# Alloy broadening of the near-gap luminescence and the natural band offset in semiconductor alloys

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**Abstract.** The inhomogeneous broadening of the near-gap emission (bound excitons (BE) and conduction-band to acceptor (CA)) in semiconductor alloys is reanalysed using the Markoff statistical theory for fluctuations of alloy composition. We give the exact relationship between the linewidth and the Bohr radius of the bound particle. The results of our theory indicate that even in the best GaAlAs samples there is still a significant contribution from other broadening mechanisms. We also show that the linewidth ratio of the CA to BE emission lines may provide a good estimate of the natural band offset in the alloy.

## 1. Introduction

We shall show how the inhomogeneous broadening of spectra in semiconductor alloys may be analysed quantitatively. Our approach follows methods applied previously to a range of spectroscopies involving many types of inhomogeneous broadening [1]. Whilst the qualitative ideas of the effect of alloy disorder are long established, our quantitative approach allows us to compare different types of spectra (here bound exciton emission and conduction-band to acceptor emission) and hence to estimate the natural band offset (NBO) for semiconductors. We also identify discrepancies between observation and common simple models. In particular, it is possible to avoid previous arbitrariness which has prevented the separation of the truly fluctuation-limited broadening component of observed linewidths.

The low-temperature emission in high-purity p-type semiconductors is dominated by bound exciton (BE) emission, with conduction-band to acceptor (CA) transitions observed at slightly lower energies.

The emission processes in high-purity ternary semiconductors are broadened relative to those in binary semiconductors. This is due to alloy disorder, since statistical fluctuations of the composition lead to fluctuation of the energies of the band edges, and thus to a broadening of all electron–hole recombination processes [2–6]. We shall calculate the relevant magnitude of the fluctuations, and will show how the resulting emission linewidth depends on the degree of localization of the quasiparticles involved in the recombination. Clearly both the length scale characterizing localization and the parameter relating energy shift to change in composition will depend on which emission is considered.

## 2. Theory of the alloy broadening of the spectra

Any quantitative approach to inhomogeneous broadening of defect spectra in an alloy (A, B) C must make assumptions about (i) the energy change produced by changing an A atom for a B atom at the sites close to the defect and (ii) the relative probabilities of A and B atoms on particular sites close to the defect. In our analysis we shall also make working assumptions, specifically for item (i) that the difference between A and B atoms can be represented by a delta-function potential. For item (ii) we shall assume a randomly disordered alloy. These working assumptions are not essential, and it is easy to extend our results to more general models.

To be specific, we may consider an alloy like $Ga_{1-x}Al_xAs$. Taking GaAs as a reference binary alloy, there is a volume density $\rho = x/\Omega$ ($\Omega$ is a unit cell volume) of the perturbing Al, and it is the many small contributions of the Al atoms close to each defect which cause broadening. For a particular defect (whether involved in BE or CA transitions), a specific Al substitution for Ga at the site $r$ contributes an individual shift

$$\delta E = \mathscr{E}_i \Omega |\Psi(r)|^2 \tag{1}$$

where $\mathscr{E}_{BE} = dE_g/dx$ and $\mathscr{E}_{CA} = dE_{vb}/dx$; $\Psi(r)$ is the wavefunction of a quasiparticle controlling the broadening.

The moments of the inhomogeneously broadened lines can be expressed in terms of integrals $S_n$, where [1]

$$S_n = \rho \int \mathrm{d}z \, p(z)(\delta E(z))^n. \qquad (2)$$

Here $z$ is just $r$, though in more complex cases other parameters may be involved (e.g. ionic charge, if that can vary and random electric fields are considered). $p(z)$ is the distribution function for the different species of perturbing ions (here $p(z)\mathrm{d}z$ is just $\mathrm{d}r$). $\delta E(z)$ is essentially $\delta E(r)$.

In the Gaussian limit, the halfwidth of the emission line is then

$$\Gamma = 2.35 \, \mathscr{E}_i\!\left(x(1-x)\Omega \int \mathrm{d}r|\Psi(r)|^4\right)^{1/2} \qquad (3)$$

with a numerical factor 2.35 relating the halfwidth $\Gamma$ of the Gaussian line to its second moment.

A formally similar result has been obtained recently by Yanchev and Bleris [7] in the context of an impurity-band formation caused by the local-potential fluctuations in $Ge_{1-x}Si_x$ alloys and by Mycielski et al [8], who studied the energy distribution of shallow donor states in mixed diluted magnetic semiconductors.

In many cases the relevant wavefunction $\Psi(r)$ can be approximated by the hydrogenic 1s wavefunction $\Psi_{1s}(r) = (\pi a_B^3)^{-1/2} \exp(-r/a_B)$. If such an approximation is valid, the halfwidth $\Gamma$ is

$$\Gamma = 2.35 \, \mathscr{E}_i\!\left(\frac{x(1-x)\Omega}{8\pi a_B^3}\right)^{1/2}. \qquad (4)$$

We may contrast this result with earlier work in which the binomial distribution for $N$ atoms was used to describe the fluctuations [2, 4, 5, 9]. In such calculations $N$ is described as the ratio of an effective volume $V$ of the perturbed quasiparticle to the cell volume $\Omega$, but no proper calculation of $V$ has been offered before. The theory given here yields

$$V = 8\pi a_B^3. \qquad (5)$$

In previous approaches the volume $V$ was approximated [2, 5, 9] by a volume of a sphere with a radius equal to a Bohr radius $a_B$. This leads to a very significant overestimation of the linewidth by a factor of $\sqrt{6}$. An alternative approach suggested by Singh and Bajaj [3] leads to an even bigger overestimation: with their critical-distance parameter $r_c$ taken to be the cation–anion distance in a zincblende lattice, the linewidth overestimation is as large as the factor $(3\pi\sqrt{3}/2)^{1/2} = 2.9$.

The linewidths from previous analyses prove to be larger than those observed, so that experiment and the simplest theories cannot be reconciled. The widths given by our more precise theory prove somewhat smaller, possibly implying an additional broadening mechanism.

The results of our theory can be directly applied to analyse the fluctuation-limited broadening observed in numerous experiments which probe defect energy levels (e.g. in deep-level transient spectroscopy or the Hall effect [9, 10]). The parameter $\mathscr{E}_i$ in equation (3) or (4) now becomes the observed composition dependence of

the defect energy levels. The Bohr radii $a_B$ cause more difficulty, not least because of uncertainties in effective masses, but mainly due to the breakdown of a hydrogenic model in the case of most deep-level defects.

## 3. Inhomogeneous broadening of bound exciton emission in AlGaAs

In figure 1 we collect the best published results [6, 11] for $Ga_{1-x}Al_xAs$ bound exciton (BE) emission linewidths. There the full curve has been calculated by using equation (4), in which the exciton Bohr radius $a_B$ has been computed in the effective-mass approximation, i.e. $a_B^c$ being inversely proportional to the effective mass $m^*$ of the bound quasiparticle. For an exciton, $1/m_e^* = 1/m_c^* + 1/m_h^*$ ($m_c^*$ and $m_h^*$ are the electron and hole effective masses respectively). The unit cell volume $\Omega$ in the zincblende lattice equals $a_0^3/4$, with $a_0$ being the lattice constant. In this simplified model all corrections related to the fact that the exciton bound at a neutral impurity is in fact a three-particle problem were neglected. It is also worth stressing that the results of the model calculations must not describe correctly a free-exciton emission broadening due to a motional narrowing. This effect is obviously absent in the case of a bound exciton.

In spite of the technological importance and advanced technology of $Ga_{1-x}Al_xAs$ alloys, there still exist serious discrepancies concerning most of the material parameters entering equation (4). The composition dependence of the energy gap has recently been strongly revised [12]. Taking into account the band-offset data, [13, 14] we used a value of 1.34 eV for $\mathrm{d}E_g/\mathrm{d}x$. For the electron effective mass we employed the results of El Jani et al [15] for the direct energy gap obtained from the Shubnikov–de Haas oscillations. The large uncertainty occurs for the hole effective mass [16], because there are no experimental data for AlAs and the alloy. Moreover, in
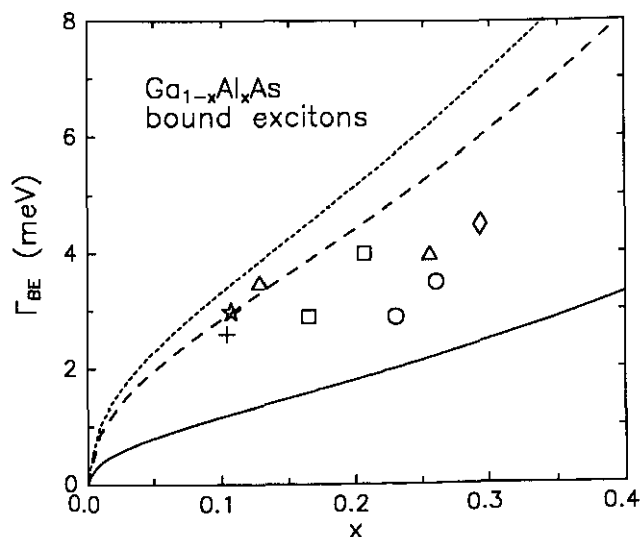
Figure 1. Comparison of the best published results of the BE luminescence half-widths in $Ga_{1-x}Al_xAs$ (taken from [6] ○ and [11] (a) □, (b) +, (c) △, (d) ☆, (e) ◇) with theory (full curve, this paper; long broken curve [2]; short broken curve [3]).

many tabulations [16] a cyclotron effective mass is quoted, which in the case of the valence band leads to an overestimation of the energetic effective mass to be used in the calculation of $m_{exc}^*$. An additional serious obstacle is the complicated structure of the valence band and the three-particle nature of the BE. A prime factor determining the exciton binding energy and its Bohr radius is the electron effective mass. The hole contribution we approximated by using as $m_h$ the average spherical heavy-hole mass computed from the most recent values of the Luttinger $\gamma_i$ parameters for GaAs and AlAs [17]. For the alloy we used a linear interpolation (see table 1).

It is clear from figure 1 that previous approaches [2, 3] grossly overestimate the BE linewidths. Our theory predicts broadening smaller than observed in the best reported samples. This conclusion does not depend on a choice of the hole effective mass (taking even an infinitely large $m_h$ produces linewidths that are still smaller than the best experimental results). We therefore suggest that there still exist mechanisms other than alloying that contribute to the linewidth. It is clear that these will always cause extra broadening, and so would make the previous workers' results worse. Among the most likely are the non-randomness in the formation of the cation sublattice and elastic terms resulting from the different cation volumes in the alloy [18]. These mechanisms could be the true limiting factors of the linewidths in the semiconductor alloys, in addition to the alloy fluctuations discussed here.

## 4. Inhomogeneous broadening of conduction-band to acceptor emission in AlGaAs

Calculation of the linewidths of the CA transition by using the above approach needs certain approximations due to the more complicated wavefunction of the acceptor. Moreover, the chemical shift, causing departure of the acceptor binding energies from the predictions of the pure hydrogenic effective mass model, affects the effective Bohr radius of the bound hole, and thus the linewidth of the CA emission (the contribution of the conduction-band electron to the linewidth can be safely neglected because the mean free path in pure $Ga_{1-x}Al_xAs$ is much larger than the effective Bohr radius of the hole bound at the acceptor [2]). Fortunately, in the purest $Ga_{1-x}Al_xAs$ considered here, the dominant acceptor is carbon

—which departs least from the hydrogen model. Its binding energy in the alloy changes as $E_b = 26.7 + 5.75x + 123x^{3.4}$ [19]. The use of a simple hydrogenic model of the acceptor is hardly acceptable. It is, however, possible to estimate the effective Bohr radius from the experimental value of the binding energy through the relation $E_b = e^2/2\varepsilon_0 a_B$. This procedure has the advantage of taking into account to some extent the chemical shift specific for a given acceptor. The value of $dE_{vb}/dx$ entering equation (4) has been taken equal to 0.45 eV according to most recent determinations of this quantity [13, 14].

Figure 2 presents a collection of the best results for the CA emission in the direct-gap $Ga_{1-x}Al_xAs$. The full curve represents the result obtained from our theory with all the approximations described above. It is again clear that the previous approaches grossly overestimate the observed linewidths.

The theory of the alloy broadening presented here can be used directly if a more realistic model of the acceptor is available. Such a model has recently been developed by one of us for the effective mass acceptors in Si and Ge [20, 21]. The model follows the method initiated by Baldereschi and Lipari [22]. It takes into account all details of the valence band of the zincblende compounds, namely warping and the existence of the spin–orbit split-off valence band. Using this model we computed the ground-state energies and the integral $I_4 = \int dr |\Psi(r)|^4$ for the effective mass acceptors in GaAs and in $Ga_{1-x}Al_xAs$ alloys. For the alloy we used the virtual crystal approximation with all relevant parameters (dielectric constant $\varepsilon_0$, the energy $\Delta$ of the spin–orbit split-off valence band and the Luttinger parameters

**Table 1.** Material parameters for $Ga_{1-x}Al_xAs$.

| | | |
|---|---|---|
| $dE_g(\Gamma)/dx$ | 1.34 eV | [12, 13] |
| $dE_{vb}/dx$ | 0.45 eV | [13] |
| $\varepsilon_0(x)$ | $12.4 - 0.28x$ | [16, 17] |
| $m_e^*(x)/m_e^0$ | $0.0657 + 0.0174x + 0.145x^2$ | [15] |
| $\gamma_1$ | $7.15 - 2.81x$ | [17] |
| $\gamma_2$ | $2.03 - 1.21x$ | [17] |
| $\gamma_3$ | $2.96 - 1.24x$ | [17] |
| $m_{hh}^*(x)/m_e^0$ | $0.51 + 0.1x$ | computed from $\gamma_1, \gamma_2, \gamma_3$ |
| $\Delta_{so}(x)$ | $341 - 66x$ meV | [16] |
| $\Omega$ | $45.1$ Å$^3$ | [16] |



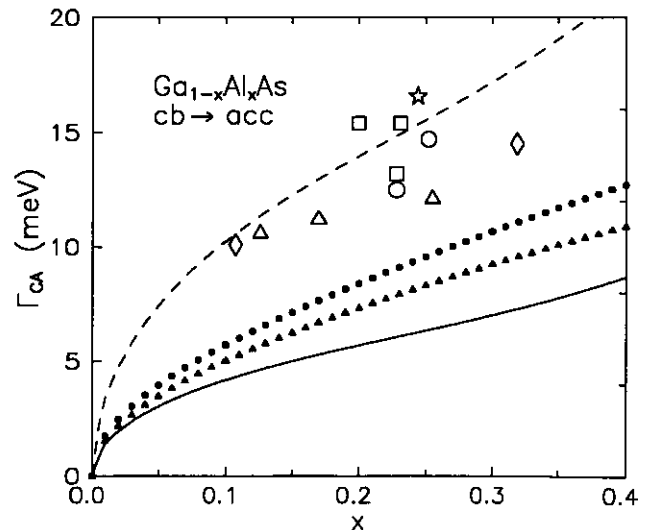**Figure 2.** Comparison of the best published results of the CA luminescence half-widths in $Ga_{1-x}Al_xAs$ (taken from [6] ○ and [11] (a) □, (c) △, (d) ◇, (f) ☆) with theory (full curve, simplified hydrogenic model of this paper; broken curve [2]; full symbols, realistic model of acceptors in GaAlAs: ● linewidth calculated from the $I_4$ integrals, ▲ 'hydrogenic' model but using calculated acceptor binding energies).

$\gamma_i$) linearly scaled between GaAs and AlAs (see table 1). We have also retained spherical symmetry of the Coulomb potential in the alloy. The major difference from the computations of the properties of acceptors in Si and Ge [20, 21] is that here we truncated the dielectric function into the dielectric constant $\varepsilon_0$ and no central-cell correction potential producing the chemical shift was used. Both approximations affect most the Coulomb potential close to the impurity site. Carbon is the shallowest acceptor, so the central-cell corrections must be smallest among all group-IV acceptors. On the other hand any chemical shift correction for carbon—the uppermost acceptor in group IV of the periodic table—should lower its binding energy in comparison with the isocoric germanium. The effect of the dielectric function is opposite. We can therefore assume that the two effects at least partially cancel each other, so our approximations should work best just for the carbon acceptor. The trial wavefunctions used in a computation were similar to those used in [20, 21].

The results of the variational computations for GaAs and several $Al_xGa_{1-x}As$ alloy compositions are presented in table 2. The acceptor binding energies follow closely the composition trend for the carbon acceptor in $Ga_{1-x}Al_xAs$. The linewidths calculated from the computed integrals $I_4$ reproduce quite well the best published experimental values. It is also worth noting how closely the crude hydrogenic model, in which we used as input the computed acceptor binding energies (see figure 2), reproduces more accurate theory. This supports a simplified procedure of estimating the Bohr radius and then the CA linewidth from a simple 'hydrogen-like' formula for the binding energy: $E_B = e^2/2\varepsilon_0 a_B$ with experimental $E_B$ values.

## 5. Band offsets and alloy broadening

We may combine the results reported above for the BE and CA to provide also a unique and simple method for the estimation of the natural band offset (NBO) in semiconductor alloys. The NBO is just the slope of the dependence of either the conduction or valence band edge energy on the composition (e.g. the valence band NBO equals $dE_{vb}/dx = Q_{vb}\,dE_g/dx$). In the case of the lattice-matched heterojunctions NBO coincides with the heterojunction band offset [14], while in the case of the lattice-mismatched heterojunctions the final band offset is a sum of the NBO and the interface strain contribu-tion [14, 23]. The current status of the theory does not allow a precise estimation of both. Various experimental techniques provide information on the total band offset only [14]. Recently a heuristic way of estimating the NBO in the alloys has been proposed and successfully tested for all reliable lattice-matched heterojunctions [13, 24]. This method uses transition-metal energy levels as the reference levels for the band alignment. The near-gap emission broadening provides a more direct way of estimating the NBO. From equation (3) or (4) it is clear that the ratio of the CA to BE linewidths gives a direct measure of the NBO, provided the exciton and acceptor wavefunctions are known. If they can be approximated by the 1s-like envelope, then the ratio of the linewidths is a simple function of the effective Bohr radii (see equation (4)). Therefore the valence band NBO is

$$Q_{vb} = [\Gamma(CA)/\Gamma(BE)](a_B^{acc}/a_B^{exc})^{3/2}. \quad (6)$$

This can be simplified even further by estimating the Bohr radii from the respective binding energies:

$$Q_{vb} = [\Gamma(CA)/\Gamma(BE)](E_B^{exc}/E_B^{acc})^{3/2}. \quad (7)$$

An alternative way to estimate the value of $Q_{vb}$ for a new material is to use a material for which the NBO is well established (e.g. $Ga_{1-x}Al_xAs$ [13, 14]) and to scale the luminescence data for the CA transition by the data known for the latter. Then, taking the acceptor Bohr radius as proportional to $\varepsilon/E_B$, a reasonable estimation of an unknown value of the NBO can be obtained. Among recent controversies concerning the band offset partition, the large discrepancies in the GaAs/InAs band offset predictions require special attention because these compounds constitute the technologically important InP-based heterojunctions [13]. As there are no data on transition metals in relatively narrow-gap InAs, the above proposal should provide an effective means of clarifying this issue.

**Table 2.** Composition dependence of the acceptor in $Ga_{1-x}Al_xAs$. Energies are in meV and $I_4$ in units of $10^{-6}\ \text{Å}^{-3}$.

| $x$ | $E_B$ [19] | $E_B^{th}$ | $I_4$ |
|-----|-----------|-----------|-------|
| 0   | 26.7 | 28.6 | 5.97 |
| 0.1 | 27.3 | 31.0 | 7.19 |
| 0.2 | 28.4 | 33.7 | 8.75 |
| 0.3 | 30.5 | 36.7 | 10.8 |
| 0.4 | 34.5 | 40.1 | 13.4 |

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