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Γ-X hybridization of donor levels in gallium arsenide under pressure

J. Leymarie, M. Leroux, and G. Neu

Laboratoire de Physique du Solide et Énergie Solaire-CNRS, rue B. Gregory, F-06560 Valbonne, France

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Levels associated with the sulfur donor are studied in GaAs under pressure by low-temperature photoluminescence. The identification of the free-to-bound and donor-acceptor pair recombinations involving the donor ground state linked to X minima gives evidence for a Γ-X hybridization. Results are analyzed within the framework of the multivalley effective-mass approximation. The ionization energy of the indirect donor ground state as well as the Γ-X coupling coefficient (respectively, 109 ± 2 and 5 ± 1 meV) are deduced.

I. INTRODUCTION

The band-structure configuration dependence of impurity levels in semiconductors is essential to understand the electronic properties of doped semiconductor alloys.[1] For donor species, the binding energy, the valley-orbit interaction in the indirect configuration, and the intervalley coupling are key parameters for models implying several levels associated with different nonequivalent minima[2,3] in III-V compounds as well as in device modeling. As theoretically stressed by Morgan,[4] the symmetry of donor levels linked to the X minima in GaP depends on the site occupied by the impurity. The electron wave function of the ground state belongs to the X_3 representation if the impurity is located on a Ga site or to X_1 for a P site substituted impurity. In this last case, the interaction matrix element $\langle \Gamma | U(r) | X \rangle$ of the impurity potential $U(r)$, which couples Γ and X, is nonvanishing.[5] Although this point was theoretically established for a long time, it was not clearly experimentally evidenced until now (even if levels that are neither linked to Γ or X minima have been observed[6-8]).

This paper investigates the coupling between the Γ and X valleys through a detailed sulfur-donor spectroscopy in bulk GaAs under pressure. GaAs is indeed a suitable material because of the following: (i) its pressure-induced band-structure modification simulates somehow the composition dependence of the band structure of III-V alloys as (Ga,Al)As and Ga(As,P) and such a study in GaAs gives some insights about donor levels in alloys;[6,7] (ii) the interaction is particularly effective at the pressure-induced crossover of Γ- and X-donor-related levels[9] and such an effect has been forwarded to interpret time decays of donor bound excitons in GaAs under pressure.[10] We report the observation of the free-to-bound transition involving the X-dependent donor level and of the hybridization of Γ and X donor levels. This allows a direct determination of the indirect ground-state energy and the Γ-X coupling coefficient. Experimental data are shown to be well described within the framework of the multivalley effective-mass approximation (EMA).

II. EXPERIMENTS

Photoluminescence (PL) experiments at low temperatures (2–60 K) and high pressure (0–5 GPa) are performed on bulk n-type (2×10^{16} cm^{-3} at 300 K), [001] Czochralski-grown GaAs doped with nitrogen and sulfur.[11,12] The recombination lines of the exciton bound to the isoelectronic nitrogen trap are used for testing the hydrostaticity in the high-pressure chamber.[13] The sample, thinned to 30 μm, is immersed in argon as a pressure-transmitting medium in a diamond-anvil cell together with ruby chips for pressure monitoring.

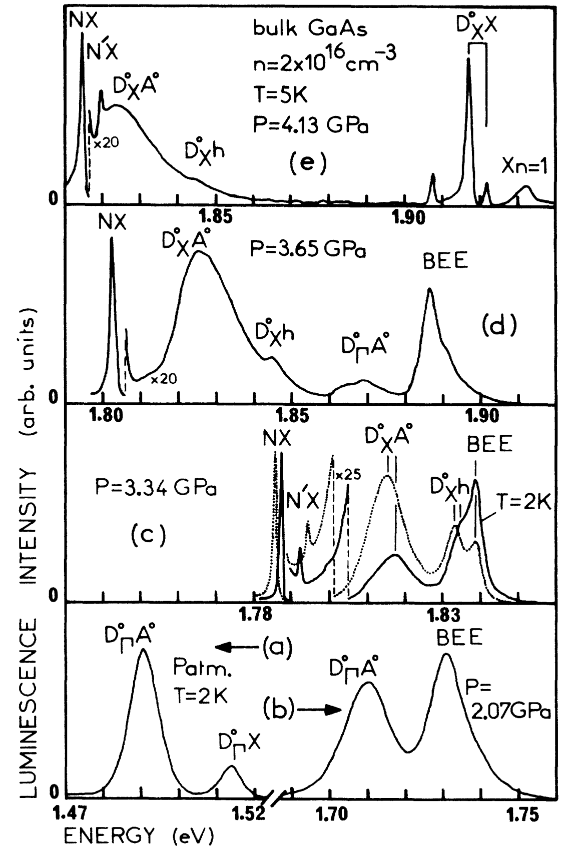

FIG. 1. High-pressure and low-temperature photoluminescence spectra of nitrogen- and sulfur-doped GaAs. In (c), spectra are shown for two values of the uniaxial stress (96 and 165 MPa), evidencing its effect on the transitions.

High-pressure PL spectra are shown in Fig. 1. Up to 2.4 GPa [Figs. 1(a) and 1(b)], PL features are not deeply modified and exhibit, as at atmospheric pressure [Fig.

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1(a)], a neutral donor-acceptor pair emission band ($D^0_\Gamma A^0$) and a high-energy line which includes nonresolved recombinations of band-edge excitons (BEE) and free-hole–neutral-donor transitions ($D^0_\Gamma h$). The energy of $D^0_\Gamma A^0$ at 0 GPa indicates that carbon is the main residual acceptor.

For pressures above 2.4 GPa and below the Γ-X band-gap crossover pressure (P = 4.2 GPa), PL spectra are modified in two ways: (i) as is well known, nitrogen potential traps an exciton (labeled NX) (Refs. 14 and 15) and (ii) the free-to-bound ($D^0_\Gamma h$) and donor-acceptor pair ($D^0_\Gamma A^0$) transitions begin to deepen at P = 3.3 GPa [Fig. 1(c)]; the near-band-gap exciton is now resolved. When the pressure is weakly nonhydrostatic, a second nitrogen-associated line labeled N′X can be observed on the high-energy side of NX. The (NX,N′X) doublet results from the splitting of the valence band under uniaxial stress and leads to estimate the deviation from hydrostaticity.[16] As an illustration, Fig. 1(c) displays two PL spectra recorded at the same hydrostatic pressure (as measured from the ruby line shift), but for different residual uniaxial stresses as shown by the amplitude of NX-N′X splittings. Since the uniaxial deformation also shifts the $D^0_X h$ and $D^0_X A^0$ bands, it has to be considered in the analysis of experimental data. Assuming that the direction of the uncontrolled uniaxial strain is along the [001] axis (which is also the diamonds axis), the modifications of the different band extrema can be quantitatively evaluated. The effect of a [001] compressive stress on the GaAs band structure is sketched in Fig. 2. $D_{\pm 3/2}$ and $D_{\pm 1/2}$ are intrinsic transitions between the Γ_{1c} minimum and the split valence-band states (the NX-N′X energy difference is the amplitude of this last splitting). The degeneracy of the X band is removed giving rise to transitions labeled $I_{\pm 1/2}$ and $I'_{\pm 1/2}$ towards the upper valence band. The calculated pressure coefficients of the direct and indirect transitions under [001] stress (S) are[17–20] $dD_{\pm 1/2}/S = 9.7$, $dD_{\pm 3/2}/S = 62$, $dI_{\pm 1/2}/S = -95$, and $dI'_{\pm 1/2}/S = 1.6$ meV/GPa. Note that the energy of the $m_J = \pm \frac{1}{2}$ exciton, which is observed at low temperature, is weakly dependent on uniaxial stress. In this work, the deviation of the direct exciton energy is less than 2 meV from hydrostatic conditions.

Near the Γ-X crossover, the neutralization of Γ- and X-like donor levels persists up to the excitonic crossover occurring at 3.90 GPa [Fig. 1(d)]. Above 4 GPa, the near-band-gap luminescence is dominated by indirect neutral-donor bound excitons D^0_XX, sometimes split by the stress. The direct free exciton is detectable up to 4.3 GPa [Fig. 1(e)].

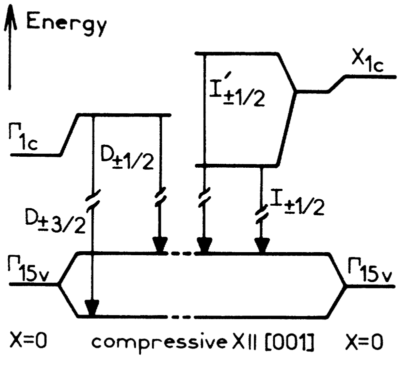

FIG. 2. Schematic illustration of the strain effect on Γ- and X-band extrema of GaAs for a compressive [001] stress.

III. DISCUSSION

PL experiments have shown that the main events occur around the Γ-X crossover, in a region where Γ-X hybridization actually influences the donor binding energies. It is then essential to clearly identify the nature of the sulfur- and carbon-related recombinations in that pressure range. Considering the inset of Fig. 3 where the PL transition energies are reported as a function of pressure measured with the ruby scale, it appears that the shallow impurity bands have, far from the Γ-X crossover, either the Γ- or X-pressure coefficient. As the acceptor binding energy weakly varies with pressure, the two bands detected in the indirect configuration can be attributed to donor-acceptor pairs and free-hole–neutral-donor transitions. The separation between both bands is 21 meV on the average, i.e., nearly the same value as at atmospheric pressure (22 meV). Other arguments in favor of this identification are given by PL experiments where the excitation intensity and the temperature are varied. As is expected for donor-acceptor pair luminescence, the $D^0_X A^0$ band shifts towards higher energies and tends to saturate when the excitation intensity is increased. In the same conditions the $D^0_X h$ intensity varies linearly. On the other hand, the thermalization of carbon acceptors is observed when the temperature is increased; at high temperature (40–50 K), only free-hole–neutral-donor transitions are detected.

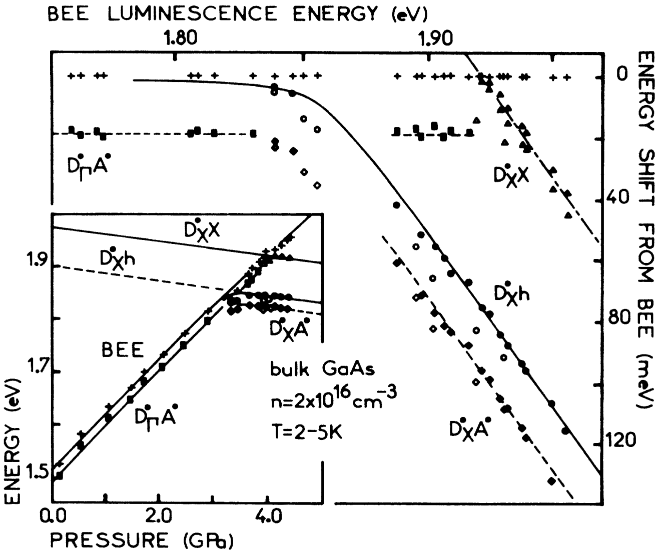

FIG. 3. Pressure dependence of PL transitions, using the direct BEE energy as an intermediate pressure scale. Solid and open symbols respectively represent results obtained under low (< 100 MPa) and high residual uniaxial stress (100–200 MPa). The solid line is calculated according to Eq. (3). In the inset, the $R1$ ruby line is used to calibrate pressure in a standard representation.

The identification of the two bands is also supported by the emergence of the D_X^0h transition from near-band-gap luminescence at the onset of the deepening of donor levels in the direct-band-gap region (Fig. 3).

In order to compare experimental data with calculations in the multivalley effective-mass approximation (EMA), it is convenient to report the energy difference between the direct-band-edge exciton lines and the impurity-related transitions in an intermediate pressure scale given by the position of the direct-band-edge excitons (Fig. 3). This representation mode eliminates the scatter of the pressure measurement from the ruby line (the remaining scatter is only due in this case to the weak residual uniaxial stresses).

The donor bound-state wave functions are expanded along a set of wave functions which are zero-order solutions in the subzones centered at the Γ and threefold-degenerated X minima of the Brillouin zone.[1] The possible "camel's back" structure of GaAs at the point X is not considered in the present calculation. The donor energy levels are obtained by solving the secular equation

$$\begin{array}{cccc} |\Gamma\rangle & |X\rangle & |X\rangle & |X\rangle \\ \left|\begin{array}{cccc} E_{D_\Gamma}-E & V & V & V \\ V & E_{D_X}-E & -\Delta & -\Delta \\ V & -\Delta & E_{D_X}-E & -\Delta \\ V & -\Delta & -\Delta & E_{D_X}-E \end{array}\right| \end{array} = 0\,, \tag{1}$$

where E_{D_Γ} and E_{D_X} are the energies of the donor levels linked respectively to Γ and X minima. The reference energy is taken at the top of the valence band. V and $-\Delta$ are intervalley coupling parameters defined by

$$V=\langle\Gamma|U(r)|X\rangle=\int\int_{\mathrm{BZ}}\phi_\Gamma^*(\mathbf{k})U_{\Gamma X}(\mathbf{k},\mathbf{k}')\phi_X(\mathbf{k}')d\mathbf{k}\,d\mathbf{k}'\,, \tag{2a}$$

$$\Delta=-\langle X|U(r)|X\rangle=-\int\int_{\mathrm{BZ}}\phi_X^*(\mathbf{k})U_{XX}(\mathbf{k},\mathbf{k}')\phi_X(\mathbf{k}')d\mathbf{k}\,d\mathbf{k}'\,. \tag{2b}$$

$U_{ij}(\mathbf{k},\mathbf{k}')$ ($i=\Gamma,X$; $j=X$) is the Bloch transform of the impurity potential as defined in Ref. 1. The resolution of Eq. (1) gives purely X-like and twofold-degenerate states $E=E_{D_X}+\Delta$ of Γ_{12} symmetry and two coupled levels of Γ_1 symmetry:

$$E\pm=\{E_{D_X}-2\Delta+E_{D_\Gamma}\pm[(E_{D_X}-2\Delta-E_{D_\Gamma})^2+3V^2]^{1/2}\}/2\,. \tag{3}$$

Neglecting the pressure-induced variations of the dielectric constant and of the Γ- and X-band effective masses, the donor binding energy $E_g(\Gamma)-E_{D_\Gamma}$ is constant and equal to his value at atmospheric pressure (6 meV). In good agreement with the data of Wolford and Goñi *et al.*, the pressure dependences of direct $E_g(\Gamma)$ and indirect $E_g(X)$ band gaps are the following [energies are expressed in eV and pressures (P) in GPa]:[6,21]

$$E_g(\Gamma)=1.519+10.8\times10^{-2}P-1.4\times10^{-3}P^2\,, \tag{4a}$$

$$E_g(X)=2.010-1.34\times10^{-2}P\,. \tag{4b}$$

Since the D_X^0h energy is uniaxial-stress-dependent, only experimental results recorded for low-stress values (< 100 MPa) are considered [though data corresponding to higher uniaxial stress in the cell (100–200 MPa) are also reported on Fig. 3 allowing the transitions of interest to be followed step by step with pressure variation]. The best fit to the D_X^0h pressure dependence is found for $E_g(X)-(E_{D_X}-2\Delta)=109\pm2$ meV and $V=5\pm1$ meV. It is worth pointing out that the calculation actually gives the D_X^0h energy relative to the valence band ($E_{D_X}-2\Delta=1901\pm2$ meV at 0 GPa) and that the donor ionization energy depends on the precise knowledge of the X band gap. However, the ionization energy of the sulfur donor in indirect-band-gap GaAs is comparable with the ionization binding energies of group-VI donors in GaP: 107, 105, and 93 meV for S, Se, and Te, respectively.[22]

The second basic parameter V, just evaluated from the adjustments of the pressure dependence of D^0h, can be estimated in another way using only the ionization energy of Γ and X donor ground states. Within the multivalley EMA, the Γ-X coupling parameter takes a simplified form,[1]

$$V=F_\Gamma(0)U_{\Gamma X}(\mathbf{k}_\Gamma,\mathbf{k}_X)F_X(0)\,, \tag{5}$$

where $F_\Gamma(0)$ and $F_X(0)$ are the core values of the zero-order envelope functions. After Bassani, Iadonisi, and Preziosi,[1] $U_{\Gamma X}(\mathbf{k}_\Gamma,\mathbf{k}_X)$ is approximated to

$$U_{\Gamma X}(\mathbf{k}_\Gamma,\mathbf{k}_X)\approx-e^2/[\epsilon_0\epsilon(\mathbf{k}_\Gamma-\mathbf{k}_X)|\mathbf{k}_\Gamma-\mathbf{k}_X|^2]\,. \tag{6}$$

$\epsilon(q)$ is the dielectric screening function which decreases to 1 when q becomes of the order of a reciprocal-lattice vector. Using hydrogeniclike envelope functions (solutions of the EMA in each subzone) gives $|V|\approx e^2a^2/4\pi^3\epsilon_0(a_\Gamma a_X)^{3/2}$, where a is the lattice parameter and a_i are the Bohr radii calculated from the ionization energy in the case of the hydrogenic system. As the intervalley X-X coupling parameter (Δ) is unknown, the ionization energy of the indirect ground state (109 meV) is used to evaluate the matrix element. The discrepancy between the calculated value ($V=3$ meV) and the one deduced from experiments can be due to the neglect of core effects on indirect donor levels in the first evaluation.

IV. CONCLUSION

We have spectroscopically investigated the sulfur-donor energy levels in GaAs as a function of the band-structure configuration. The effect of the intervalley mixing of the conduction band upon the ground state occurs well below the Γ-X gap crossover. The Γ-X hybridization of anion site substituted donor levels, as theoretically predicted by Morgan in GaP, is clearly evidenced in GaAs and the multivalley effective-mass approximation well accounts for this behavior.

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