VALLEY-ORBIT SPLITTING OF THE NITROGEN-BOUND

EXCITON IN GaP : N

H. Mathieu, L. Bayo, J. Camassel, P. Merle and A. Raymond

Centre d'Etudes d'Electronique des Solides, Université des Sciences et Techniques du Languedoc, 34060 - MONTPELLIER-CEDEX, FRANCE

We report the first measurement of the valley-orbit splitting of the N-bound exciton in GaP. We obtain $E_{12} = 24$ meV.

Alt**p**ough considerable attention has been given to the theoretical description of the binding of excitons to nitrogen both in GaP and GaAsP (Faulkner [1], Kleiman et al [2], Hsu et al [3], Ross et al [4], Jaros et al[5]) no conclusive solution exists. From the more recent calculations [5], it appears that the computed composition of the wavefunction, i.e. the coefficients Ank (eq.(2-15) in Ref.[5]) shows that most of the coefficients are very small except those located near F-X line in the Brillouin zone. Moreover the states of X, conduction band valleys have large wavefunction coefficients (see table [1) or Ref.[5]. It results that, according to the existence of three equivalent X_1 minima, the valley-orbit coupling splits the triplet ground state into a singlet 1s (Γ_1) and a doublet 1s (Γ_{12}). Now in both the one-band one-site approximation and in more elaborated computer calculations [1,5] the excited state due to the intervalley mixing, 1s (Γ_{12}) , is found to the unbound. But any experimental confirmation has been given up to date. We present the first measurement of the valley-orbit splitting $E_{12} = E(\Gamma_{12}) - E(\Gamma_{1})$. It is rather difficult to get E_{12} directly from experimental optical spectra for several reasons. First in visible spectroscopy (creation or recombinaison of bound excitons) the only state which is radiative is the Γ_1 ground state because of a strong admixture whith the direct minimum of the conduction band. In contrast the antisymetric Γ_{12} state, which is not admixed, has zero no-phonon oscillator strength. Second in infrared spectroscopy the transition $\Gamma_1 \rightarrow \Gamma_{12}$ is dipole for-bidden. Third the electronic Raman scattering which has been used to obtain E_{12} for donor in GaP : S, Se, Te [6]may not be used because the Γ_1 ground state is empty without optical excitation. And fourth if the T_{12} state is unbound as suggested by theoretical calculations [1,5] it must be observed above the threshold of the excitonic band gap, this is very difficult. As a consequence, up to date, no report of E_{12} has been given. Under calibrated uniaxial stress we have found possible to determine E_{12} unambiguously.

The N-exciton state corresponds to the electron bound by the short-range nitrogen potential and the hole bound by the long-range Coulomb attraction of the electron. The ground state is made of an electron localised in the Γ_{1} nitrogen state and a hole associated with the Γ_{8} valence band maximum. To zero-order, the wave function which corresponds is a product of the electron wave function by the hole wave function times an envelope function. The resulting zero-order exciton states next couple by j-j interaction to form a J = 1 triplet of energy $E = E_{0} + 5/8 \gamma$ and, at lower energy, a J = 2 quintet of energy $E = E_{0} - 3/8 \gamma$. The transition between these states and the J = 0 crystal ground state lead to the A line (dipole allowed) and B line (dipole forbidden). The energy difference between A and B has been measured to be $\gamma = 0.9$ meV. The effect of the crystal field is a mixing of the exciton basis states and hence a splitting which is

expected to be very small has not been observed.

The stress dependence of a given bound-exciton state can be written as the sum of three different contributions : i) a simple hydrostatic dependence A_h ; ii) a shear dependence of the bound electron, E (Γ_1) , which reflects the change in degeneracy on the conduction band valleys; iii) a shear dependence of the |JM > states related to be splitting of the Γ_{g} hole states :

i) the hydrostatic component induces only a shift of the center of gravity of the exciton, given by: $A_h = a (S_{11} + 2 S_{12}) X$,

(1)

where a is the hydrostatic deformations potential of the bound exciton and S it the elastic compliance constants of the crystal.

ii) the shear strain lifts the degeneracy of the three conduction band valleys and modifies the exciton states by the so-called "valley-repopulation effect". This, shifts and mixes between them the Γ_1 and Γ_2 valley-orbit split states, giving rise to a nonlinear stress-induced shift of the ground state of the bound exciton. The treatment, based on the "valley-repopulation" model has been developped by Price [7] for donors on Germanium and successfully used by Wilson and Feher [8] for donors in silicon, by Onton and Morgan [9] for Bi-excitons in GaP : Bi, and by Mathieu et al [10,11] for (D°X) complexes in GaP : S. The shear strain dependence of the electron state of the exciton is given by [10] :

$$E(\Gamma_1) = \frac{1}{2} \Delta \left[-1 + x - 3 \left(1 + \frac{2}{3} x + x^2 \right)^{1/2} \right], \quad (2)$$

with

 $x = \frac{E_2 S}{6 \wedge}$.

 $\Delta = \frac{E_{12}}{3}$ is the intervalley-coupling matrix element and E_2 the shear deformation potential of the conduction band.

 $s = 2 (s_{11} - s_{12}) X \text{ for } X // [001]$ = $-(S_{11} - S_{12}) \times \text{for } \times //[110]$

= 0 for X // [111].

iii) taking account of the stress-induced coupling between Γ_{8v} and the spin-orbit split-off valence band, the splitting of the Γ_8 hole state into the V₁ (M = ± 1/2) and V₂ (M = ± 3/2) sublevels is given by :

$$V_1 = \varepsilon + 2 \frac{\varepsilon'^2}{\Delta_0 + \varepsilon} ; \quad V_2 = -\varepsilon ,$$

where $\boldsymbol{\Delta}_{\boldsymbol{\alpha}}$ is the spin-orbit splitting of the valence band. $\boldsymbol{\varepsilon}$ and $\boldsymbol{\varepsilon}'$ which have been measured to be isotropic are given by :

$$\varepsilon = \frac{d_1 + 2 d_2}{2 \sqrt{3}} S_{44} X = (b_1 + 2 b_2) (S_{11} - S_{12}) X ,$$

$$\varepsilon' = \frac{d_1 - d_2}{2 \sqrt{3}} S_{44} X = (b_1 - b_2) (S_{11} - S_{12}) X .$$

b1, b2, d1 and d2 are the deformation potentials defined in Ref. [12].

The splitting of the valence band separates the J = 1 and J = 2 exciton states into series of sublevels (one for each value of [M] quantized along the stress axis) and mixes those having the same value of M[9] . Now, for N-exciton, on account of the relative magnitudes of the j-j interaction

($\mathbf{X} = 0.9 \text{ meV}$) and of the valence band splitting (2 $\varepsilon \simeq 4 \text{ meV/Kbar [12]}$), the nonlinear behavior resulting from the stress induced mixing of the $|\text{JM}\rangle$ states will be only found under very low stress conditions.

In the high stress range, $\epsilon >> \gamma$ the stress dependence of the sublevels are simply given by :

E	(1 ± 1>)	=	3 γ/8 - V ₂	,	(3-a)
E	(1 0>)	=	5 $\gamma/8 - v_1$,	(3-b)
E	(2 ± 2>)	=	- 3 y/8 - V ₂	,	(3-c)
E	(2 ± 1>)	=	$- \gamma/8 - V_1$,	(3-d)
E	(2 0 >)	=	- 3 y/8 - V1		(3-e)

The resulting stress dependence and selection rules of the bound exciton ground state is then given by :

$$A' = E_{o} + A_{h} + E (\Gamma_{1}) + E (|1 \pm 1\rangle) \sigma , \quad (4-a)$$

$$A^{-} = E_{o} + A_{h} + E (\Gamma_{1}) + E (|1 0 \rangle) \sigma \pi , \quad (4-b)$$

$$B^{+} = E_{o} + A_{h} + E (\Gamma_{1}) + E (|2 \pm 2\rangle) \quad \text{forbidden}, \quad (4-c)$$

$$B^{-} = E_{o} + A_{h} + E (\Gamma_{1}) + E (|2 \pm 1\rangle) \sigma , \quad (4-d)$$

$$B^{+-} = E_{o} + A_{h} + E (\Gamma_{1}) + E (|2 \pm 0\rangle) \quad \text{forbidden}, \quad (4-e)$$

 E_{o} is the zero-order threefold degenerate energy state of the bound exciton and corresponds to the absence of intervalley mixing and j-j interaction.

In order to obtain the valley-orbit coupling matrix element we must extract the shear dependence E (Γ_1) from the resulting stress dependence of the exciton state. This is done in the following way :

$$\mathbf{A}_{001} - \mathbf{A}_{111} = \mathbf{E} \left(\Gamma_1 \right)_{001} - \mathbf{E} \left(\Gamma_1 \right)_{111} = \frac{1}{2} \Delta \left[3 + \mathbf{x} - 3 \left(1 + \frac{2}{3} \mathbf{x} + \mathbf{x}^2 \right)^{1/2} \right] .$$
(5)

In the same manner

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$$A_{110} - A_{111} = E(\Gamma_1)_{110} - E(\Gamma_1)_{111}.$$
 (6)

The experimental results are given in Figs. 1 and 2. The full lines (Fig.2) correspond to the calculated curves (eqs. (5), (6)) using for the shear deformation potential E_2 the value 6.9 eV which corresponds, within the experimental error, to the value measured for the free excitons [12]. The best fit is obtained by using a stress-dependent value of the intervalley coupling matrix element Δ giving by :

$$\triangle (X) = \triangle + kX.$$

We find $\Delta = 8$ meV and k = 0.4 meV/Kbar. X is negative for a compression.

The zero-stress value $\Delta = 8$ meV gives for the valley-orbit splitting of the bound exciton the value $E_{12} = 24$ meV. It is to be note that this value confirms that the first excited state of the N-exciton is degenerated with the free excitons continuum. This result is in agreement with Faulkner's and Jaros et al [15] calculations.





Fig.2 Shear dependence of the bound-electron ground state (Γ_1) : The calculated curves correspond with an intervalley-coupling matrix element : Δ (X) = (8 + 0.4X) meV (X is expressed in kbar and negative for a compression).

Fig.1 Effect of a uniaxial stress along the (111), (110) and (001), crystallographic directions on the A and B absorption lines: A and B appear only with $E \perp X$ (σ polarization). A appears only with E // X (π polarization). A is associated with the heavy $\lfloor 3/2 , \pm 3/2 \rangle$ hole state. A and B are associated with the light $\lfloor 3/2, \pm 1/2 \rangle$ hole state.

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