Effect of Exciton Localization and Delocalization on Magnetic-Field-Dependent Photoluminescence Linewidths in Semiconductors*

S. K. Lyo, E. D. Jones and S. R. Kurtz

Sandia National Laboratories, Albuquerque, N. M. 87185

Theory and data are presented for the photoluminescence linewidth in ordered and disordered semiconductor alloys at low temperatures. In disordered (ordered) systems, the linewidth is due to exciton localization (exciton-impurity scattering) and increases (decreases) as a function of the field in agreement with the data.

Keywords: Magnetic field, Exciton linewidth, Semiconductors

Running Title: Exciton Linewidths in Semiconductors

Correspondence: S. K. Lyo, Sandia National Laboratories, Dept. 1112, Albuquerque, N.M., 87185, Phone: (505) 844-3718

Introduction

Currently much attention is focused on the effect of order and disorder on the band-gap changes in III-V alloys such as $In_{0.48}Ga_{0.52}P$ (lattice-matched to GaAs). In this paper we present theoretical and experimental evidence to show that the magnetic-field (B) dependence of photoluminescence (PL) linewidths (LWs) yields valuable information on exciton localization and delocalization arising from order-disorder effects at low temperatures. In a disordered system, low energy excitons are localized at different regions of the sample. The alloy composition inside the volume occupied by one exciton is different from that inside the volume of another exciton, yielding inhomogeneously broadened exciton energy and thus PL LW. The LW is given by the mean-square deviation of the bandgap fluctuation inside the exciton volume. Because the B-field shrinks the volume inside the exciton wave function, the LW is expected to rise with the field [1]. Here, the electron-hole energy gap is nonlocal and the radius of the exciton localization (R_0) is arbitrary in contrast to previous treatments where only local energy gap and $R_0 = 0$ were considered. The field dependence as well as the magnitude of the LW is found to be sensitive to R_0.

In an ordered system, on the other hand, we assume that the LW is from free excitons and is due to homogeneous broadening arising from exciton-impurity scattering at low temperatures with some inhomogeneous background arising from the possible presence of ordered domains in the sample. The B-field shrinks the size of the exciton volume, affecting the scattering cross section. We show that the scattering cross section and thus the homogeneous LW can decrease with the field in agreement with the data.

PL Linewidth from Localized Excitons

The deviation of the random local alloy potential from the mean value is given by $V_\alpha(\mathbf{r}_\alpha) = \Sigma_i E_\alpha(i)\Delta(\mathbf{r}_\alpha - \mathbf{R}_i)$, where $\alpha = e$, h and $\mathbf{r}_e$ ($\mathbf{r}_h$) stands for the electron (hole) coordinate. The quantity $\mathbf{R}_i$ denotes the cation positions occupied, for example, by In and Ga atoms in $In_{0.48}Ga_{0.52}P$. The function $\Delta(\mathbf{r}_\alpha - \mathbf{R}_i)$ is unity when $\mathbf{r}_\alpha$ lies inside a cell of volume $\Delta V = a^3/4$ around $\mathbf{R}_i$ and is zero otherwise. Here a is the lattice constant. The quantity $E_\alpha(i)$ represents the conduction ($\alpha=e$) and valence ($\alpha=h$) band-edge fluctuations from cell to cell given by $E_\alpha(i) = [(1-x)\hat{\mathbf{n}}_i - x(1-\hat{\mathbf{n}}_i)]dE_\alpha/dx$, where $x = \langle \hat{\mathbf{n}}_i \rangle$, $\hat{\mathbf{n}}_i (= 0,1)$ is the occupancy of the cell, say, by an In-atom and dE_α/dx is the band-edge shift per concentration change.

Excitons are localized by the random alloy potential. However, the localization radius of the center-of-mass (CoM) wave function turns out to be very large for $In_{0.48}Ga_{0.52}P$ (and in general for other III-V systems), yielding negligible LWs [2]. Therefore, we consider other mechanisms of exciton localization, for example, by pinning centers such as acceptor or donor centers and isoelectronic impurities. The total wave function equals $\Psi = \Phi(\mathbf{R})\psi(\mathbf{r})$ where $\psi(\mathbf{r})$ is the wave function of the relative coordinate $\mathbf{r} = \mathbf{r}_e - \mathbf{r}_h$ given by

$$\left(-\nabla^2 - 2/r + \frac{\gamma^2}{4} r^2 \sin^2\theta\right)\psi(\mathbf{r}) = \varepsilon\psi(\mathbf{r}) \qquad (1)$$

and $\Phi(\mathbf{R})$ is the wave function for the CoM coordinate $\mathbf{R}$. Here $\nabla = \partial/\partial\mathbf{r}$, $r = |\mathbf{r}|$ and θ is the polar angle with respect to $\mathbf{B}$. The length, energy and the reduced field γ are, respectively, given in (1) in units of the Bohr radius $a_B = \kappa\hbar^2/\mu e^2$, exciton binding energy $\epsilon_B = \mu e^4/(2\kappa^2\hbar^2)$ and $\gamma = \hbar\omega_c/2\epsilon_B$, where $\omega_c = eB/\mu c$. Here κ, e and c are the dielectric constant, electronic charge and the speed of light. The reduced mass equals $\mu = m_e m_h/(m_e + m_h)$, where m_e and m_h are electron and hole effective masses. The function $\Phi(\mathbf{R})$ is not known in general and it is sufficient for our purpose to assume $\Phi(\mathbf{R}) = (\pi R_o^2)^{-3/4}\exp(-R^2/2R_o^2)$. The basic ingredient of the phenomenological wave function $\Phi(\mathbf{R})$ is the localization radius R_o. The quantity R_o is independent of B, because the CoM motion is insensitive to B

due to the charge neutrality of the exciton.

The first-order correction for the alloy-fluctuation energy for a given exciton is given by $\delta E = \langle \Psi | V_e(\mathbf{r}_e) + V_h(\mathbf{r}_h) | \Psi \rangle$. The mean-square deviation equals:

$$\langle \delta E^2 \rangle = \frac{\Delta V}{(2\pi)^2} \int \zeta_{\mathbf{k}}^2 \left[\langle E_e^2 \rangle \rho_{\mathbf{k}_e}^2 + \langle E_h^2 \rangle \rho_{\mathbf{k}_e}^2 + 2 \langle E_e E_h \rangle \rho_{\mathbf{k}_h} \rho_{\mathbf{k}_e} \right] d^3k, \qquad (2)$$

where $\mathbf{k}_\alpha = m_\alpha \mathbf{k}/M$, $M = m_e + m_h$, $\rho_{\mathbf{k}} = \int \rho(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r}) d^3r$ and $\zeta_{\mathbf{k}} = \int \zeta(\mathbf{r}) \exp(i\mathbf{k}\cdot\mathbf{r}) d^3r$. Here $\rho(\mathbf{r}) = |\psi(\mathbf{r})|^2$, $\zeta(\mathbf{r}) = |\Phi(\mathbf{r})|^2$ and $\langle E_\alpha(i) E_\beta(i') \rangle = \langle E_\alpha E_\beta \rangle \delta_{i,i'}$, dropping the site index from $E_\alpha(i)$. The brackets $\langle\rangle$ denote the spatial average and $\delta_{i,i'}$ Kronecker's delta. Using the expression for $E_\alpha(i)$, we find $\langle E_e^2 \rangle = \eta^2 E_o^2$, $\langle E_h^2 \rangle = (1 - \eta)^2 E_o^2$ and $\langle E_e E_h \rangle = \eta(1 - \eta) E_o^2$, where $E_o^2 = (dE_g/dx)^2 x(1 - x)$ and $\eta = (dE_e/dx)/(dE_g/dx)$ is the fractional conduction-band-edge shift. The result in (2) yields a Gaussian line shape in agreement with the data. The full-width-at-half-maximum (FWHM) equals $\Delta\epsilon_{FWHM} = 2.355(\langle \delta E^2 \rangle)^{1/2}$.

In the following we evaluate $\Delta\epsilon_{FWHM}$ for $In_{0.48}Ga_{0.52}P$ using $m_h = 0.44$, $m_e = 0.091$ (in units of free electron mass), $a = 5.66$ Å, $\kappa = 11.6$ and $dE_g/dx = 1.15$ eV [3]. The probability density function $\rho(\mathbf{r})$ is obtained numerically from (1), using a five-point difference equation approach [2]. Equation (2) was evaluated numerically, assuming $m_h \gg m_e$. The parameters (R_o, η) are used as adjustable parameters. In Fig. 1 we plot the FWHM as a function of B and compare with the data from disordered $In_{0.48}Ga_{0.52}P$ [4]. Primary evidence of order and disorder comes from TEM and bandgap data. In Fig. 1, the solid, long-dashed and short-dashed curves represent (R_o, η) = (0, 0.96), (0.22, 0.89) and (0.34, 0.78), respectively. The slope of the curve is sensitive to R_o (given in units of a_B). For large R_o >> 1, the FWHM becomes small, because the energy fluctuation, being inversely proportional to the square-root of the exciton volume, is small. The agreement between the theory and the data is good. A more detailed description of the work is given elsewhere [2].

The LW arising from localized excitons was studied earlier. In earlier work, δE in (2) was defined as a sum of local bandgap deviations [1, 5]. In the present work, δE is given by the sum of $V_e(\mathbf{r}_e) + V_h(\mathbf{r}_h)$ which is a **nonlocal** bandgap deviation. Earlier results [1, 5] correspond basically to the first term of (2) with the restriction (R_o, η) = (0, 1).

PL Linewidth from Free Excitons

Our low-temperature PL data from ordered $In_{0.48}Ga_{0.52}P$ and InAs show PL LWs decreasing as a function of B. Since the PL LW from localized excitons is shown to increase with B in the previous section, we consider only free excitons to explain the LW

decreasing with B. In the following, we propose a model which yields such a behavior for the homogeneous exciton LW arising from exciton-impurity scattering; The observed LW consists of homogeneous and inhomogeneous contributions.

We consider only exciton scattering with charged impurities. More complicated neutral-impurity scattering will be studied elsewhere. The potential energy between an exciton and an impurity of negative charge -|e| at the origin, averaged over the angular coordinate (Ω) of the CoM position vector **R**, is given by $V(R,r) = (e^2/\kappa)\langle 1/r_e - 1/r_h\rangle_\Omega$. This potential is attractive and saturates to a constant value $-(M\Delta m/m_h m_e)e^2/\kappa r$ for $R < m_e r/M$, equals $(e^2/\kappa)[M/m_h r - 1/R]$ in the range $m_e r/M < R < m_h r/M$ and vanishes for $m_h r/M < R$, where $\Delta m = m_h - m_e$. The scattering potential $V(R)$ is then given by averaging $V(R,r)$ with a weighting factor $\rho(\mathbf{r})$ obtained from (1).

The total scattering cross section σ from $V(R)$ is obtained through a phase-shift analysis [6], which converges very fast with increasing angular momentum quantum number ℓ with a negligible contribution from $\ell \geqq 3$. The LW is estimated from the kinetic formula $\hbar\tau^{-1} = \hbar v\sigma N$ where N is the impurity density, v is the velocity obtained from exciton-photon momentum conservation $v = nE_g/Mc$ and n is the refractive index. The polariton effect was not observed possibly due to large LWs and is not considered here.

We first discuss the LW in ordered $In_{0.48}Ga_{0.52}P$. For negatively charged impurities, σ is very large and sensitive to B for low-energy excitons. For example, σ drops from $550a_B^2$ ($116a_B^2$) to nearly zero as B increases from zero to 5 T for the incoming exciton energy $10^{-3}\epsilon_B$ ($10^{-2}\epsilon_B$). A similar effect is obtained if we reduce the size of the wave function instead of applying the field; For the incoming energy $10^{-3}\epsilon_B$, for example, the total σ drops from $550a_B^2$ to almost zero, if the Bohr radius of the field-free 1s wave function is reduced by about 10%. For positively charged impurities, σ is much smaller and less sensitive to B; σ is about $14.9a_B^2$ ($14.3a_B^2$) at $B = 0$ for the incoming energy $10^{-3}\epsilon_B$ ($10^{-2}\epsilon_B$) and decreases slowly to $5.3a_B^2$ ($5.2a_B^2$) at $B = 15$ T. In Fig. 2, the theoretical result is compared with the data for negatively charged impurities of the density $N = 3\times10^{16}\ cm^{-3}$. An inhomogeneous background is added to fit the data, although this is strictly valid only for Lorentzian lines. For positively charged impurities, much larger density is necessary. The negative charge centers may be ionized acceptors due to compensation.

For InAs, σ is smaller for negatively charged impurities and oscillates with B, because the effective kinetic energy is enhanced by a factor m_h/m_e, which is very large in

InAs. On the other hand, σ behaves similarly to $In_{0.48}Ga_{0.52}P$ and is larger than that in $In_{0.48}Ga_{0.52}P$ for positively charged ions. Therefore, we plot the LW, assuming positively charged impurities in Fig. 3 and compare with the data, employing the standard mass m_e = 0.023 and $N = 5\times10^{16}\ cm^{-3}$ (dashed curve) and the observed mass $m_e = 0.033$ (through field-dependent line shift) and $N = 10^{17}\ cm^{-3}$ (solid curve). Again, a constant background LW is added to fit the data. Standard parameters $m_h = 0.4$ and $\kappa = 14.6$ are used. The InAs sample was n-doped to about $5\times10^{16}\ cm^{-3}$. The total σ due to ionized donors is comparable to that calculated for neutral donors at zero field [7] owing to the large donor orbit. Therefore the theoretical results in Fig. 3 may be valid for neutral donors as well. This question is under investigation.

This work supported by the Division of Materials Science, Office of Basic Energy Science, U.S. DOE under Contract No.DE-AC04-76DP00789.

References

[1] R. A. Mena, G. D. Sanders, and K. K. Bajaj, J. Appl. Phys. **70**, 1866 (1991).
[2] S. K. Lyo, Phys. Rev. B (1993), to be published.
[3] Landolt-Bø¨rnstein Series III, edited by O. Madelung (Springer, New York, 1987), Vol. 22a, p. 141.
[4] E. D. Jones, R. P. Schneider, Jr., S. M. Lee, and K. K. Bajaj, Phys. Rev. B **46**, 7225 (1992).
[5] S. M. Lee and K. K. Bajaj, Appl. Phys. Lett. **60**, 853 (1992) and references therein.
[6] S. E. Koonin and D. C. Meredith, *Computational Physics, Fortran Version* (Addison-Wesley, New York, 1990), p. 104.
[7 J. Lee, E. S. Koteles, M. O. Vassell, and J. P. Saleerno, J. Lum. **34**, 63 (1985).

Figure Captions

Fig. 1 FWHM as a function of the magnetic field.

Fig. 2 FWHM as a function of the reduced field for ordered $In_{0.48}Ga_{0.52}P$.

Fig. 3 FWHM as a function of the reduced field for InAs. The solid and dashed curves correspond to different electron mass and impurity density (given in the text).

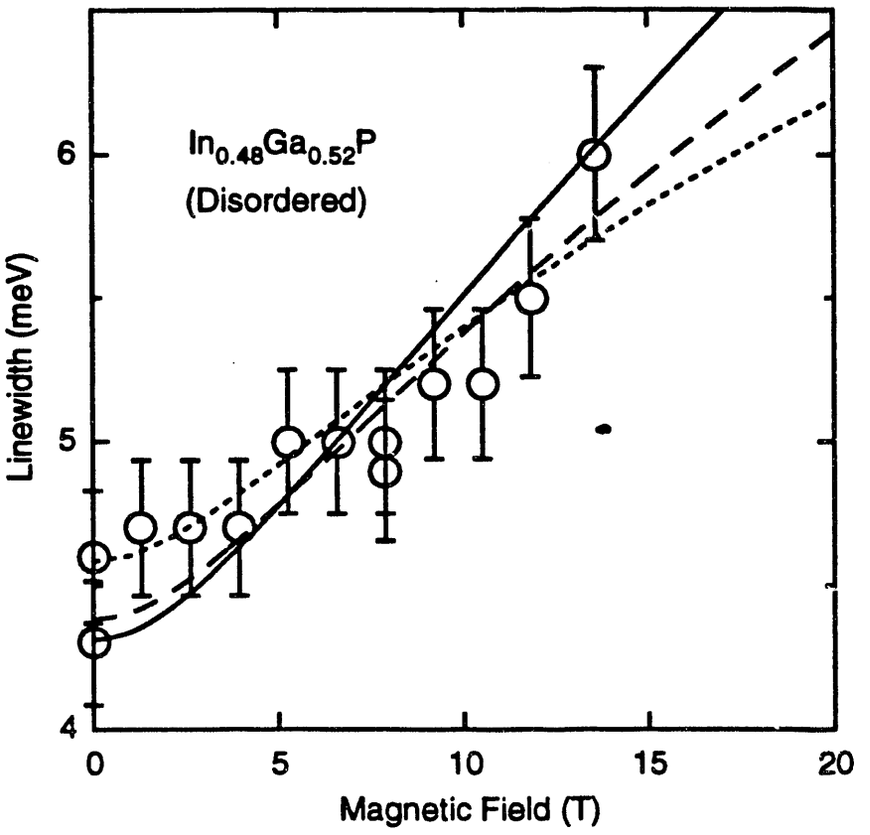
$In_{0.48}Ga_{0.52}P$
(Disordered)
Linewidth (meV)
Magnetic Field (T)
4
5
6
0
5
10
15
20

Fig. 1

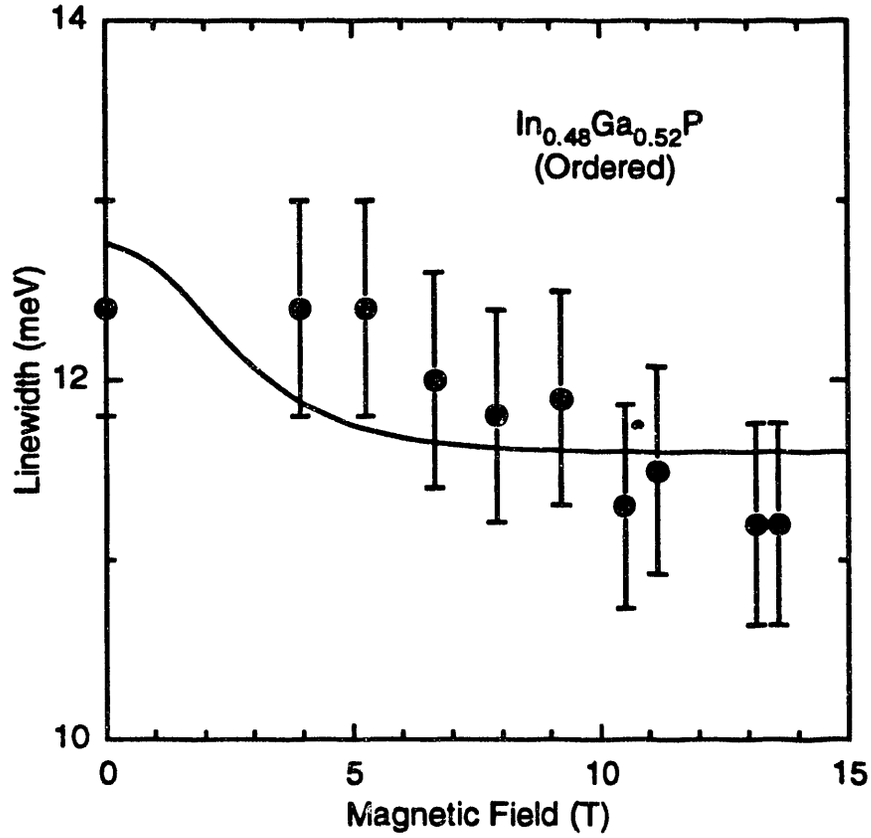
14
12
10
Linewidth (meV)
$In_{0.48}Ga_{0.52}P$
(Ordered)
0
5
10
15
Magnetic Field (T)

Fig. 2

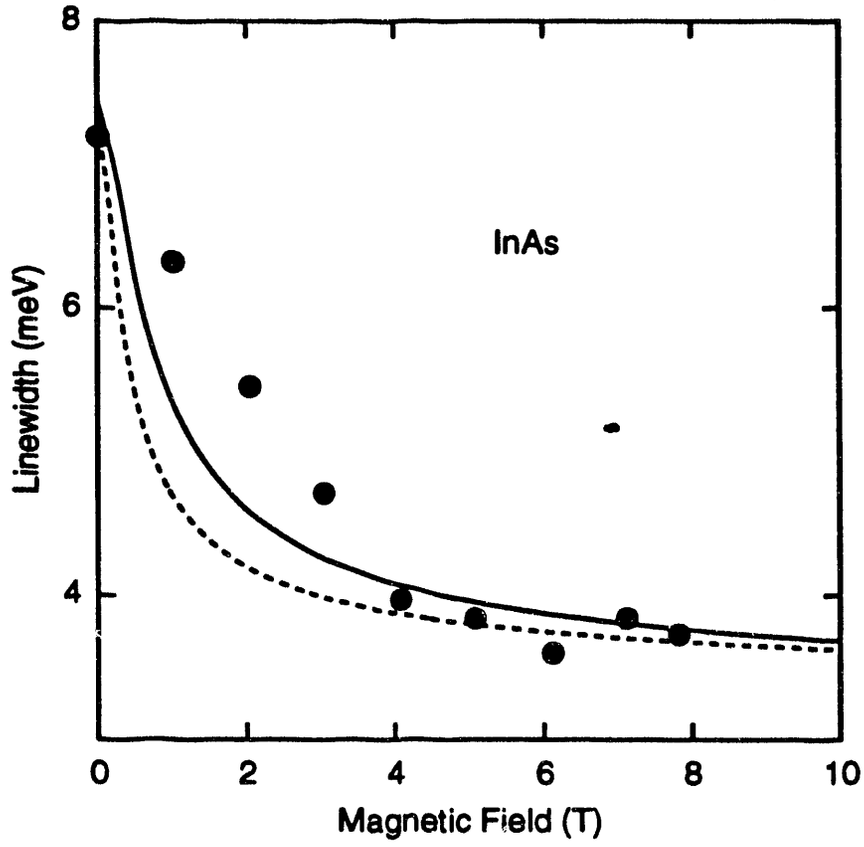

Fig. 3

END

DATE FILMED

10/29/93