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Spin-Exchange Interaction in ZnO-based Quantum Wells

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Abstract: Wurtzitic ZnO/(Zn,Mg)O quantum wells grown along the (0001) direction permit unprecedented tunability of the short-range spin exchange interaction. In the context of large exciton binding energies and electron-hole exchange interaction in ZnO, this tunability results from the competition between quantum confinement and giant quantum confined Stark effect. By using time-resolved photoluminescence we identify, for well widths under 3 nm, the redistribution of oscillator strengths between the A and B excitonic transitions, due to the enhancement of the exchange interaction. Conversely, for wider wells, the redistribution is cancelled by the dominant effect of internal electric fields, which dramatically reduce the exchange energy.

Exchange interaction energy naturally appears in quantum mechanics whenever one has to deal with identical interacting particles. This interaction is important for understanding particle physics, interpreting small energy splittings in atoms and to describe spin-related excitonic fine structure in condensed matter. In this latter case, a prerequisite to the interpretation of the overall optical properties of pure solids has been the definition of the short-range and long-range contributions to this interaction¹.

As a recent evidence of the importance of this issue, the particularly large (4.7 meV) electron-hole (e-h) short-range exchange interaction energy γ in ZnO, has been proved to be a crucial ingredient that explains the nature (the symmetry) of the states involved in the fundamental band-gap of this solid². This provided a physical explanation to the series of advanced experimental investigations^{4,5} which recently ended up a more than 40 year old controversy. This particularly large value of γ specificity of ZnO opens new perspectives if we think of using this compound in quantum nanostructures: to what extent could such artificial systems allow us to tune the exchange interaction?. Could we then get, by using this new degree of freedom a better control of the symmetry of eigenstates and therefore of spin-related optical properties?

In this letter, we present novel results that provide quantitative elements for further investigations of these questions. We emphasize the importance of e-h exchange interaction to explain time-dependent photoluminescence (PL) properties of narrow wurtzite ZnO / (Zn,Mg)O quantum wells (WQWs). In such objects, the strong built-in electric field induces an exponential increase of decay time with well width (L_W), for the wide WQWs⁶. The situation is more complex for narrow WQWs as we already noticed it⁶. It is the purpose of this letter to explain it. We show that the enhanced e-h exchange interaction redistributes oscillator strengths among exciton states built from different valence bands in a way that depends on well width. To do so, we provide a good description of our results by using a model that accounts for the intricate effects of Coulomb attraction, of the internal electric field and of the e-h exchange interaction. This being quite

complex and this resulting from different origins, we therefore begin this letter by a review of these phenomena and of their respective impacts in the context of low-dimensional semiconductor systems.

Generally, the reduction of dimensionality blue-shifts the band-gap of the system, but it also modifies the excitonic properties: enhancement of binding energy^{7,8}, participation to valence-band state mixing⁸, re-distribution of oscillator strengths among the various excited states (including unbound states)⁹, enhancement of the electron-hole exchange interaction¹⁰⁻¹³,... The latter effect is expected to influence, in particular, the spin-relaxation time of excitons¹⁴. In this context, for a quantum system of interest, it is crucial to have the best possible knowledge of the symmetry and spin-related properties of excitonic eigenstates. It has been pointed out¹², in particular, that exciton spin relaxation should be sensitive to the presence of an electric field along the growth axis of the QW.

Such electric fields were found to result naturally in WQW structures, from some symmetry reduction. The latter can induce piezoelectric fields, *e.g.* in strained QWs based on zincblende III-V or II-VI semiconductors, grown away from the (001) direction¹⁴⁻¹⁶. The resulting "quantum-confined Stark effect" (QCSE) reduces the 1s-exciton binding energy but still red-shifts the corresponding optical transition. It reduces the exciton oscillator strength by separating the wavefunctions of the electron and hole and by loosening the Coulomb attraction that controls the extension of their in-plane relative motion¹⁷. Giant effects of the same nature have been studied in the past few years in quantum nanostructures based on semiconductors of wurtzite crystal symmetry. For instance, group-III nitride semiconductors exhibit particularly large coefficients of both spontaneous and piezoelectric polarizations (comparable to those of ZnO)¹⁸ and thus can generate internal fields of several MV/cm. For wide enough nitride WQWs (above a few nanometers, in practice), the QCSE is so strong that it can counteract the quantum confinement and

therefore can push the fundamental transition *below* the natural excitonic gap of the WQW material¹⁹. Two regions of well widths can be defined:

- for narrow WQWs, the quantum confinement dominates, yielding large emission energies and typical excitonic lifetimes of nanoseconds, or slightly less,
- for wide enough WQWs, the QCSE dominates and the emission energy decreases almost linearly with increasing L_W , whereas the exciton lifetime increases (its oscillator strength decreases) almost exponentially.

The exchange interaction participates to the partial lifting of exciton degeneracy, being superposed to crystal-field and internal strain effects and to spin-orbit interaction¹. For group III-nitride WQWs, due to excessive inhomogeneous broadening effects²⁰, the short-range electron-hole exchange interaction was not identified as an important issue although it plays, for micrometric epilayers²¹, a role in the mixing of the excitonic states that originate from the different valence-bands. In the case of wurtzite ZnO epilayers, after Reynolds et al. and Adachi et al.^{4,5} ended the longstanding controversy on the valence-band ordering, Gil and co-workers^{2,3} have established, by using a model considering the appropriate symmetry, *that the weak oscillator strength of the A-exciton compared to the B-exciton results, in particular, from quantum beat oscillations that are extremely efficient due to the giant magnitude of the short-range electron-hole exchange interaction energy*, $\gamma = 4.7$ meV, to be compared to 0.69 meV for GaN²¹ or 0.02 meV²² for GaAs. Quantum confinement is known to enhance this interaction by a factor that is inversely proportional to the squeezed volume occupied by the confined exciton wave-function. For quantum wells, the amplification factor is given by¹⁰:

$$\mathbf{a} = \mathbf{p} a_{3D}^{-3} W_{eh} |\mathbf{j}_1(0)|^2 \quad (1),$$

where a_{3D} is the excitonic effective Bohr radius for the bulk material. The exciton relative motion is described by the product of envelope-functions $f_e(z_e)$ and $f_h(z_h)$ describing the electron and hole confinement along the QW growth axis, by the two-dimensional hydrogenic term

$j_1(\mathbf{r}) = (\sqrt{2/p}/l) \exp(-\mathbf{r}/l)$, where \mathbf{r} is the in-plane relative coordinate. The z-dependent factor is given by:

$$W_{eh} = \int_{-\infty}^{+\infty} dz [f_e(z) f_h(z)]^2 \quad (2).$$

From Eqs. (1) and (2) it is obvious that, in any case of on-axis separation of the electron and hole, the α factor may become smaller than unity and even vanish with increasing L_W , in presence of a longitudinal electric field.

Due to large spontaneous and piezoelectric polarization parameters⁶, WQWs based on wurtzite ZnO, like ZnO-(Zn,Mg)O QWs, are thus expected to materialize the unprecedented situation where *both* large internal electric fields *and* giant exchange interaction terms are present. To face this situation, competitive effects of confinement and electric fields on the large exciton binding energy (~ 60 meV), have to be properly considered. Samples as well as the growth and other experimental conditions were described in a previous paper²³.

Figure 1 shows, for four different QW widths, the time-integrated photoluminescence (PL) spectra obtained under pulsed excitation. The repetition rate was adapted to the slowness of the observed decay, *thus allowing for a full de-excitation between two consecutive pulses*.. Inserts in Fig.1 show the band profiles, energy levels and envelope functions for electrons and heavy holes that we calculate for two extreme situations, namely narrow and wide QWs. A very good agreement is obtained between our variational “one band” excitonic calculation¹⁷ and the experimental PL energies, as shown in Fig. 3 of reference 6, when we include an electric field of 0.9 MV/cm.

The well width dependence of the oscillator strength is usually considered to be the same as that of quantity $f = |\mathbf{j}_1(0)|^2 I_{eh}^2$, where $I_{eh} = \int_{-\infty}^{+\infty} dz f_e(z) f_h(z)$ is the envelope-function overlap integral. So, in this first approach, we can readily see how fast the oscillator strength is expected to decrease: when the QCSE becomes dominant, we obtain a drop of more than 7 orders of magnitude

between $L_W = 2$ and 7 nm. In practice, if the excitonic lifetime (inversely proportional to f) for our narrowest QWs is of some nanoseconds, we expect tens of milliseconds for our widest QW⁶.

Experimentally, things are a little more complicated, especially for narrow QWs, as reported in Ref. 6 and now shown in Fig. 2. Wide QWs indeed show very large PL decay times, at $T = 8\text{K}$, and they grow almost exponentially with L_W , as we show below. On the other hand, Fig. 2(b) shows that the PL dynamics exhibits two characteristic times, for the two QWs emitting above the ZnO gap. Typically, a first decay occurs with a slightly sub-nanosecond time, followed by a second one, with decay time of a few tens of nanoseconds. We have checked that the slower part of this dynamics was not induced by a slow carrier transfer from the barriers: TR-PL from these barriers revealed much slower decay times, on orders of hundreds of microseconds.

We explain these results by the superposition of two radiative mechanisms related to the two fundamental excitonic ground states, usually referred to as the A and B excitons, in the bulk material. As explained above, the e-h exchange interaction mixes the G_5 exciton states that are dipole allowed in the present s-polarization²⁴. The off-diagonal exchange energy, $\Delta = 4.73\text{meV}$ is fixed for bulk ZnO but it becomes strongly well-width dependent for the present QWs, as illustrated by the left hand bottom insert in Fig. 3. The latter presents the changes of both the exciton binding energy and the e-h exchange energy, Δ , calculated from Eqs. (1) and (2), versus L_W . For narrow enough QWs, the confinement enhances both direct Coulomb and short-range exchange energies. But they both become smaller than their bulk value for QW widths larger than $\sim 2\text{-}3\text{nm}$.

Concerning the oscillator strengths of excitonic transitions, the case of wide QWs (dominating QCSE) is rather simple: having nearly no exchange coupling means that the oscillator strengths of confined states built upon the G_{5A} and G_{5B} states are nearly equal, in s-polarization. The only difference arises from the mixing of G_{5B} and G_{5C} states via spin-orbit off-diagonal terms in the Hamiltonian. Therefore, the oscillator strengths of these quantized states should follow together the well width dependence of the "envelope term" plotted in Fig. 2. On the other hand, for narrow

QWs, the mixing of the two fundamental G_5 states necessarily redistributes some oscillator strength from the A exciton to the benefit of the B exciton, like it is the case³ for bulk ZnO, but more strongly, since in that case, the exchange energy is enhanced. To describe the case of our samples, we have used an adapted version of the formalism presented in Ref.3, for G_5 states. More specifically, as we did in Ref.6, we assume, for simplicity, equal on-axis effective masses for the so-called heavy- and light-holes. *This warrants that, even for QWs, the energy difference between diagonal terms for these two types of holes is independent of the well width.* We assume, too, that the bulk binding energies are equal for A, B and C excitons, and so this will remain true for all QW widths. Again, this permits that the energy separation of diagonal terms in the G_5 excitonic Hamiltonian of Ref. 3 is kept constant. We assume, moreover, that internal strain effects are negligible, in first approximation, or that we can mimic them by our choice of the Γ_1 crystal-field parameter. Finally, we consider a single confined state for electrons as well as for each of the three hole bands, which is reasonable in view of the band profiles sketched in Fig. 1.

With such hypotheses, we are left with the resolution of the following matrix:

$$\begin{pmatrix} |\Gamma_{5A}\rangle & |\Gamma_{5B}\rangle & |\Gamma_{5C}\rangle \\ E^* - \Delta_1 - \Delta_2 + \mathbf{ag} / 2 & \mathbf{ag} & 0 \\ \mathbf{ag} & E^* - \Delta_1 + \Delta_2 + \mathbf{ag} / 2 & -\sqrt{2}\Delta_3 \\ 0 & -\sqrt{2}\Delta_3 & E^* - \mathbf{ag} / 2 \end{pmatrix} \quad (3).$$

Here, the bulk-like $a\Gamma$ term is simply the one that is plotted in Fig. 3 and E^* is an energy which accounts for the band-gap, augmented by the confinement energies of the electron and the hole and reduced by the size-dependent binding energy. Within our approximations, the B line remains a few meV above the fundamental A line. In fact, some L_w dependency (left hand top insert in Fig. 3) is only obtained for $L_w < 3$ nm and the maximum separation of these lines is of 12 meV, which is rather small, if compared to the PL linewidths for the two narrower QWs, comprised between 25 and 35 meV. *These inhomogeneous linewidths result from the fluctuations of Mg concentration in the barriers and of strain along the QW plane.* We thus understand that, for all well widths,

including the smaller ones, the observed PL lines correspond to the superposition of the two unresolved, transitions, that we may still call "A" and "B". These transitions correspond to well-width dependent combinations of $|\Gamma_{5A}\rangle$ and $|\Gamma_{5B}\rangle$ states, both dipole-allowed in s-polarization.

Coming to the oscillator strengths –thus PL decay times– of these transitions for the narrower QWs, exchange-induced mixings now have the same kind of effect as for ZnO epilayers: reduction of oscillator strength for the ground state "A" to the benefit of "B". For each of these two transitions, the eigenstate of the matrix in Eq.(3) has the general form: $u(L_w)|\Gamma_{5A}\rangle + v(L_w)|\Gamma_{5B}\rangle + w(L_w)|\Gamma_{5C}\rangle$. Owing to spin-flip effects³, the oscillator strengths in s-polarization are proportional to $[u(L_w) + v(L_w)]^2$ multiplied by the envelope factor f , calculated above. The L_w dependency lies essentially, here, on the variation of the a? off-diagonal term.

Figure 3 is a plot of a quantity inversely proportional to the calculated oscillator strengths for the two lower-lying optical transitions, versus L_w . A factor has been applied to this quantity in order to fit the experimental PL decay times for the 5.2 and 7.1 nm wide QWs. For the two narrower QWs, two decay times have been plotted, resulting from the detailed measurements shown in Fig. 2.

The double-exponential PL decays measured for narrow QWs (and the single one for wide QWs) are well explained by the superposition, within the same line, of two exciton states having different recombination rates. We thus assign this observation –the first of its kind, as far as we know– to the exciton state mixing induced by the enhanced (or reduced) e-h exchange interaction. Obviously, a full quantum-mechanical calculation of exciton states in this type of QWs is now necessary. It will have to include correctly the difference in confinement and excitonic energies for the three different valence bands and the effects of possible internal strains. The calculation of exchange-induced matrix elements and the boundary conditions in the presence of strong internal electric fields will necessarily be more complicated than in our preliminary approach and, as

pointed out by Coli and Baja²⁴, the coupling of excitons to phonons will certainly play an important role, for such polar compounds.

In summary, the first quantitative measurement of the impact of quantum confined short range spin exchange interaction on the optical properties of wurtzitic ZnO / (Zn,Mg)O quantum wells. For well widths smaller than 3 nm, it manifests via a double exponential decays that we have explained by the redistribution of oscillator strengths between the two lower lying excitonic transitions. This effect disappears for well widths larger than 3 nm, due to the presence of the strong electric field. In the current context of growing interest towards ZnO based nanostructures for spintronics, this work provides a first glance of the important issues that will have to be faced, in the future.

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FIGURE CAPTIONS

Figure 1: Time-integrated photoluminescence spectra obtained under pulsed excitations for four different WQW widths and the band profiles, energy levels and envelope functions for electrons and heavy holes that we calculate for two extreme situations, namely narrow and wide WQWs.

Figure 2: Photoluminescence decay time for a wide well (right hand plot), and photoluminescence decay times for a narrow well (left hand plot). *Note the different time scales*

Figure 3: Measured (dots) and computed decay times versus well width. Right hand top insert: the computed A-B splitting versus well width to be compared with widths of photoluminescence lines. Left hand bottom insert: short-range exchange energy in meV

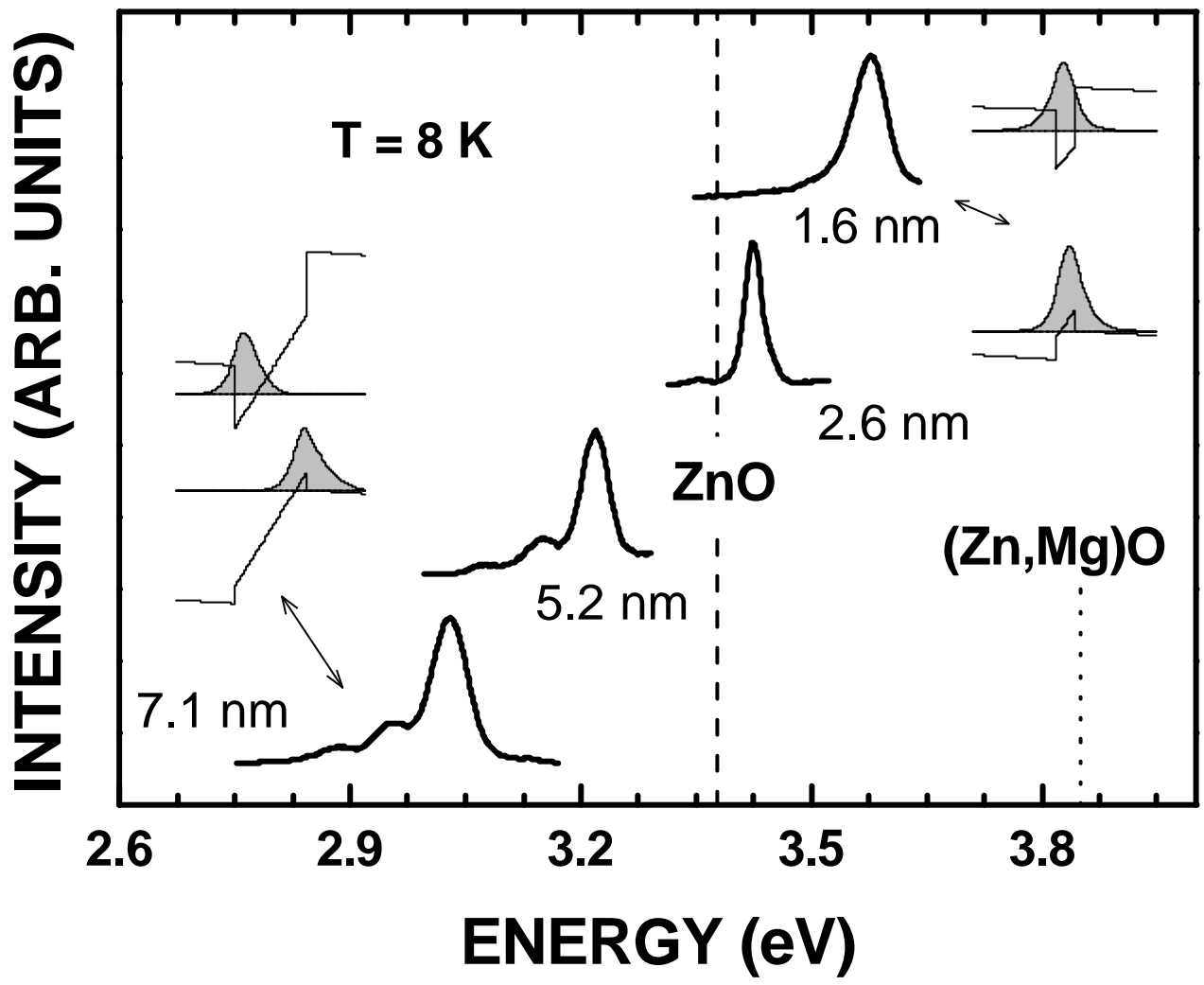


FIGURE 1

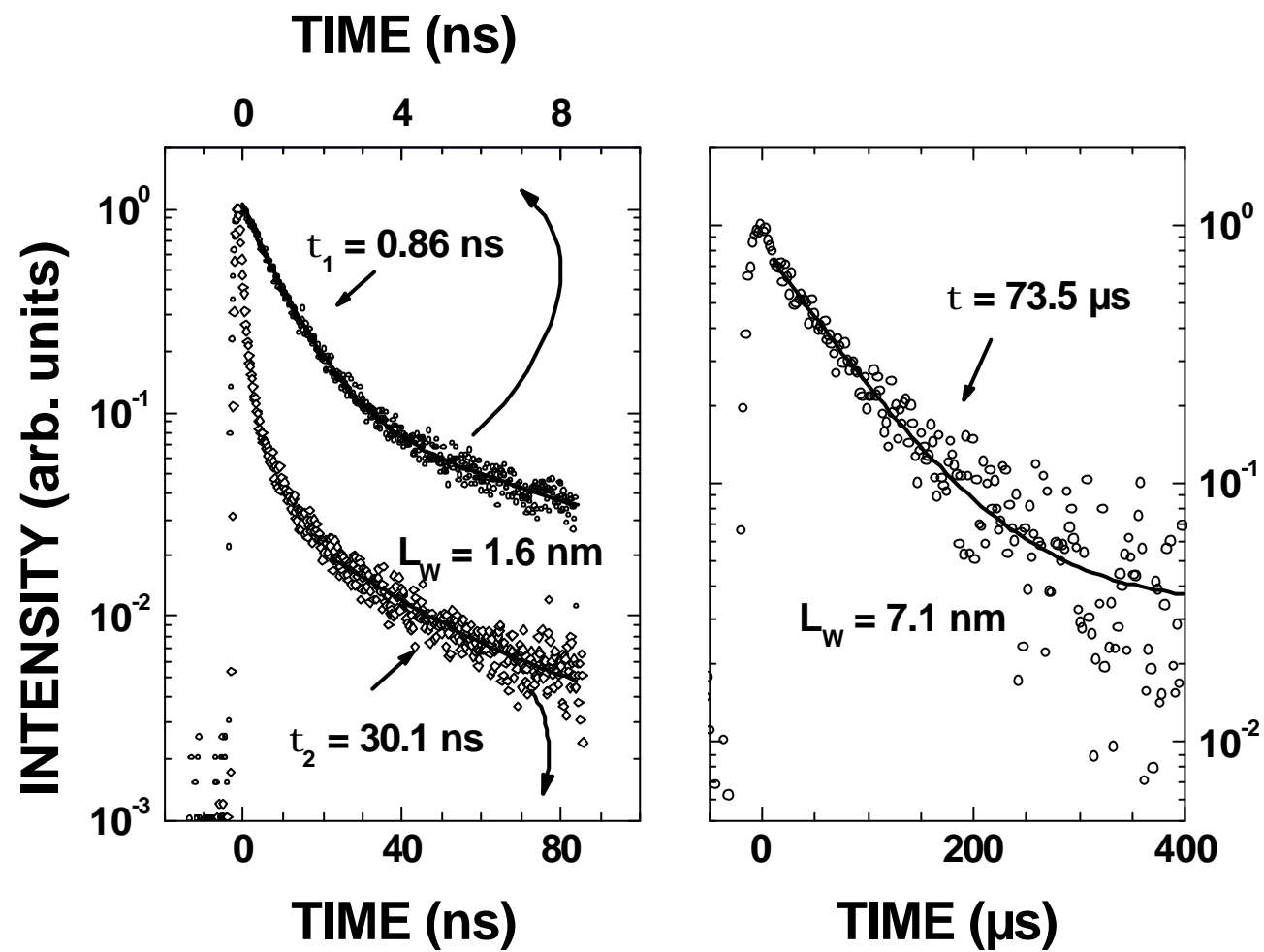


FIGURE 2

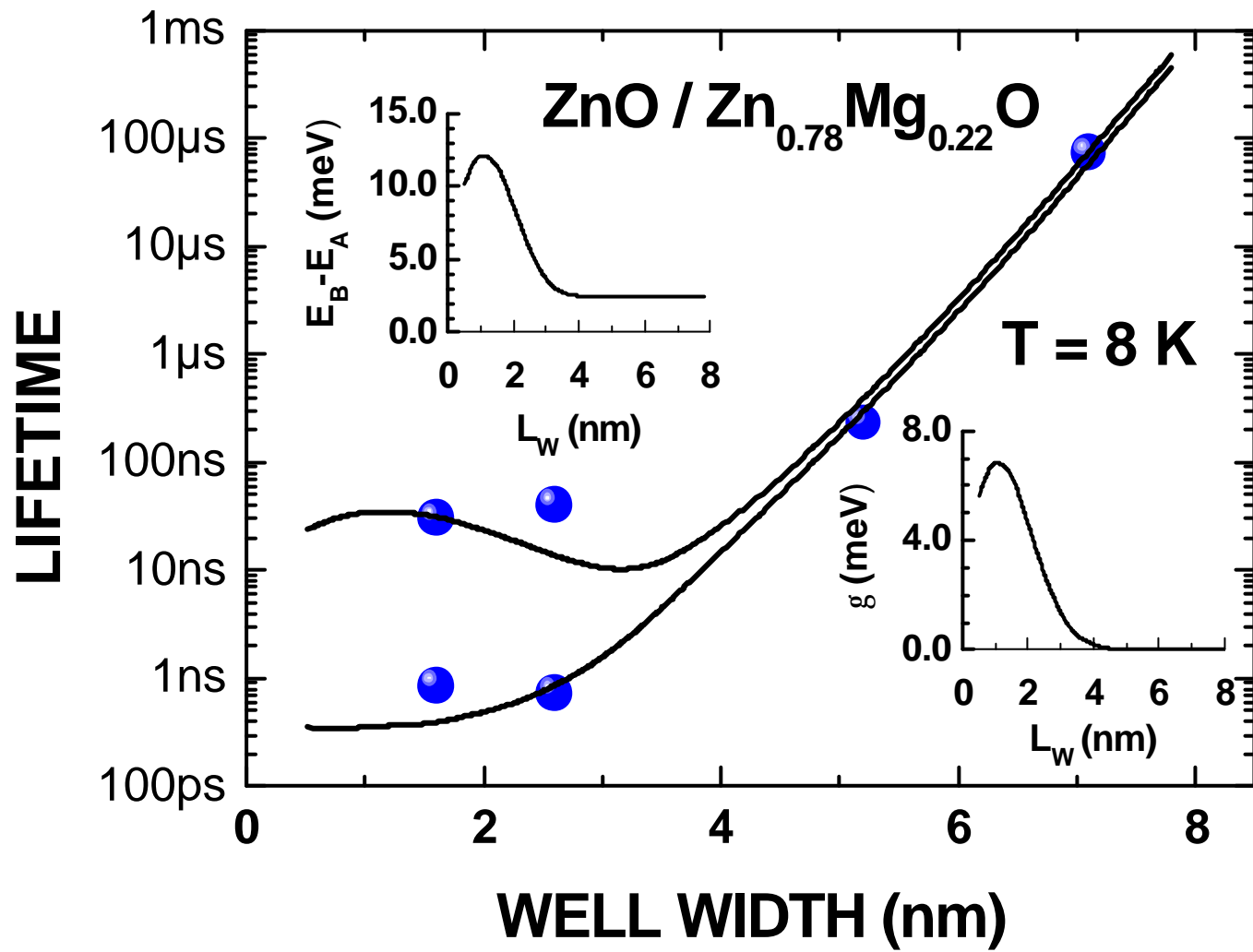


FIGURE 3