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1997 J. Phys.: Condens. Matter 9 7667

(http://iopscience.iop.org/0953-8984/9/36/014)

J. Phys.: Condens. Matter **9** (1997) 7667–7674. Printed in the UK PII: S0953-8984(97)80646-7

Two-photon absorption coefficient measurements in $ZnSe–ZnS_{0.18}Se_{0.82}$ strained-layer superlattices

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Received 3 January 1997, in final form 9 June 1997

Abstract. The two-photon absorption (TPA) coefficient $\alpha^{(2)}$ of $ZnSe–ZnS_{0.18}Se_{0.82}$ strained-layer superlattices has been measured in different samples at excitation energies related to heavy- and light-hole excitons associated with $n = 1, 2$ subbands in the TE polarization. A comparison between the experimental results and the predictions of analytical theories on TPA processes including quasi-bidimensional excitonic effects has been carried out. A satisfactory agreement with the numerical values has been shown by one of these theories. Finally, the imaginary part of the third-order susceptibility $\chi_I^{(3)}$ has been evaluated from the $\alpha^{(2)}$ experimental values.

At present intensive experimental and theoretical attention is focused on optical nonlinearities near the band gap of $ZnSe–ZnS_xSe_{1-x}$ strained-layer superlattices (SLSs) in order to exploit these synthetic structures for optoelectronic applications in the blue spectral region [1]. Two-photon absorption (TPA) spectroscopy has been proved to be a very efficient means for extracting detailed information on the optical properties of these low-dimensional systems. In fact, the complementarity of its selection rules with respect to the one-photon absorption ones provides a key to explore exciton states not accessible in conventional linear spectroscopy techniques, allowing the experimental determination of important parameters such as the exciton binding energy [2, 3]. Moreover, TPA, and the nonlinear index of refraction (n_2) associated with it, have been shown to affect significantly the operation of devices working in the fast nonresonant regime [4]. In particular, TPA introduces parasitic losses hindering the effectiveness of the material in different ways depending on the polarization vector ($\hat{\epsilon}$) of the incident radiation that can be perpendicular (TE) or parallel (TM) to the growth axis ($\hat{z}$) of the multiquantum well [5]. This suggests the importance of a quantitative study of TPA processes in $ZnSe–ZnS_{0.18}Se_{0.82}$ SLSs.

For this reason the aims of the present work are

(i) to measure the TPA coefficient value $\alpha^{(2)}$ in some $ZnSe–ZnS_{0.18}Se_{0.82}$ samples at different excitation energies corresponding to the allowed excitonic transitions in the TE polarization,

(ii) to compare the experimental results with the theoretical ones obtained by two analytical theories on TPA in low-dimensional systems [5–7] which give $\alpha^{(2)}$ values in the energy range near the half-gap, avoiding the lengthy calculations involved in other more accurate methods [8] and

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0953-8984/97/367667+08$19.50

(iii) to determine the imaginary part of the third-order susceptibility $\chi_I^{(3)}$ from the $\alpha^{(2)}$ experimental values.

The measurements have been performed on two different samples of ZnSe–$ZnS_{0.18}Se_{0.82}$ SLSs having equal well and barrier thickness $L_W = L_B = 37$ Å and 100 Å and a total SL thickness 0.8 μm. The well widths of the samples (37 and 100 Å) were deliberately chosen to be so different in order to study TPA in two representative cases. In fact, 37 and 100 Å SLSs have well separated or closely spaced subbands, respectively, and consequently the exciton oscillator strengths for optical transitions are different in the two heterostructures [5, 6]. Moreover, previous experimental studies [2, 3] have allowed a complete characterization of these samples by means of photoluminescence one-photon absorption (OPA) and TPA photoluminescence excitation (PLE), and so they are the ideal candidate for this kind of quantitative investigation.

The $\alpha^{(2)}$ values have been measured by means of the comparative nonlinear luminescence (CNL) technique. Although this technique is indirect, it is one of the most reliable in the case of a thin sample with opaque substrates [9]. Photoconductivity, for example, is another indirect technique that is available for these samples but it requires the insertion of good electrical contacts and the knowledge of many other physical parameters. Consequently, if a waveguide operation mode allowing the use of a nonlinear transmission technique cannot be implemented, CNL will be a suitable technique. This method allows the quantitative determination of $\alpha^{(2)}$ by comparing the intensities of the one- and two-photon excited luminescence signals in the same sample and by assuming a quantum efficiency independent of the pumping mechanism when $\hbar\omega_1$ is nearly equal to $2\hbar\omega_2$. In fact, the OPA and TPA give optical transitions having final states at the same energy. Therefore the thermalization process towards the emitting state may be assumed to be similar in both cases. In particular, the luminescence intensities $L^{(1)}$ and $L^{(2)}$ induced respectively by OPA and TPA at the detection energy $\hbar\omega_L$ (PL peak) are given by [10]

$$L^{(1)} = C_1\xi_1 T_L \alpha_1 I_{01}\, \mathrm{e}^{-\alpha_L l}\frac{1-\mathrm{e}^{-(\alpha_1-\alpha_L)l}}{\alpha_1-\alpha_L} \tag{1}$$

$$L^{(2)} = C_2\xi_2 T_L \alpha^{(2)} I_{02}^2 \frac{1-\mathrm{e}^{-\alpha_L l}}{\alpha_L} \tag{2}$$

where I_{01} and I_{02} are the exciting radiation intensities at the energies $\hbar\omega_2 < E_G \leqslant 2\hbar\omega_2$ (E_G being the energy band gap), α_1 is the OPA coefficient at the excitation energy $\hbar\omega_1$ and T_L and α_L are the transmission and the OPA coefficients at $\hbar\omega_L$, respectively. C_i ($i = 1, 2$) are the calibrating constants relative to the experimental configuration used in detecting the luminescence, ξ_i ($i = 1, 2$) are the quantum efficiencies and l is the active thickness of the sample. It must be noted that the equation (2) is valid provided that the OPA coefficient α_2 at $\hbar\omega_2$ is actually negligible. With this assumption and by arranging the same experimental configuration it is possible to obtain $\alpha^{(2)}$ directly from the ratio $L^{(2)}/L^{(1)}$:

$$\alpha^{(2)} = \frac{L^{(2)}}{L^{(1)}}\frac{I_{01}}{I_{02}^2}\frac{\alpha_1\alpha_L}{\mathrm{e}^{\alpha_L l}-1}\frac{1-\mathrm{e}^{-(\alpha_1-\alpha_L)l}}{\alpha_1-\alpha_L}. \tag{3}$$

We measured $L^{(1)}$ and $L^{(2)}$ signals at $T = 10$ K in the excitation configuration in which the polarization vector $\hat{\epsilon}$ of the incoming electromagnetic field is perpendicular to the SLS growth axis $\hat{z}(\hat{\epsilon} \perp \hat{z})$. The detection energy was set at the fundamental exciton energy $\hbar\omega_L = 2.814$ eV for the S100 sample and $\hbar\omega_L = 2.837$ eV for the S37 sample, independently determined by photoluminescence measurements [2]. For excitation we used energies in resonance with 2p exciton transitions associated with subbands having the same

principal quantum number, as allowed by the selection rules for TPA processes in the $\hat{\epsilon} \perp \hat{z}$ polarization [2, 3]. Such energies were determined by means of two-photon absorption excitation luminescence (TPA–PLE) measurements, as reported in [2].

The source of one- and two-photon luminescence measurements was a 10 Hz Quantel Datachrome dye laser (pulse duration of 9 ns, tuning accuracy of 2 Å, maximum peak power of about 20 MW cm^{-2} after focusing) pumped by the third and the second harmonic of a Nd:YAG laser, respectively. The dye laser was equipped with a low-pressure H_2 Raman shifter to give the near-infrared radiation employed for TPA measurements. In particular for $L^{(1)}$ measurements Stilbene 420 dye was used, while DCM dye was employed for $L^{(2)}$ measurements. Much care was used to reduce and to test the influence of the non-uniformity of the power distribution across the laser section on the $\alpha^{(2)}$ values. The emitted radiation was detected perpendicularly to the excitation radiation by an S20 extended-response photomultiplier tube, while the incident beam was monitored by a fast-response photodiode. Both signals were sent to a digital oscilloscope for a further processing. The signal-to-noise ratio was better than 200:1 for each run.

In figure 1(i) and (ii) we show the dependence of the $L^{(1)}$ and $L^{(2)}$ luminescence intensities detected at $\overline{h}\omega_L = 2.814$ eV on the excitation densities I_{01} and I_{02}, respectively. This was obtained from the S100 sample using the excitation energies of the excitons E^{2p}_{11h} ((a), $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.846$ eV), E^{2p}_{22h} ((b), $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.858$ eV) and E^{2p}_{11l} ((c), $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.867$ eV), as reported in figure 1 [2]. (We have used for designating optical transitions the notation $E^{q}_{i,j,h(l)}$, where i is the electron subband, j is the hole subband, h and l stand for heavy and light, respectively, and q indicates the state of the exciton, 1s, 2s, 2p, etc). In the $\overline{h}\omega_1$ excitation case the experimental points exhibit the expected linear behaviour which is consistent with the OPA process. On the other hand the slope of two for the $2\overline{h}\omega_2$ excitation energies indicates a two-photon process. All experimental datapoints fit their relative regression curves within 3%. Similar results have been obtained for the S37 sample, as shown in figure 2(i) and (ii), in which $L^{(1)}$ and $L^{(2)}$ luminescence signals detected at $\overline{h}\omega_L = 2.837$ eV versus their relative excitation densities I_{01} and I_{02} are represented. The energies used for excitation were the ones associated with exciton transitions E^{2p}_{11h} ((a), $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.865$ eV) and E^{2p}_{11l} ((b), $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.888$ eV), as reported in figure 2 in [2].

The linear absorption coefficients α_1 and α_L, to be used in equation (3), have been evaluated from optical density measurements independently performed and reported in tables 1 and 2 and in their captions for the S100 and the S37 samples, respectively. Moreover, as required by equation (3), for all two-photon excitation energies $\alpha_2 \sim 0$ and for both samples an active thickness equal to the geometrical one has been assumed. The $\alpha^{(2)}$ values have been obtained by equation (3) and have been reported in tables 1 and 2 for the S100 and the S37 samples, respectively. It can be observed that the $\alpha^{(2)}$ experimental values of the S37 sample are greater than the ones of the S100 sample by about an order of magnitude on average. This is probably due to the presence of a non-negligible component of the polarization vector of the impinging beam which is parallel to the growth axis even in the $\hat{\epsilon} \perp \hat{z}$ excitation configuration for the S37 sample. This has been observed in [2] and, according to [8], this component would enhance TPA absorption because of the continuum contribution which becomes significant in the $\hat{\epsilon} \| \hat{z}$ polarization.

The experimental values of $\alpha^{(2)}$, reported in tables 1 and 2, show an increasing behaviour when $2\overline{h}\omega$ increases as in the TPA–PLE spectra reported in [2] and the TPA coefficient augments when the well width becomes smaller for a given exciton transition.

Experimental data have been compared with theoretical values obtained from [6], [7] and

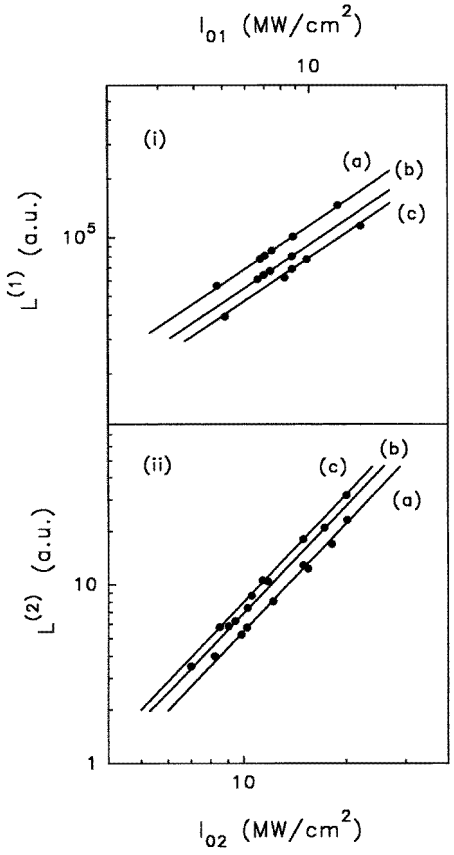

Figure 1. (i) OPA and (ii) TPA luminescence intensity from the S100 sample at $\overline{h}\omega_L = 2.814$ eV against I_{01} and I_{02} laser input power respectively, using the excitation energies (a) $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.846$ eV (E^{2p}_{11h}), (b) $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.858$ eV (E^{2p}_{22h}) and (c) $\overline{h}\omega_1 = 2\overline{h}\omega_2 = 2.867$ eV (E^{2p}_{11l}).

Table 1. Linear absorption coefficients α_1, experimental results of $\alpha^{(2)}$ values and imaginary part of the third-order susceptibility $\chi^{(3)}_I$ for the S100 sample. $2\overline{h}\omega_2$, α_1 and $\alpha^{(2)}$ and $\chi^{(3)}_I$ are expressed in eV, cm^{-1}, cm MW^{-1} and esu, respectively. For the linear absorption coefficient at $\overline{h}\omega_L = 2.814$ eV $\alpha_L = 7.92 \times 10^4$ cm^{-1}has been employed. For the physical parameter values used in the calculations see [14].

Transition	$2\overline{h}\omega_2$	α_1 ($\times 10^4$)	$\alpha^{(2)}_{exp}$ ($\times 10^{-3}$)	$\chi^{(3)}_I$ ($\times 10^{-12}$)
E^{2p}_{11h}	2.846	16.09	1.3 ± 0.3	2.2 ± 0.5
E^{2p}_{22h}	2.858	16.09	2.1 ± 0.5	3.4 ± 0.8
E^{2p}_{11l}	2.867	16.09	2.8 ± 0.7	4.6 ± 1.1

[5]. The last two papers give analytical expressions for $\alpha^{(2)}$ taking into account excitonic contribution, while the first one considers only intersubband transitions. For sake of brevity, we report only one of these formulae. In particular, according to Shimizu's theory, when

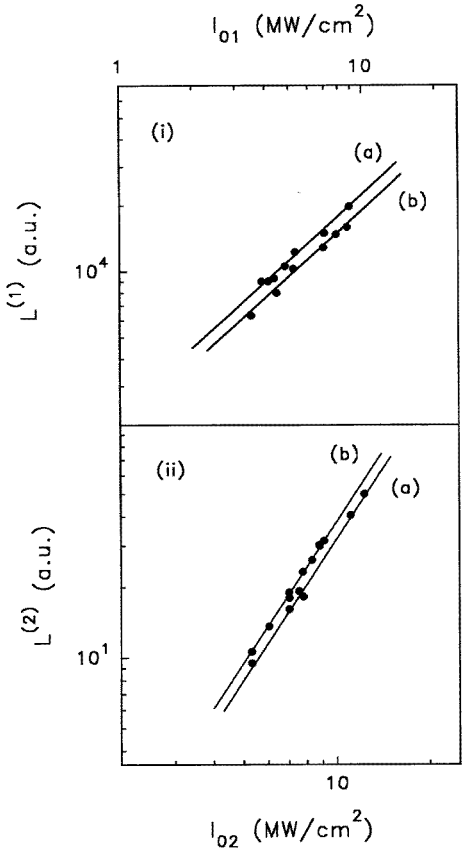

Figure 2. (i) OPA and (ii)TPA luminescence intensity from the S37 sample at $\hbar\omega_L = 2.837$ eV against I_{01} and I_{02} laser input power respectively, using the excitation energies (a) $\hbar\omega_1 = 2\hbar\omega_2 = 2.865$ eV (E_{11h}^{2p}) and (b) $\hbar\omega_1 = 2\hbar\omega_2 = 2.888$ eV (E_{11l}^{2p}).

Table 2. The same as table 1 for the S37 sample. For the linear absorption coefficient at $\hbar\omega_L = 2.837$ eV $\alpha_L = 8.83 \times 10^4$ cm^{-1} has been employed.

Transition	$2\hbar\omega_2$	α_1 ($\times 10^4$)	$\alpha_{exp}^{(2)}$ ($\times 10^{-2}$)	$\chi_I^{(3)}$ ($\times 10^{-11}$)
E_{11h}^{2p}	2.865	9.78	5.9 ± 1.5	9.8 ± 2.4
E_{11l}^{2p}	2.888	10.35	7.2 ± 0.8	11.7 ± 2.9

the absorbed photons are of the same frequency ω and for $\hat{\epsilon} \perp \hat{z}$ polarization:

$$\alpha^{(2)}\ (\text{cm MW}^{-1}) = \frac{10^{13} 2^8 \pi^3 e^4 \hbar^3 M^2}{c^2 \eta^2 (\hbar\omega)^3 m_e^4 E_G^2 (L_Z + L_B)} \sum_v q_x^v \left(\frac{m_e}{\mu_\parallel^v}\right)^2 \sum_{\alpha,\beta} |I_{\alpha\beta}|^2 \left(\frac{\hbar^2}{a_{\alpha\beta}}\right)^2 \times \left[(1 - \Theta_{\alpha\beta}) \sum_{n \geqslant 2} \frac{2n(n-1)}{\pi a_{\alpha\beta}^2 (n - 1/2)^5} S_{n1}^{\alpha\beta} + \Theta_{\alpha\beta} \frac{\mu_\parallel^v (1 + \lambda_{\alpha\beta}^2/4)\, e^{\pi/\lambda_{\alpha\beta}}}{\pi \hbar^2 \cosh(\pi/\lambda_{\alpha\beta})}\right] \quad (4)$$

where $\Theta \equiv \Theta(2\hbar\omega - E_G^{\alpha\beta})$ is a unit step function with $E_G^{\alpha\beta}$ being the quantized band gap energy, η is the refractive index of the material acting as a quantum well, $\mu_\parallel$ is the reduced

exciton mass for the motion in the xy plane, $I_{\alpha\beta}$ is the overlap integral between the subband envelope functions, $a_{\alpha\beta}$ is the exciton Bohr radius and $S_{n1}^{\alpha\beta}$ is a line-shape function of the involved exciton which accounts for the discrete behaviour of the exciton spectra for energies below the subband energy gap. In actual superlattices $S_{n1}^{\alpha\beta}$ is a Gaussian-like function whose full width at half maximum (FWHM) is essentially due to exciton–phonon interactions and to quantum well imperfections. All other symbols have the meaning reported in [7]. All quantities are expressed in esu. The expression for $\alpha^{(2)}$ in the $\hat{\epsilon} \perp \hat{z}$ polarization due to Obeidat and Khurgin [5] is quite similar to formula (4). Some differences between the two theories considering the exciton effects are related to the line functions describing this contribution that have been included in the $\alpha^{(2)}$ analytical expressions. In Shimizu's model [7] the excitonic contribution is described by a Gaussian line function whose FWHM is related to the imperfections of the SLSs and to the exciton–phonon interactions. Instead in Obeidat's model [5] a Lorentzian line function is included in the expression in order to reproduce the exciton resonance [11]. It is worth noting that in both cases the FWHMs included in the calculations of the two different line functions were the experimental values of the excitonic peaks [3] of the spectra of [2]. These values range from 4 to 10 meV for both samples. The $\alpha^{(2)}$ theoretical values obtained from formula (4) are reported in tables 3 and 4. On the other hand, the values obtained with the expression of [5] are systematically much smaller than the experimental ones even though the exciton effect is considered and for this reason are not reported in tables 3 and 4.

Table 3. $\alpha^{(2)}$ (cm MW^{-1}) theoretical values for S100. The $\alpha_{th,a}^{(2)}$ have been calculated according to the expression by Shimizu taking into account the excitonic contribution. The $\alpha_{th,b}^{(2)}$ values have been calculated according to the expression by Khurgin without taking into account the excitonic contribution.

Transition	$2\bar{h}\omega_2$	$\alpha_{th,a}^{(2)}$ ($\times 10^{-3}$)	$\alpha_{th,b}^{(2)}$ ($\times 10^{-3}$)
E_{11h}^{2p}	2.846	1.30	0.34
E_{22h}^{2p}	2.858	1.95	0.48
E_{11l}^{2p}	2.867	2.91	0.64

Table 4. The same as table 3 for the S37 sample.

Transition	$2\bar{h}\omega_2$	$\alpha_{th,a}^{(2)}$ ($\times 10^{-2}$)	$\alpha_{th,b}^{(2)}$ ($\times 10^{-2}$)
E_{11h}^{2p}	2.865	0.41	0.38
E_{11l}^{2p}	2.888	0.62	0.50

For comparison also the theoretical $\alpha^{(2)}$ values obtained by [6] have been evaluated and reported in tables 3 and 4. It must be noted that the model of [6] related to intersubband transitions (without exciton enhancement) allows the evaluation of the TPA coefficient also for excitation energies less than the first intersubband transition because this model considers the contribution of the bulk material constituting the well. As expected, these values underestimate the experimental ones. Conversely, the values obtained with the expression of Shimizu (including excitonic effects) show a satisfactory agreement with the experimental ones, in particular for the S100 sample. Moreover, formula (4) confirms the experimental trend of TPA coefficient with well width for a given excitonic transition.

Finally, the knowledge of the $\alpha^{(2)}$ experimental values has allowed us to determine the imaginary part of the third-order susceptibility, $\chi_I^{(3)}$, which is originated by a TPA process and is related to $\alpha^{(2)}$ by the following expression [12]:

$$\chi_I^{(3)} = \frac{9 \times 10^8 \epsilon_0 \eta_0^2 c^2}{4\pi\omega} \alpha^{(2)} \tag{5}$$

where ϵ_0 is the vacuum permittivity, η_0 is the linear refractive index and c is the speed of light in vacuum. Here $\chi_I^{(3)}$ is expressed in esu and all other quantities in MKS units. Using formula (5), we obtained the $\chi_I^{(3)}$ values reported in tables 1 and 2 for the S100 and S37 samples, respectively.

It is worth noting that TPA measurements allow us to evaluate the absolute value of the ratio of real and imaginary components of the third-order susceptibility when used in conjunction with nonlinear refractive experiments [13]. This physical parameter represents an important figure of merit useful in the charcterization of the behaviour of devices employed in the field of high-speed optical switching, logic and nonlinear optical signal processing.

In conclusion we have presented first experimental results for the TPA coefficient of ZnSe–$ZnS_{0.18}Se_{0.82}$ SLSs obtained in the excitonic region by the nonlinear luminescence technique. An extensive use of this method has pointed out the need of better experimental evaluation of quantum efficiency in TPA and OPA processes. On this topic further work is still in progress. However, it is comforting that the $\alpha^{(2)}$ experimental values are in fairly good agreement with one of the theories [7] and a correct dependence on the thickness of the well and barrier in the ZnSe–ZnS_xSe_{1-x} SLSs has also been shown in the case of TPA coefficient measurements. Furthermore, we have determined the imaginary part of the third-order susceptibility whose knowledge assumes considerable interest in view of the potential technological applications of the investigated material in fast nonlinear optoelectronic devices.

Acknowledgments

The authors are pleased to thank Professor Shimizu for helpful discussions.

This work was partially supported by MURST (Ministero dell'Universitá e della Ricerca Scientfica e Tecnologica), GNEQP CNR (National Research Council) and INFM (Istituto Nazionale per la Fisica della Materia).

References

[1] Nurmikko A V and Gunshor R L 1994 *Solid State Commun.* **92** 113
[2] Tommasi R, Lepore M, Netti M C and Catalano I M 1994 *Phys. Rev.* B **49** 14 367
[3] Lepore M, Netti M C, Tommasi R and Catalano I M 1994 *Solid State Commun.* **92** 695
[4] Aitchson J S, Oliver M K, Kapon E, Colas E and Smith P W E 1990 *Appl. Phys. Lett.* **56** 1305
[5] Obeidat A and Khurgin J 1995 *J. Opt. Soc. Am.* B **12** 1222
[6] Khurgin J 1994 *J. Opt. Soc. Am.* B **11** 624
[7] Shimizu A 1989 *Phys. Rev.* B **40** 1403
Shimizu A, Ogawa T and Sakaki H 1992 *Phys. Rev.* B **45** 11 338
[8] Pasquarello A, Quattropani A 1990 *Phys. Rev.* B **41** 12 728
Pasquarello A, Quattropani A, 1991 *Superlatt. Microstruct.* **9** 157
[9] Catalano I M, Cingolani A, Lepore M, Cingolani R and Ploog K 1990 *Phys. Rev.* B **41** 12 937
[10] Catalano I M, Cingolani A, Ferrara M and Lugará M 1980 *Opt. Acta* **27** 625
[11] Elliott R J 1957 *Phys. Rev.* **108** 1384

[12] Canto E J, Hagan D J, Young J and Van Stryland E W 1991 *IEEE J. Quantum Electron.* **QE-27** 2274
[13] Sheik-Bahae M, Said A A, Wei T H, Hagan D J and Van Stryland E W 1990 *IEEE J. Quantum Electon.* **QE-26** 760
[14] *Landolt–Börnstein New Series* 1982 Group III, vol 17, ed O Madelung (Berlin: Springer) pp 61–157