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MANGANESE LEVELS IN GaAs UNDER HYDROSTATIC PRESSURE, IN AlGaAs, AND IN GaAs/AlGaAs QUANTUM WELLS - A COMPARATIVE STUDY

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ABSTRACT

Manganese-doped GaAs is investigated under hydrostatic pressure up to p=7.2 GPa. We use the low temperature photoluminescence to characterize the samples. The binding energy of the Mn acceptor increases with pressure, and the internal $^4T_1 - ^6A_1$ transition of Mn^{2+} is detected for $p \geq 2.8$ GPa. A comparison is made with the position of the internal transition in AlGaAs-alloys and GaAs/AlGaAs quantum wells.

1. INTRODUCTION

Manganese is known in GaAs to form an acceptor level ~110 meV above the valence band edge.[1] The low temperature photoluminescence spectra of Mn doped GaAs exhibit a characteristic donor-acceptor pair recombination of donor-bound electrons with distant Mn acceptor holes.[1]

A different luminescence process is detected in Mn-doped II-VI compound semiconductors[2] and in GaP[3]. Intra-atomic 3d-3d transitions within the Mn^{2+} ion give rise to sharp zero-phonon transitions along with broader related side-bands. However, these transitions were not observed in GaAs:Mn, due to the degeneracy of the excited states of Mn^{2+} with the conduction band.[4] The degeneracy can be removed by enlarging the band gap of GaAs by means of alloying, carrier confinement in quantum wells, and hydrostatic pressure. In fact, a new luminescence band occurs in $Al_xGa_{1-x}As$:Mn with $x>0.3$ [4] and in Mn-doped AlGaAs/GaAs quantum wells with a well-width smaller than 30 Å.[5] These new transitions are attributed to the intra-atomic $^4T_1 - ^6A_1$ transition of Mn^{2+}.

In this paper, we report the observation of the internal Mn^{2+} transition in GaAs subjected to hydrostatic pressure, and compare our results with the behavior of this optical transition in Mn-doped AlGaAs-alloys and quantum wells.

2. EXPERIMENTAL CONDITIONS

The GaAs samples used in this study are grown by liquid phase epitaxy (LPE) from a gallium solution containing 1% manganese. The concentration of Mn atoms in the sample ranges from 10^{18} to 10^{19} cm^{-3} depending on the growth temperature.

For the measurements under hydrostatic pressure, the GaAs substrate is removed by mechanical polishing to give a final sample thickness of 50 μm. The platelets are cleaved into cubes with faces of area $\sim$100 μm^2, and loaded into a diamond anvil cell together with a ruby crystal and xenon, which is used as transparent pressure transmitting medium.

Photoluminescence measurements are performed with the diamond cell cooled to $\sim$ 5 K by He gas in an optical cryostat. We achieve hydrostatic pressures up to $\sim$ 3 GPa. A precise pressure calibration is possible using the shift of the ruby emission.[6] The GaAs samples are excited by the 530.9 nm line of a Kr$^+$-laser. The photoluminescence (PL) signal is dispersed by a 3/4 m - Spex monochromator, and detected by a cooled photomultiplier with S1-cathode.

3. RESULTS

Typical low temperature PL spectra of Mn-doped GaAs samples subjected to hydrostatic pressure are given in figure 1. The maximum of the $(D^\circ, A^\circ)_{Mn}$ transition at p=0 GPa appears at 880 nm under our excitation conditions. The pair transition experiences a drastic reduction in intensity, a broadening, and a shift to higher energies with increasing pressure. At 2.2 GPa, the linewidth of the pair-band is larger than 70 meV, and the structure due to the LO phonon replica is no longer visible.

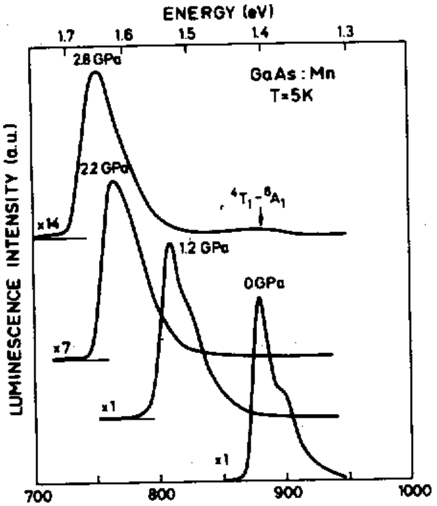

Figure 1: *Low temperature photoluminescence spectra of Mn-doped GaAs at hydrostatic pressures* $p \leq 2.8$ *GPa.*

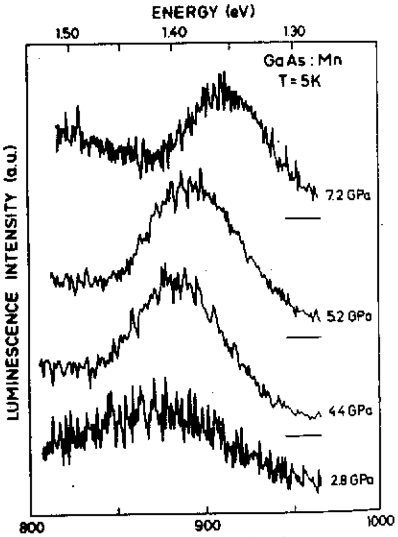

Figure 2: *Low temperature photoluminescence spectra of Mn-doped GaAs at hydrostatic pressures* $p \geq 2.8$ *GPa.*

In addition to the pair-band at 750 nm, a new transition appears at 880 nm for p=2.8 GPa. This weak band is also detected at pressure values greater than 2.8 GPa. (See figure 2.) In contrast the pair-band, the new band shifts to lower energies with increasing pressure.

The hydrostatic pressure dependences of the transition energies for the $(D^\circ, A^\circ)_{Mn}$ transition, near band gap excitonic recombination, and the new PL band are given in figure 3. We label new band in this figure according to the identification given in the next section as an internal $T_1 -^6 A_1$ transition.

The $(D^\circ, A^\circ)_{Mn}$ band exhibits a linear shift with p according to

$$E(D^\circ, A^\circ)_{Mn}(p) = \alpha + \beta p \qquad (1)$$

with α=(1.42±0.01)eV and β=(86±3)meV/GPa.

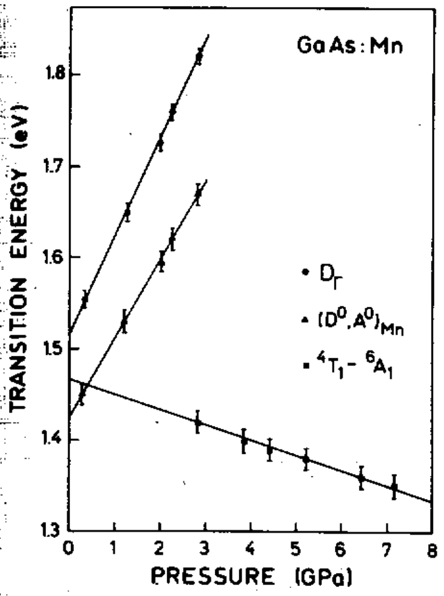

Figure 3: *Photoluminescence peak energies of Mn-doped GaAs versus applied hydrostatic pressure.*

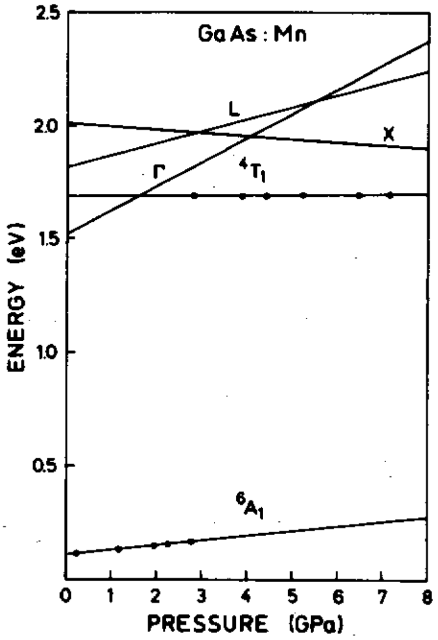

Figure 4: *Energy level diagram of Mn-doped GaAs under hydrostatic pressure. The hydrostatic pressure dependences of the Γ, X, and L conduction band minima are taken from Ref. 8.*

The transition energy of the new band exhibits the following dependence upon p

$$E_{trans}(p) = \gamma - \delta p \tag{2}$$

with γ=(1.47±0.01)eV and δ=(17±3)meV/GPa.

3. DISCUSSION

Our low temperature PL studies on Mn-doped GaAs show the well-known $(D^{\circ}, A^{\circ})_{Mn}$ pair transition in the pressure regime below 3 GPa. From the spectra, the hydrostatic pressure dependence of the binding energy $E_b^{Mn}(p)$ of the Mn-acceptor groundstate can be determined.[7]

$$E_b^{Mn}(p) = Eg(p) - E(D^{\circ}, A^{\circ})_{Mn}(p) - E_b^{D}(p) + \Delta E \tag{3}$$

The band gap energy Eg(p) is determined from the position of the near band gap PL (D_{Γ}) of our samples, and is in agreement with literature values.[8]. (See figure 3.) The binding energy of the neutral donor $E_b^{D}(p)$ is assumed to be constant with a value of 6 meV. The pairing interaction term ΔE represents the Coulomb interaction between the impurity levels, and is typically of the order of 20 meV for our samples. Experimentally, we find

$$E_b^{Mn}(p) = a + bp \tag{4}$$

with a=110 meV and b=(20±3)meV/GPa. We point out that our value of b is almost a factor of 2 larger than that reported in Ref. 9. However, the reason is still under debate.

At pressures $p \geq 2.8$ GPa, the new PL band appears. This band is identical to a luminescence band in Mn-doped AlGaAs and small quantum wells, and was identified as the intra-atomic $^4T_1 - ^6A_1$ transition of Mn^{2+}. In all three cases, the new band appears when the $^4T_1$ state crosses the conduction band minimum. Since we cannot observe the zero-phonon line of the internal transition, we determine the energetic position of the $^4T_1$ state with respect to the valence band minimum using

$$E(^4T_1)(p) = E_b^{Mn}(p) + E_{trans}(p) + \Delta E(PM) \tag{5}$$

$\Delta E(PM)$ is the energy separation between the PL band maximum and the high energy onset of the band, and is ~100 meV. This is similar to the value of 110 meV found for GaP:Mn.[3] The positions with respect to the valence band of the excited $^4T_1$ state, the $^6A_1$ groundstate, and the various conduction bands with respect to the valence band as function of pressure are shown in figure 4. If we extrapolate the $^4T_1$ level to zero pressure, we find the position of the $^4T_1$ state in GaAs to be (1.69±0.03) eV. This value agrees with the value of 1.72 eV determined from the extrapolation to x=0 of the $^4T_1$ level in AlGaAs-alloys.[10]

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Hydrostatic pressure leads to variations in the GaAs band structure similar those found with Al-alloying. In both cases, the binding energy of the Mn-acceptor increases. However, the energy of the internal transition behaves differently in these two cases. Whereas under hydrostatic pressure the $^4T_1 - ^6A_1$ transition energy decreases, an increase is found with alloying.[10] A qualitative explanation for the different behavior under pressure and alloying can be given. Hydrostatic pressure decreases the lattice parameter, which, in turn, increases the crystal field strength. However, as shown in Ref. 11, increasing the crystal field strength decreases the transition energy. In the AlGaAs-alloys, the lattice constant remains approximately fixed. However, the ionicity decreases from GaAs to AlAs, leading to an increase in the internal transition energy.

Another mechanism to increase the band gap energy is to form small quantum well structures. No change in the crystal field splitting of the internal transition is expected, and therefore, the excited $^4T_1$ level should cross the conduction band at a quantum well thickness of ~30 Å. Indeed, the internal $^4T_1 - ^6A_1$ transition for quantum wells with $L_z = 30$Å has been detected.[5]

In summary, we have reported the hydrostatic pressure shift of the Mn levels in GaAs. An increase with pressure in the acceptor binding energy, but a decrease in the intra-atomic Mn^{2+} transition energy was found.

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