Magnetoluminescence study on the effective mass anisotropy of CuPt$_B$-ordered GaInP$_2$ alloys

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Photoluminescence measurements in a magnetic field between 0 and 13.6 T were carried out on CuPt$_B$-ordered GaInP at liquid-helium temperature. Four samples of different degrees of ordering (η, varying from 0 to 0.54) were studied. Experimental results show that the ordering not only induces a band-gap reduction and valence-band splitting, it also causes changes in effective masses and an effective mass anisotropy. By measuring and analyzing the magnetoluminescence with the magnetic field aligned along both ordering (the $[111]$) and growth (the $[001]$) directions, we demonstrate that, for the band-edge excitonic state, the reduced mass in the plane perpendicular to the ordering direction is smaller than that in the ordering direction and also smaller than that of a disordered alloy. The exciton binding energy is found nearly independent of the degree of ordering, in agreement with theoretical predictions. © *1997 American Institute of Physics.* [S0021-8979(97)03106-X]

I. INTRODUCTION

It has been well established that, under proper growth conditions, epitaxially grown Ga$_x$In$_{1-x}$P alloys ($x\sim0.5$) exhibit CuPt ordering along the $[111]_B$ directions.[1] The most prominent ordering-induced changes in the band structure of the GaInP alloy, such as band-gap reduction and valence-band (VB) splitting, have been investigated both experimentally[1,2,3] and theoretically.[4,5] However, these studies only addressed the band-edge energies of the conduction band (CB) and the VB and not the effective masses, which are defined by

$$m^{-1}=\frac{1}{\hbar^2}\frac{\partial^2 E}{\partial k^2}.$$

The effective masses are very important parameters for device applications such as solar cells and semiconductor lasers. Only recently, the effective masses of the Brillouin-zone center of the ordered alloy have been studied theoretically[6–8] and experimentally.[9,10] It is pointed out in Ref. 7 that near the band edges the energy dispersions of both the CB and the VB have an ellipsoidal form. In the VB, the effective mass anisotropy is caused mainly by an ordering-induced change in the crystal symmetry,[7] which is much more significant than the nonspherical effect (so-called warping) in cubic crystals.[11] For the CB, the ordering-induced coupling to the VB,[7,8] together with the folded CB from the L valley,[6,8] causes the effective-mass anisotropy.

On one hand, all three models[6–8] predict that the CB effective mass in the ordering direction ($m_{c_\parallel}$) is larger than the effective mass in the plane perpendicular to the ordering direction ($m_{c_\perp}$). On the other hand, these models differ with respect to the dependence of both masses on the ordering parameter. A two-band model,[6] which considers the $\Gamma-L$ coupling, predicts an increase of both mass components as ordering occurs, i.e., $m_{c_\parallel}>m_{c_\perp}>m_{c0}$ (m_{c0} being the Γ-point effective mass of the disordered alloy). This is the result of the $\Gamma-L$ repulsion and is correlated with the anisotropy in the effective masses at the L point ($m_{L_\parallel}>m_{L_\perp}>m_{c0}$). However, an eight-band $\mathbf{k}\cdot\mathbf{p}$ model,[7] considering the CB–VB coupling at the Γ point, predicts a decrease of the mass components with an increasing degree of order ($m_{c0}>m_{c_\parallel}>m_{c_\perp}$), which can be understood as a result of the band-gap reduction and the VB anisotropy. A first-principles calculation[8] using the local-density approximation shows that $m_{c_\parallel}>m_{c0}$ and $m_{c_\perp}<m_{c0}$. As for the topmost VB, Ref. 7 predicts that $m_{h_\parallel}$ does not change with ordering, but $m_{h_\perp}$ becomes significantly smaller than that of the disordered alloy. For the reduced masses, $\mu^{-1}=m_e^{-1}+m_h^{-1}$, of the excitonic state in the ordered alloy, one also expects that $\mu_\parallel>\mu_\perp$, because of $m_{c_\parallel}>m_{c_\perp}$ and $m_{h_\parallel}>m_{h_\perp}$.

To the best of our knowledge, there have been only two attempts to study the effect of ordering on the effective masses in GaInP experimentally. Emanuelsson *et al.* presented optically detected cyclotron resonance measurements[9] and concluded that the CB effective mass in an ordered GaInP sample decreases to $m_c=0.088\pm0.003$ from $m_c=0.092\pm0.003$ in the disordered alloy (without giving the orientation of the magnetic field). All effective masses are given in units of the free-electron mass. Since the ordering was relatively weak (with a 56 meV band-gap reduction),

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TABLE I. Properties of the samples used in this work.

Sample No.	Growth temperature (°C)	Order parameter η	Band-gap reduction (meV)	Valence-band splitting (meV)
1	840	0	0	0
2	750	0.32	35	13
3	720	0.44	94	2
4	660	0.54	129	30

the mass difference was relatively weak. Moreover, the magnetic field was presumably oriented along the [001] direction[12] and, therefore, the determined effective mass was an average. Also, a previous magnetoluminescence study by Jones *et al.*,[10] with the magnetic field oriented along the [001] direction, showed a reduction of the averaged exciton-reduced mass μ_{avg} because of ordering.

In this article, we present a magnetophotoluminescence (PL) study of ordered GaInP with varying degrees of order[13] from $\eta=0$ to $\eta=0.54$. To determine the ordering dependence of the effective masses, as well as their anisotropy, we studied the diamagnetic shift of the excitonic PL emission in the magnetic field oriented parallel to the ordering direction [111] as well as parallel to the growth direction [001]. A theoretical analysis to the data was carried out to determine the exciton-reduced masses and binding energy as functions of the order parameter.

II. EXPERIMENT

The samples used in this study are a set of four GaInP layers (2 μm thick). The samples were grown by metal-organic vapor-phase epitaxy in a horizontal reactor with a gas foil rotating susceptor at a reactor pressure of 100 hPa and a V/III ratio of about 240. The ordered samples were grown undoped on GaAs substrates misoriented by 6° toward a $[111]_B$ direction. This choice of substrate is known to yield single-variant samples. The disordered sample was grown on a 6° toward $[111]_A$-misoriented substrate. The lattice mismatch of each of the samples has been determined by high-resolution x-ray diffractometry and was found to be better than 10^{-3}. This means that the Ga content of the samples was 0.510 ± 0.005.

To vary the order parameter η, the growth temperature was changed, as indicated in Table I. As previously published,[3] η was obtained by fitting the experimentally determined VB splitting (VBS) to a theoretical curve VBS(η), given by Wei and co-workers.[5] The values are given in Table I.

The experimental setup consisted of a conventional ^{4}He-flow cryostat (base temperature 1.4 K) and an Oxford Instruments superconducting magnet system ($B_{\mathrm{max}}\approx 14$ T). PL data were taken by coupling the exciting laser light into a 100 μm core diameter optical fiber that was attached to the [001] growth surface of the sample. The PL emission was collected by the same fiber, directed to a Spex 0.85 m double-grating monochromator, and detected by a cooled GaAs photomultiplier tube. The samples were excited by a dye laser operated with DCM dye at a wavelength of 620 nm. The cw-excitation power density was 150 mW/cm^2. By using a sample holder that allowed the sample to rotate with respect to the magnetic field direction, the ordered samples were measured in two configurations: $\mathbf{B}\|[001]$ and $\mathbf{B}\|[111]$. When aligning the sample with respect to the field, the substrate misorientation was taken into account.

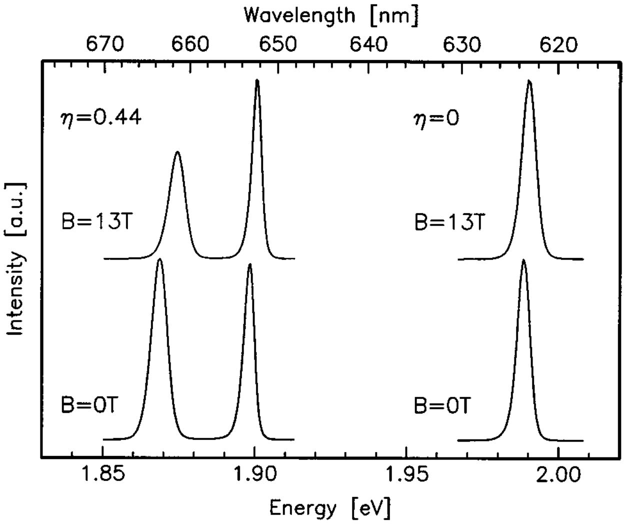

FIG. 1. PL spectra from a disordered sample (right-hand side) and an ordered sample ($\eta=0.44$, left-hand side), taken at zero magnetic field (bottom) and at 13 T (top). The spectra are normalized and shifted on the intensity axis.

III. RESULTS

Figure 1 shows a few typical PL spectra from an ordered—and the disordered—GaInP sample, measured at zero magnetic field and at $B=13$ T. The disordered sample shows one PL line (linewidth ~4.9 meV), whereas the ordered sample (as well as the other two ordered samples) displays two PL lines. The peak at higher energy (linewidth ~4.0 meV) is associated with the recombination of the band-gap exciton, as previously discussed.[14] The peak at lower energy represents the below-band-gap emission usually observed in ordered GaInP.[10,14,15] The origin of this peak is not clearly understood. In what follows we only focus on the high-energy peak. In our experiments we did not find any systematic increase or decrease of the PL linewidth with varying the magnetic field as reported earlier by Jones *et al.* for ordered and disordered GaInP.[16]

Figure 2 shows the shift of the excitonic PL peak as a function of the magnetic field. In Fig. 2(a) we compare the disordered sample with the most ordered sample ($\eta=0.54$). Here, as in all other cases, we observe a larger magnetic blue shift with ordered samples than with the disordered sample. This implies, in agreement with the theoretical predictions of Refs. 7 and 8 that the reduced mass in the ordered alloy is smaller than in the disordered alloy (see Sec. IV). Figure 2(b) shows a comparison of the magnetic blue shift with the [111]-oriented field to that with the [001] field for an ordered sample ($\eta=0.44$). In general, the [111] field gives larger shifts than the [001] field, which indicates that the in-plane

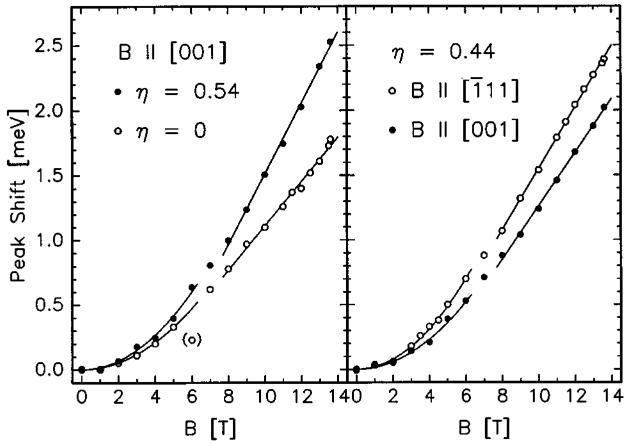

FIG. 2. Energy shift δE of the PL peak with increasing magnetic field. (a) Comparison of the disordered with the most ordered sample; (b) comparison of the peak shift with **B**‖[001] and with **B**‖[111]. Lines are fits to the data: For 0 T$\leqslant B \leqslant$6 T, a parabola ($\delta E = a_1 B^2$) fits the data, whereas a linear magnetic shift ($\delta E \propto a_2 B$) describes the data well for 8 T$\leqslant B <$14 T.

reduced mass $\mu_\perp$ is smaller than the out-of-plane reduced mass $\mu_\parallel$. This agrees qualitatively with the above-mentioned predictions of Refs. 6–8.

Furthermore, it can be seen from Fig. 2 that the energy shift δE of the PL peak can be described very well by a simple quadratic behavior $\delta E = a_1 B^2$ for magnetic fields $B \leqslant 6$ T, and that there appears to be a linear dependence $\delta E \propto a_2 B$ for stronger fields $B \geqslant 8$ T. As discussed in greater detail in the following section, the quadratic behavior can be well understood in terms of the diamagnetic properties of excitons in a weak magnetic field (i.e., where the magnetic energy $\frac{1}{2}\hbar\omega_0$ ($\omega_0 = eB/\mu_\perp$) is smaller than the exciton binding energy). For a very strong field, a linear magnetic shift is to be expected because of the formation of Landau levels. We do not assume, however, that this field range was reached in our experiment, i.e., the linear fits of Fig. 2 are of purely heuristic nature. The information on the magnetic shift observed for both magnetic-field orientations and the four samples is summarized in Table II in terms of the fitted parameters a_1 and a_2.

TABLE II. Quadratic (a_1) and linear (a_2) coefficients of the magnetic blue shift of the PL peak of the samples investigated.

Sample No.	η	a_1 **B**‖[001] (μ eV/T^2)	a_2 **B**‖[001] (μ eV/T)	$\underline{a_1}$ **B**‖[111] (μ eV/T^2)	$\underline{a_2}$ **B**‖[111] (μ eV/T)
1	0	13.1 (±0.3)	169(±4)	not measured	not measured
2	0.32	16.4 (±0.5)	211(±3)	19.1 (±0.8)	224 (±5)
3	0.44	14.7 (±0.5)	201(±4)	18.8 (±0.9)	234 (±2)
4	0.54	14.1 (±1.0)	257(±20)	18.3 (±1.0)	272 (±6)

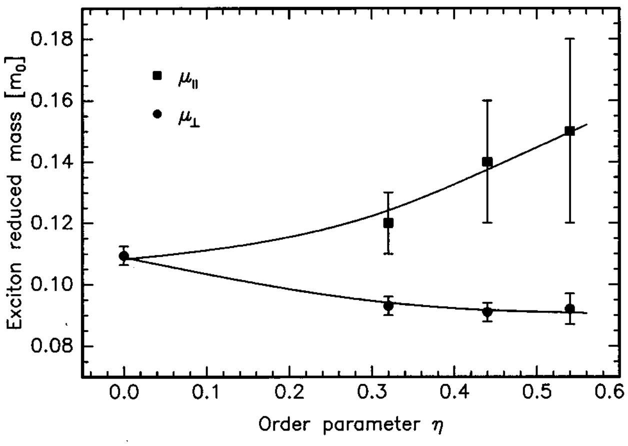

FIG. 3. Anisotropic exciton reduced masses as a function of order parameter η, derived from the experimentally determined diamagnetic shift of the excitonic PL transition.

IV. THEORETICAL ANALYSIS

At zero field, the excitonic state in an ordered alloy can be described by[17]

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\gamma\frac{\partial^2}{\partial z^2}+\frac{2}{r}\right)f(x,y,z)=E(\gamma)f(x,y,z), \tag{1}$$

where $\gamma = \mu_\perp/\mu_\parallel$, $a_B = \hbar\epsilon/\mu_\perp e^2$, and $E_0 = e^2/2a_B\epsilon$ are the units for the length and energy in Eq. (1), respectively. Equation (1) can be solved variationally by using a trial wave function[17]

$$f(x,y,z)=\left(\frac{a^2 b}{\pi}\right)^{1/2}\exp[-\sqrt{a^2(x^2+y^2)+b^2 z^2}],$$

with a and b as variational parameters and z the spatial coordinate in the ordering direction. The exciton binding energy is given as $E_b = E_{\text{hydrogen}}\epsilon^{-2}\mu_\perp E(\gamma)$, where E_{hydrogen} is the binding energy of a hydrogen atom and ϵ is the dielectric constant. With increasing order parameter, $\mu_\perp$ decreases as suggested by the above experimental results, but $E(\gamma)$ increases because of the enhancement in γ, which yields a weak dependence of the exciton binding energy on the ordering parameter.

The diamagnetic shift (the low-field behavior) of an exciton state can be derived from a general theory[18] and given as follows:

$$\delta E_{[\bar{1}11]}=\frac{e^2B^2}{8\mu_\perp c^2}\langle f|x^2+y^2|f\rangle, \tag{2}$$

$$\delta E_{[001]}=\frac{e^2B^2}{8\mu_\perp c^2}\,\frac{1}{3}\langle f|x^2+y^2+2z^2|f\rangle+\frac{e^2B^2}{8\mu_\parallel c^2}\,\frac{1}{3}\times\langle f|x^2+y^2|f\rangle, \tag{3}$$

for the $[\bar{1}11]$ and [001] fields, respectively. Because $\mu_\parallel > \mu_\perp$, it is expected that $\delta E_{[\bar{1}11]} > \delta E_{[001]}$. The low-field portions of Fig. 2 can be well described by Eq. (2) or (3), but the high-field portions, which are the transition regions between ‘‘diamagnetic shift’’ to ‘‘Landau level shift,’’ are less easy to model. By fitting Eqs. (2) and (3) to the low-field regions ($B \leqslant 6$ T), we obtain reduced masses as a function of order parameter. These results are shown in Fig. 3.

As the alloy becomes ordered, the in-plane reduced mass $\mu_\perp$ decreases and the out-of-plane reduced mass $\mu_\parallel$ seems to

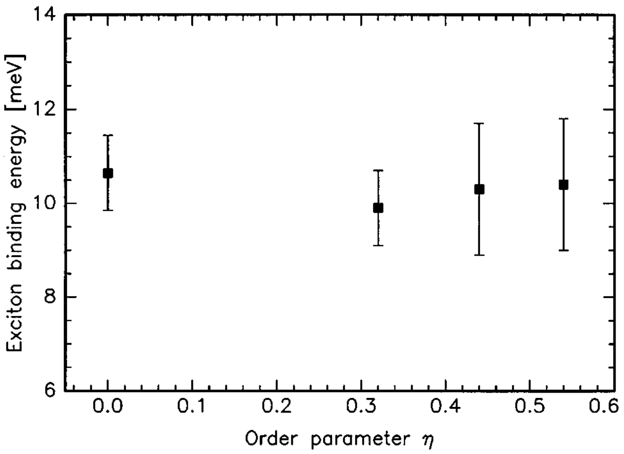

FIG. 4. Exciton binding energies as a function of order parameter η, derived from the exciton reduced masses shown in Fig. 3.

increase. Note that because the VB out-of-plane effective mass does not change because of the ordering,[7] the trend of the CB mass change is the same as that of the reduced mass. Thus, Fig. 3 implies, within experimental uncertainty, that the CB out-of-plane mass increases with increasing ordering parameter, as predicted by Ref. 8. Using the obtained reduced masses, we find that the exciton binding energy is nearly independent of order parameter and around 10 meV, as shown in Fig. 4.

V. SUMMARY

We have shown by magneto-optical measurements that in ordered $GaInP_2$ alloys the exciton reduced mass is significantly anisotropic. In agreement with theoretical predictions, it is found that the reduced mass is larger in the ordering direction than in the plane perpendicular to it. The in-plane reduced mass is lower than that of the disordered alloy, whereas the out-of-plane mass increases with an increasing degree of order. The exciton binding energy is found nearly independent of the ordering parameter.

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