Oscillator strengths of *A*, *B*, and *C* excitons in ZnO films

Bernard Gil

Université de Montpellier II, Groupe d'Etude des Semiconducteurs, case courrier 074, 34095 Montpellier cedex 5, France
(Received 3 August 2001; published 26 October 2001)

We examine how the short-range part of the electron–hole exchange interaction influences the strain-induced variations of the oscillator strength in ZnO films. Our model enables us to account for the surprisingly small oscillator strength of the *A* exciton in $E \perp c$ polarization without having to invoke any inverted valence-band scheme. We then conclude that the valence-band physics is very similar in both ZnO and GaN.

The optical properties of wide band-gap semiconductors are currently subject of tremendous investigations, in response to the industrial demand for optoelectronic devices that could operate at short wavelengths. Zinc oxide is an interesting wurtzitic semiconductor. From its natural tendency to be grown under fairly high residual *n* type, one still meets some difficulty to achieve easily its *p*-type doping but its dramatic potential for spintronics properties renders him among the most fascinating semiconductors of the near future. This motivates in-depth investigations of its optical properties. In the present communication, we show that any examination of the optical properties of ZnO films that ignores the excitonic nature of the transitions, and that, in particular does not include internal excitonic quantum effect like the short-range electron-hole exchange interaction leads to mis-interpretation of the valence-band physics. In this communication, we also address the theoretical ingredients required to infer the recent identification of the valence-band ordering recently proposed by Reynolds *et al.*[1] from photoluminescence and reflectance spectroscopy.[2]

Bridging the theory to the experiment requires to recall some basic physics concepts and some general properties of *A*-*B* binary semiconductors.[3] In a spinless description, cubic zincblended semiconductors are known to have a threefold degenerated valence band and their optical response is isotropic. Such a degeneracy is lifted as soon as the semiconductor experiences any symmetry-breaking perturbation like an anisotropic strain. This can be easily achieved by application of an external stress to the crystal or by epitaxy of the semiconductor on a heterosubstrate. The situation is more complex for wurtzite crystals since the low symmetry splits the threefold valence states into a singlet ($|Z\rangle$-like) and a doublet ($|X\rangle$-like and $|Y\rangle$-like.). Related to the basis of the zone center valence-band states, the matrix element Δ_1 that describes this effect is called the crystal field-splitting parameter. The optical response is anisotropic and one has to distinguish the situation when the electronic states are coupled with the electric field along the *Z* direction (π polarization) and (or) with an electric field perpendicular to it (σ polarization). Things are even more complicated in reality since the comprehension of the valence-band physics requires to include the two-parameter (Δ_2 and Δ_3) spin–orbit interaction. Including the spin–orbit interaction boosts the valence-band symmetries into the double group representations. One then obtains one doublet that transforms like $\mathbf{\Gamma}_9$ ($J=3/2$, $m_J=\pm 3/2$ in the angular momentum representation) and two $\mathbf{\Gamma}_7$ doublets.

The band-to-band transition between the *s*-type $\mathbf{\Gamma}_7$ conduction band and the $\mathbf{\Gamma}_9$ valence band is forbidden in π polarization, which is a strong identification criterion since the two other band-to-band transitions are allowed in both polarizations. Gil *et al.*[3–5] have utilized this effect to elucidate the ordering of the valence band states in GaN epilayers grown on various substrates. One important result of the band-to-band transition formalism in σ polarization is the fact that the transition between the *s*-type $\mathbf{\Gamma}_7$ conduction band and the $\mathbf{\Gamma}_9$ valence band has a strain-independent oscillator strength (0.5 in arbitrary units) that exceeds those of the two remaining transitions.

Gil *et al.*[6] have recently reported the reversal nature of the valence-band states in ZnO crystals and heteroepitaxies, similarly to the GaN case. In general, the topmost of the ZnO valence-band maximum is the $\mathbf{\Gamma}_9$ state, in contrast to common belief,[7–17] but in very good agreement with the recent proposal of Reynolds *et al.*[1,2] Reversed ordering[10] requires strong biaxial tensions.[6] The interesting feature observed in reflectance spectroscopy in ZnO under σ polarization[2] conditions is the weakness of the *A*-exciton transition ($\mathbf{\Gamma}_9$-related), compared to the one of *B* in straightforward contradiction with the predictions of a band-to-band theory.

There is in general a larger splitting between the (*A*,*B*) and the *C* excitons than between the *A* and *B* excitons in ZnO. This indicates that, at first order, and if limiting the influence of the spin orbit interaction with respect to those of the crystal field-splitting, *C* transition originates from a valence band state that has a strong $|Z\rangle$ characteristics, while *A* and *B* should be considered like a couple of states essentially built from $|X\rangle$ and $|Y\rangle$. Obviously the weakness of line *A* in σ polarization and its absence in π polarization indicate that this way to consider the things is not appropriate. An excitonic model that includes the short-range electron–hole interaction (and eventually the nonanalytical long-range part) will be more appropriate as we show below.

Noticing that actual optical transitions occur between the crystal ground state and the exciton state, Gil *et al.*[3–5] had

TABLE I. Parameters of the model. Compression is a positive quantity.

Δ_1 (meV)	30.5	δ_1 (meV/kbar)	1.93
Δ_2 (meV)	4.2	δ_2 (meV/kbar)	−1.59
Δ_3 (meV)	11.5	γ (meV)	4.73
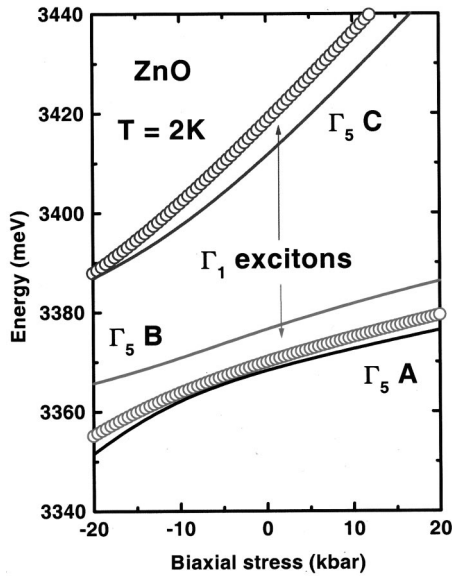
FIG. 1. Stress-induced variation of the Γ_5 (full lines) and Γ_1 (circle lines) excitonic energies in ZnO at 2 K.

FIG. 3. Stress-induced variations of the oscillator strength for Γ_1 excitons in ZnO at 2 K.

introduced the short-range electron–hole exchange interaction in their modeling of the optical properties of GaN. They found that the effect had a modest influence on the oscillator strengths in GaN, since this value is in turn fairly small[18] (0.69 meV) although the exciton binding energy is of the order of 25–27 meV. We extend this approach to ZnO for which the exciton binding energy and the short-range exchange interaction have large values (60 meV[2] and ~4.7 meV,[6] respectively).

We have first computed the eigenenergies and wave functions of Γ_5 excitons according to equations in Refs. 3 and 5. To get the oscillator strength, we sum the contributions of the
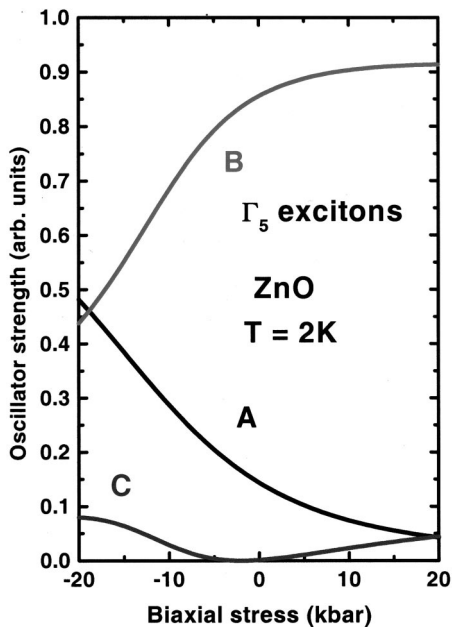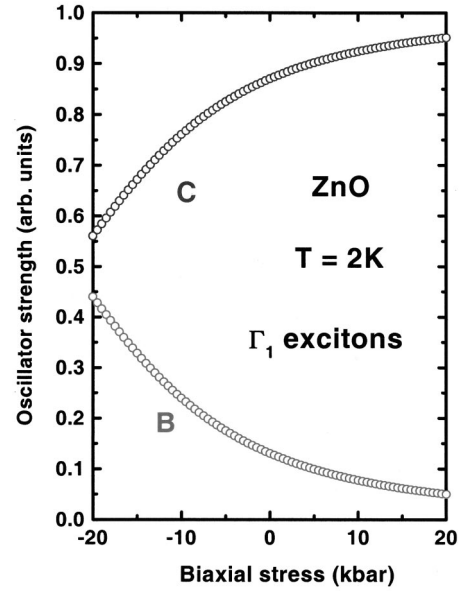
two nonspin-flip eigenvectors and get a quantity proportional to $(\omega + \bar{\omega})^2/2$. *Note the typing error in Ref. 5.* Then we compute the eigenenergies and eigenvectors for the Γ_1 symmetry still according to Ref. 5. In both calculations we assumed that the modification of the transition energies reported in the literature are due to a biaxial strain. At this stage, one could argue that biaxial stress gives a special relationship between δ_1 and δ_2. But although we agree with this point, we wish to emphasize the fact that this does not have a great impact at the scale of the spirit of this paper, although it does have a *slight* impact at the scale of the numerical results.

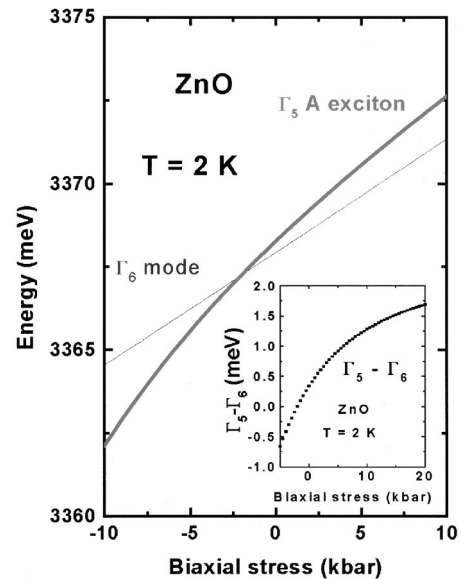Values we used are taken from Ref. 6 (see Table I). To

FIG. 2. Stress-induced variations of the oscillator strength for Γ_5 excitons in ZnO at 2 K.

FIG. 4. Stress-induced variation of the $\Gamma_5 A$ (thick line) and Γ_6 (thin line) excitonic energies in ZnO at 2 K. Inset: The stress-induced variation of the $\Gamma_5 A - \Gamma_6$ energy splitting.

obtain the transition energies the eigenvalues of the 3 $\times$3 (Γ_5) and 2$\times$2 (Γ_1) matrices were subtracted to 3405 meV.

Figure 1 shows the plot of the radiative transition energies as a function of the biaxial stress in ZnO. Note the relative orderings of Γ_5 (full lines) and Γ_1 (circles) modes given by this model and the strong anticrossings produced by the large value of the short-range electron–hole interaction.

Figure 2 shows the strain-induced evolution of the oscillator strength for Γ_5 modes. Note that A line is always weaker than B in straightforward contradiction with the predictions of the band-to-band calculation but in agreement with experiment.[2]

For the sake of completeness Fig. 3 plots on the oscillator strength of Γ_1 modes that are coupled with a π-polarized electromagnetic field. Again, the agreement with experiment[2] is very good.

An important experimental feature is the relative energy position of the Γ_6 forbidden and of the Γ_5 (A) radiative states. We have computed their strain-induced shifts as shown in Fig. 4 as well as their relative position (inset in Fig. 4). The agreement between the recent result of Reynolds *et al.*[1] and our theoretical approach is very good.

In conclusion, we have shown in this communication that the overall set of optical properties of ZnO films are in general compatible with the natural valence-band ordering: Γ_9-Γ_7–Γ_7. Reversal of this ordering requires ZnO films that experience high biaxial tension, a situation fairly rare, to date.[10] The orderings and splitting of all radiative and nonradiative (Γ_6 excitons that are detected by photoluminescence) energy levels *cannot be obtained out of the context of an excitonic modeling* and are ruled by the short range electron–hole interaction. It has a dominating contribution at the scale of the oscillator strengths *in both σ and π polarizations*.

[1] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, T. C. Collins, M. T. Harris, M. J. Callahan, and J. S. Bailey, J. Appl. Phys. **86**, 5598 (1999).

[2] D. C. Reynolds, D. C. Look, B. Jogai, C. W. Litton, T. C. Collins, G. Cantwell, and W. Harsch, Phys. Rev. B **60**, 2340 (1999); J. L. Birman, Phys. Rev. Lett. **2**, 157 (1959).

[3] For a general review see Bernard Gil, in *Semiconductors and Semi-metals* (1999), Vol. 57, Chap. 6, p. 209 (1999).

[4] B. Gil, O. Briot, and R. L. Aulombard, Phys. Rev. B **52**, R17028 (1995); B. Gil, F. Hamdani, and H. Morkoç, Phys. Rev. B **54**, 7678 (1996).

[5] B. Gil and O. Briot, Phys. Rev. B **55**, 2530 (1997).

[6] B. Gil, A. Lusson, V. Sallet, R. Triboulet, and P. Bigenwald, Jpn. J. Appl. Phys. Lett. (to be published).

[7] D. G. Thomas, J. Phys. Chem. Solids **15**, 86 (1960).

[8] Y. S. Park, C. W. Litton, T. C. Collins, and D. C. Reynolds, Phys. Rev. **143**, 512 (1966).

[9] C. F. Klingshirn in *Semiconductor Optics* (Springer Verlag, Berlin-Heidelberg-New York, 1995), and references therein.

[10] T. V. Butkhuzi, T. G. Chelidze, A. N. Georgiobiani, D. L. Jashiasvhili, T. G. Khulordava, and B. E. Tsekvava, Phys. Rev. B **58**, 10 692 (1998).

[11] W. Y. Liang and A. D. Yoffe, Phys. Rev. Lett. **20**, 59 (1968).

[12] K. Hümmer, Phys. Stat. Solidi B **56**, 249 (1973).

[13] J. Wrzesinski and D. Föhlich, Phys. Rev. B **56**, 13 087 (1997).

[14] J. F. Muth, R. M. Kolbas, A. K. Sharma, S. Oktyabrsky, and J. Narayan, J. Appl. Phys. **85**, 7884 (1999).

[15] T. Makino, C. H. Chia, N. T. Tuan, H. D. Sun, Y. Segawa, M. Kawasaki, A. Ohtomo, K. Tamura, and H. Koinuma, Appl. Phys. Lett. **76**, 3549 (2000), *ibid.* erratum **77**, 1405 (2000).

[16] H. J. Ko, Y. F. Chen, T. Yao, K. Miyajima, A. Yamamoto, and T. Goto, Appl. Phys. Lett. **77**, 537 (2000).

[17] G. E. Jellison and L. A. Boatner, Phys. Rev. B **58**, 3586 (1998).

[18] M. Julier, J. Campo, B. Gil, J. P. Lascaray, and S. Nakamura, Phys. Rev. B **57**, R6791 (1998).