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Optical anisotropy investigation in $Zn_{1-x}Cd_xSe/ZnSe$ multi-quantum wells by two-photon spectroscopy

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Abstract. The light polarization dependence of two-photon absorption (TPA) near half the band gap has been experimentally investigated in $Zn_{1-x}Cd_xSe/ZnSe$ strained-layer multi-quantum wells. A detailed analysis of their TPA photoluminescence spectra, measured for two different polarization configurations of the exciting laser beam (perpendicular and parallel to the QW growth axis z), permitted us to sensitively probe the exciton anisotropy in quasi-bidimensional (Q2D) heterostructures. Fundamental and excited exciton states of different symmetry have been selectively detected by exploiting the strong anisotropic selection rules for TPA processes. In particular, the polarization along the z axis allowed us to obtain the first clear experimental evidence of higher-order light-hole excitons. Our experimental results are in good agreement with theoretical predictions of an analytical model of TPA in Q2D exciton systems, demonstrating the usefulness of a simplified approach for the case of photon energies close to half the band gap.

$Zn_{1-x}Cd_xSe/ZnSe$ strained multi-quantum wells (MQWs) are becoming an attractive opportunity for utilization in the technological area of short-wavelength semiconductor lasers operating in the green to blue spectral region [1]. In order to improve the device characteristics of this material, a full understanding of its optical and electronic properties is required.

Two-photon absorption (TPA) spectroscopy represents a very powerful tool to investigate these heterostructure systems, particularly in exploring states not accessible in linear absorption and in exciting large volumes in materials. The flexibility of this technique is increased by the wealth of information which may be obtained by varying the polarization direction of the radiation beam with respect to the carrier confinement direction. Both the selection rules and the shape of the absorption curve for intersubband transitions are predicted to sensitively change for polarization along or perpendicular to the QWs growth axis z [2, 3]. This permits us to selectively probe exciton states of different symmetry, providing alternative and complementary information on the excitonic contribution in quasi-bidimensional (Q2D) systems. It is also of technological interest to investigate the non-linear response anisotropy of Q2D structures in view of the realization of polarization insensitive strained quantum well gain medium for lasers and optical amplifiers [4].

The purpose of this paper is to study the polarization spectral dependence of degenerate TPA in $Zn_{1-x}Cd_xSe/ZnSe$ strained-layer MQWs in the energy range of the quantized states in the well in order to detect the anisotropy of excitonic properties. We conducted this study

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in two samples of $Zn_{1-x}Cd_xSe/ZnSe$ MQWs having the same configurational parameters, but different composition. Changes in Cd concentration x cause sensitive variations in the depth of the well and the value of the elastic strain within the ternary alloy layers [5], allowing us to investigate the Q2D exciton behaviour in two different quantum confinement situations. The nonlinear photoluminescence excitation (PLE) technique has been used under selective polarization configurations with the polarization vector $\hat{\varepsilon}$ of the incoming electromagnetic field parallel or normal to the carrier confinement direction z ($\hat{\varepsilon} \perp \hat{z}$ and $\hat{\varepsilon} \parallel \hat{z}$, respectively). We will describe our experimental results and compare them with theoretical predictions of a simple analytical theory [6, 7] for low-dimensional structures in the limit of strong confinement (well width smaller than 3D exciton Bohr radius). This model has the practical advantage of a quick determination of two-photon transition rate for Q2D excitons, avoiding the lengthy variational calculations involved in more sophisticated methods [8, 9] which turn out to be rather expensive in terms of memory and computation times.

The samples studied in this work were grown by solid source molecular beam epitaxy (MBE) on (001)-orientated GaAs substrates and consist of a 0.5 mm thick GaAs(001)2×4 epitaxial layer grown at 580 °C, a 1.5 mm thick ZnSe buffer layer deposited at 290 °C, followed by ten $Zn_{1-x}Cd_xSe/ZnSe$ QWs. The details on the crystal growth are described in [10]. The QWs are characterized by a nominal cadmium content x equal to 0.10 or 0.26. Each period consists of a ternary well and a binary barrier that are 3 nm and 20 nm wide, respectively. Both the investigated heterostructures adapt the zinc-blende crystallographic structure of their substrate. Owing to the values of the layer thicknesses, the MQWs are expected to be in the pseudomorphic regime, with mainly relaxed barriers and wells under a compressive stress due to the lattice mismatch (0.8–1.6% for $x = 0.10$–0.26) with ZnSe.

The TPA–PLE measurements were carried out for the $\hat{\varepsilon} \perp \hat{z}$ and $\hat{\varepsilon} \parallel \hat{z}$ polarization geometries by monitoring the luminescence signal at the peak in the PL band (represented by the dashed curve in figures 1 and 2 for the $x = 0.10$ and $x = 0.26$ samples, respectively) as the energy of the pump is varied in the region of half the band gap. All the spectra were obtained at $T = 10$ K by measuring the luminescence signal every 2 meV on average. The excitation source was a 10 Hz Quantel Datachrome dye laser pumped by a frequency-doubled Nd:YAG laser, operating with a 9 ns pulse duration and a 2 Å tuning accuracy. The useful spectral range for TPA processes in our samples was achieved by using a low-pressure H_2 Raman shifter pumped by the dye laser. The output beam had a linear polarization and a peak power density of the order of 10 MW cm^{-2} after focusing. Two different excitation configurations were adopted with the polarization vector $\hat{\varepsilon}$ of the incoming electromagnetic field perpendicular or parallel to the QW growth axis $\hat{z}$. The luminescence was detected normally to the exciting radiation by means of a RCA 4832 photomultiplier tube, while the incident beam was monitored by a fast-response photodiode. Data acquisition was performed in a single-shot configuration by using a double-channel digital oscilloscope. The signal-to-noise ratio was better than 200:1 for each run. In the TPA measurements the luminescence signal was normalized to the second power of the reference signal in order to reduce the effects of the fluctuations in the input beam intensity. Moreover, we also verified the quadratic behaviour of the detected luminescence intensity versus the excitation intensity at all wavelengths. For each experimental point several measurement runs were carried out and a quadratic regression analysis was performed. The Slope-2 fits the experimental points within 3% at all wavelengths.

In order to obtain the exact positions of the 1 s excitons and to unambiguously assign the observed TPA excitonic transitions, one-photon absorption (OPA) PLE measurements were performed on the same samples and will be briefly discussed here. It can be noticed that the

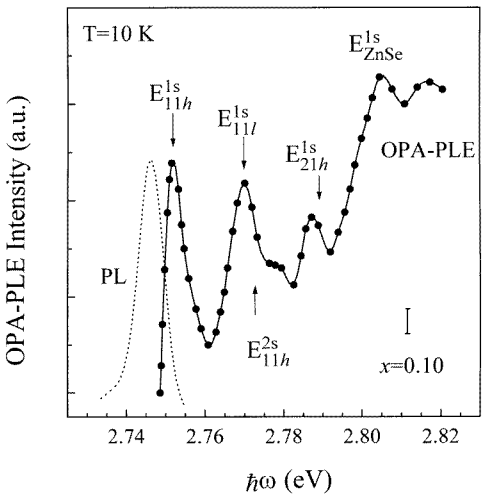

Figure 1. Photoluminescence (PL, dashed line) and one-photon absorption induced photoluminescence excitation (OPA–PLE) spectra for $Zn_{0.90}C_{0.10}Se/ZnSe$ multi-quantum wells at $T = 10$ K. The arrows mark the position of the theoretical excitonic energies calculated taking strain and confinement effects into account. The vertical error bar was estimated from the signal-to-noise ratio and from a regression analysis of the experimental points.

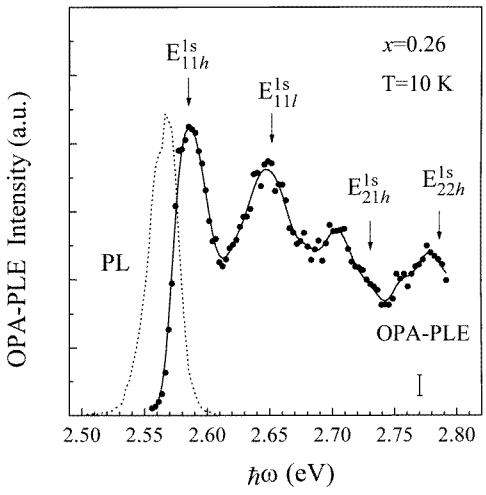

Figure 2. The same as figure 1 for the $Zn_{0.74}Cd_{0.26}Se/ZnSe$ sample.

linear spectra have been investigated only in the $\hat{\varepsilon} \perp \hat{z}$ configuration, since their polarization dependence comes only from the interband matrix element. As a consequence, they cannot give additional information to those of the TPA spectra which reflect the anisotropies of both the band structure and the Q2D exciton envelope function, allowing a sensitive probe of the effects due to the breakdown of the translational symmetry along the z-axis [7].

The OPA–PLE spectrum of the $x = 0.10$ sample is reported in figure 1. It was obtained by monitoring the PL intensity peak at 2.745 eV in the excitation energy range 2.749 eV $\leqslant \hbar\omega \leqslant$ 2.820 eV. It exhibits sharp excitonic peaks superimposed on the typical

step-like continuum following the density of states in the interband transition probability. Hereafter the exciton transitions will be classified by means of the standard notation $E^{q}_{ijh(l)}$ where i is the electron subband, j the hole subband, h and l stand for heavy and light hole, respectively, and q indicates the state of the exciton, 1s, 2s, 2p etc. The two main structures at 2.753 eV and 2.770 eV have been ascribed to the E^{1s}_{11h} and E^{1s}_{11l} exciton transitions, respectively, whereas the shallow shoulder at 2.775 eV has been attributed to the 2 s state of the c1–hh1 exciton, which has been observed for the first time in this type of heterostructure. These attributions have been made in agreement with the selection rules for OPA processes and the theoretical transition energies, calculated by taking confinement and strain effects into account [11] and with the material parameters given in our previous work [12]. We assumed a conduction-to-valence band offset ratio of 75:25 which was found to better reproduce our experimental data and that represents an average of the values available in the literature. The exciton binding energies were evaluated by using the model of the fractional-dimensional space [13]. According the predicted confinement energies, the resonance at 2.787 eV may be attributed to the parity-forbidden E^{1s}_{21h} transition, which could be probably due to the lack of inversion symmetry of the zinc-blende lattice. These attributions enable the interpretation of the TPA–PLE spectrum features by directly comparing them with the OPA–PLE ones.

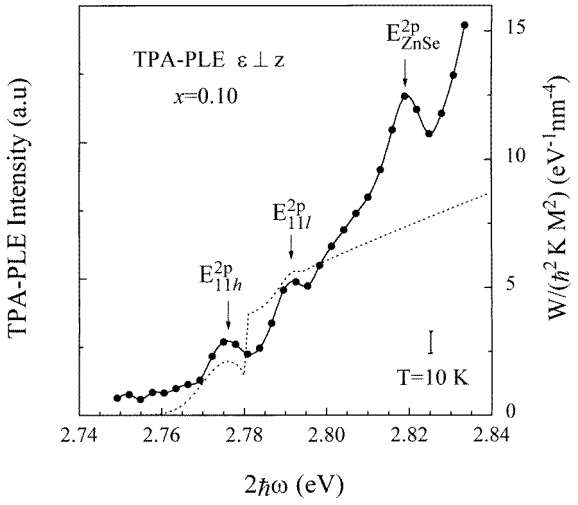

Figure 3. Two-photon absorption photoluminescence excitation (TPA–PLE) spectrum from $Zn_{0.90}Cd_{0.10}Se/ZnSe$ multi-quantum wells at $T = 10$ K, obtained with the $\hat{\varepsilon} \perp \hat{z}$ polarization configuration (solid line). The arrows indicate the TPA-allowed transitions. The vertical error bar was estimated as in figure 1. The dashed line represents the theoretical TPA transition rate $W_{\perp}$ calculated by (1).

Figures 3 and 4 show the TPA–PLE spectra (solid curves) of the $x = 0.10$ sample measured for the $\hat{\varepsilon} \perp \hat{z}$ and $\hat{\varepsilon} \parallel \hat{z}$ and configurations, respectively, in the energy range of 2.749 eV $\leqslant 2\hbar\omega \leqslant$ 2.843 eV. In the case of the radiation polarized in the QW layer planes (figure 3), the TPA intensity increases linearly with the photon energy following the linear dependence of the intraband dipole matrix element on the wavevector $\hat{k}$ [2]. On the linear absorption background there are additional excitonic peaks, that are about 23 meV blue-shifted with respect to the corresponding ones in the linear spectrum. This energy shift can be explained in terms of the parity selection rules for TPA processes involving

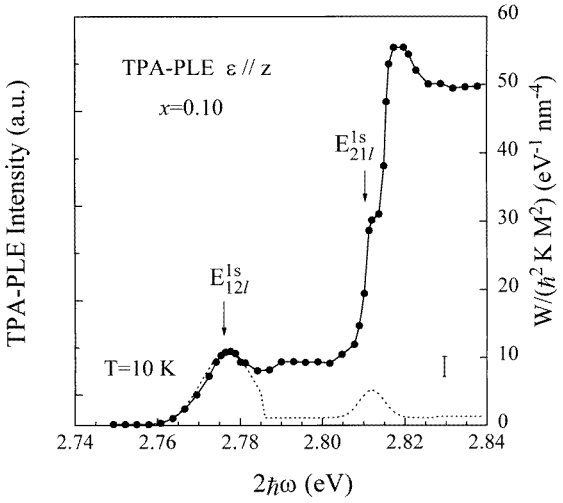

Figure 4. The same as figure 3 for the $\hat{\varepsilon} \parallel \hat{z}$ polarization configuration. The theoretical TPA transition rate $W_{\parallel}$ (dashed line) has been calculated by (2).

2p exitonic transitions with $i = j$ in this particular configuration. Hence the excitonic structures at 2.775 eV and 2.792 eV have been attributed to the E^{2p}_{11h} and E^{2p}_{11l} respectively, whereas the sharp feature at 2.820 eV has been ascribed to the 2p state of the ZnSe exciton in the barrier. A significantly different line shape is exhibited from the TPA–PLE spectrum (figure 4) measured for the beam polarization along the growth axis. It shows a step-like behaviour, with an abrupt rise at 2.777 eV which may be attributed to the 1s state of the c1–lh2 exciton in agreement with the parity selection rules for such polarization that predict 1s excitonic transitions with $i \neq j$ and related only to light-hole excitons. A faint shoulder can be noticed at the energy 2.812 eV, theoretically predicted for the 1s exciton associated with the $n = 2$ conduction subband, which is about 7 meV over the continuum edge, and the first $n = 1$ light-hole subband. The distinct resolution of such a delocalized exciton transition is prevented by the rising absorption continuum. The plateau between the E^{1s}_{12l} and the onset of the ionization continuum reflects the independence of the intraband dipole matrix element of $\hat{k}$ [2]. It is worth noting the $\hat{\varepsilon} \parallel \hat{z}$ configuration allowed us to obtain the first experimental evidence of excited light-hole excitons which are confined only by means of coulombic interaction in this type of heterostructure because of their small valence band-offset.

A systematic analysis of the TPA–PLE spectra in the energy range 2.610 eV $\leqslant 2\overline{h}\omega \leqslant$ 2.830 eV for both the polarization geometries has been performed for the $x = 0.26$ sample, which is characterized by a total band offset nearly three times large as that the $x = 0.10$ sample because of the higher Cd content. The OPA–PLE spectrum of this sample is shown in figure 2. It was obtained by detecting the PL intensity peak at 2.560 eV in the excitation energy range 2.556 eV $\leqslant \overline{h}\omega \leqslant$ 2.792 eV The three sharp structures at 2.585 eV, 2.650 eV and 2.780 eV have been attributed to the E^{1s}_{11h}, E^{1s}_{11l} and E^{1s}_{22h} transitions according the same calculation as for the other sample. The peak centred around 2.710 eV cannot be attributed to any exciton transition predicted by the theoretical calculation. Thus it may be probably caused by surface impurities in this sample. The shallow shoulder at 2.730 eV has been attributed to the parity-forbidden E^{1s}_{21h} transition. It is worth noting the decrease in the luminescence at higher energies that inhibits the detection of the ZnSe-related structure. This

effect may be probably due to the presence of non-radiative channels owing to composition fluctuations and interface roughness. The high degree of structural disorder is also confirmed by the large full width at half maximum (FWHM) of the PL (30 meV) and the considerable Stokes shift (25 meV). The inavoidable broadening induced by local inhomogeneities in the well would also justify the lack of any feature associated with the 2s state of the exciton in this spectrum. The application of non-linear absorption processes permits the reduction of the non-radiative effects thanks to the TPA characteristic of producing a uniform carrier concentration throughout the excited volume rather than in the thin penetration depth usually achieved in linear absorption processes.

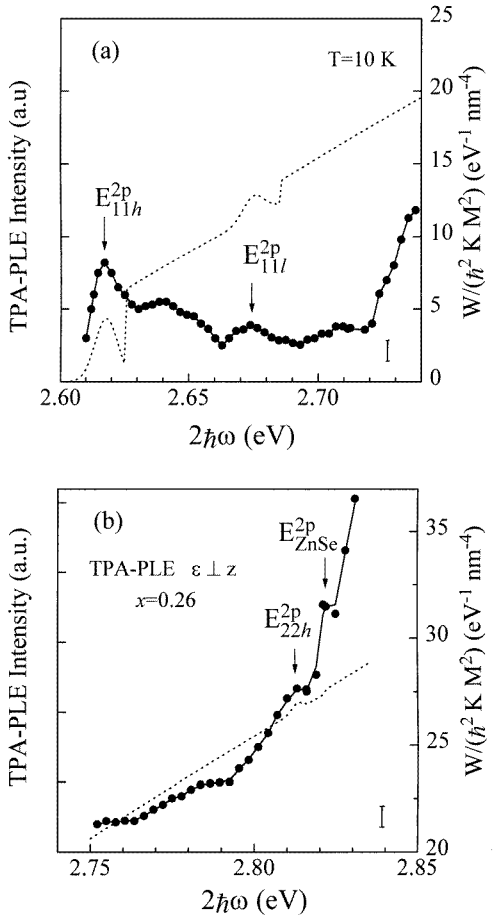

Figure 5. The same as figure 3 for the $Zn_{0.74}Cd_{0.26}Se/ZnSe$ sample. Panels (a) and (b) show the low- and the high-energy part of the spectrum, respectively.

Figures 5(a) and 5(b) show the TPA–PLE spectrum (solid line) of the $x = 0.26$ sample for the $\hat{\varepsilon} \perp \hat{z}$ configuration. The low- and the high-energy sides of this spectrum have been separately reported in figures 5(a) and 5(b), respectively, because of the large spectral range and the strong enhancement of the luminescence at high energies. The two distinct excitonic peaks at 2.628 and 2.675 eV have been ascribed to the E^{2p}_{11h} and E^{2p}_{11l} transitions respectively, being blue-shifted by about 38 meV from the corresponding ones in the OPA–PLE spectrum.

On the linear background of the high-energy side of the spectrum two excitonic structures are clearly evident at 2.810 eV and 2.825 eV and have been attributed to the E^{2p}_{22h} and E^{2p}_{ZnSe}. Another interesting feature of this spectrum is the presence of a shoulder centred at 2.650 eV corresponding to the 1s state of the c1–lh1 exciton. As discussed before, this transition is allowed in the $\hat{\varepsilon} \parallel \hat{z}$ polarization. A possible origin of this structure is the absorption of a weak component parallel to the z-axis of the polarization vector projected by the laser beam impinging on the sample surface at 45° angle. Therefore, it is reasonable to attribute the excitation of the observed $\Delta n \neq 1$, 1s exciton transition to this polarization component, even if it is expected to be very small since the strong variation of the refractive index at the surface of the sample is not favourable for guiding radiation along the z-direction. The $\hat{\varepsilon} \parallel \hat{z}$ TPA–PLE spectrum of the $x = 0.26$ sample is reported in figure 6 (solid line). As in the case of the $x = 0.10$ sample, it agrees with theoretical expectations, showing a plateau between the c1-lh2 and c2-lh1 interband transitions, corresponding to 1s excitonic resonances, centred respectively at 2.650 eV and 2.800 eV.

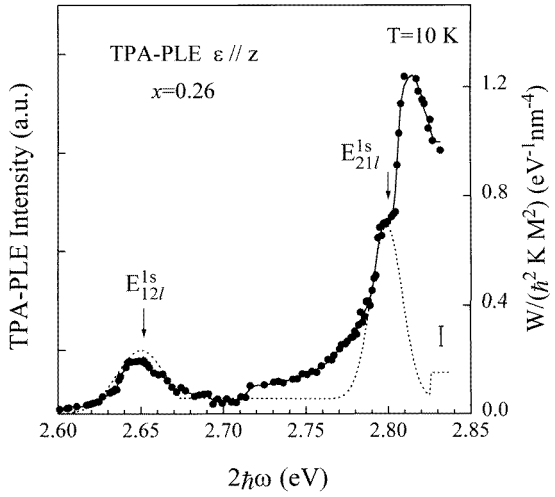

Figure 6. The same as figure 4 for the $Zn_{0.74}Cd_{0.26}Se/ZnSe$ sample.

We have compared our non-linear measurements with the predictions of the simple model of [6] which allows the analytical evaluation of TPA spectra for Q2D systems near half the band gap energy and with excitonic effects included. In the case of the $\hat{\varepsilon} \perp \hat{z}$ polarization the two-photon transition rate per unit time and per unit volume is given by:

$$W_\perp = KM^2 \sum_v q_x^v \left(\frac{m}{\mu_\parallel^v}\right)^2 \sum_{\alpha,\beta} |I_{\alpha,\beta}|^2 \left(\frac{\overline{h}}{a_{\alpha\beta}}\right)^2 \left[(1-\Theta_{\alpha\beta}) \sum_{n\geqslant 2} \frac{2n(n-1)}{\pi a_{\alpha\beta}^2 (n-1/2)^5} S_\nu^{\alpha\beta} + \Theta_{\alpha\beta} \frac{\mu_\parallel^v (1+\lambda_{\alpha\beta}^2/4)\, \mathrm{e}^{\pi/\lambda_{\alpha\beta}}}{\pi \overline{h}^2 \cosh(\pi/\lambda_{\alpha\beta})}\right] \tag{1}$$

where $\Theta = \Theta(2\overline{h}\omega - E_G^{\alpha\beta})$ is a unit step function with $E_G^{\alpha\beta}$ being the quantized band gap energy, $\mu_\parallel$ is the exciton reduced 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 $S_{\alpha\beta}^v$ is a line-shape function of the exciton associated with the subbands α (of electron) and β (of hole) with relative quantum number v. All other symbols have the meaning reported

in [6]. In actual MQWs the line-shape functions have a Gaussian-like profile with an FWHM essentially determined by the exciton–phonon coupling and to QW imperfections such as alloy fluctuations and interface roughness. In our calculations we assumed an overall Gaussian broadening with a standard deviation equal to the experimental linewidth of the excitons.

The spectra calculated by (1) for the $x = 0.10$ and $x = 0.26$ samples are reported for comparison in figures 3 and 5, respectively. The theoretical curves (dashed lines) reproduce the linear growing behaviour exhibited by the experimental ones except for the low-energy side of the spectrum related to the sample with higher Cd content because of the non-radiative effects previously discussed for this sample. Moreover the steeper increase of the luminescence shown by the experimental spectra near the barrier energy range is due to the contribution of the ZnSe-related 2p exciton which is not taken into account in the theoretical calculation. It is worth noting that the adopted model is able not only to reproduce the overall trend of the intersubband non-linear absorption, but also the 2p exciton contributions in the well. In particular, for the $x = 0.10$ sample the predicted ratio between the E^{2p}_{11l} and E^{2p}_{11h} transition rates turns out to be greater than the experimental one. This could be due to the enhancement of the first excitonic peak observed in the experimental spectrum caused by the additional contribution of the transition E^{1s}_{12l} which is energetically overlapped on the transition E^{2p}_{11h}. The excitation of such transition may be due to the small polarization component parallel to the z-axis which is always present in our experimental configuration. This would also explain the larger FWHM of the first excitonic structure in the TPA–PLE spectrum with respect to the FWHM of the transition.

For the $\hat{\varepsilon} \parallel \hat{z}$ polarization the theoretical two-photon transition rates $W_{\parallel}$ of the $x = 0.10$ and $x = 0.26$ samples are reported in figures 4 and 6 respectively (dashed lines). They have been calculated by means of the following formula:

$$W_{\parallel} = KM^2 \sum_v q_z^v \left(\frac{m}{\mu_z^v}\right)^2 \sum_{\alpha\beta} |P_{\alpha\beta}|^2 \left[(1 - \Theta_{\alpha\beta}) \sum_n [\pi a_{\alpha\beta}^2 (n - 1/2)^3]^{-1} S_v^{\alpha\beta} + \Theta_{\alpha\beta} \frac{\mu_{\parallel}^v \, \mathrm{e}^{\pi/\lambda_{\alpha\beta}}}{2\pi\hbar^2 \cosh(\pi/\lambda_{\alpha\beta})} \right]. \tag{2}$$

The spectra obtained by (2) reproduce the experimental step-like behaviour with evident excitonic peaks superimposed. In particular it can be seen that for the $x = 0.10$ sample the calculated E^{1s}_{21l} transition rate turns out to be much smaller than the E^{1s}_{12l} one, since it is related to a transition involving a delocalized exciton state. The contribution of the E^{1s}_{21l} transition rate is very small also in the experimental spectrum and its absorption edge marks only weakly the onset of ZnSe absorption.

In conclusion, a detailed investigation of the TPA–PLE spectra and their anisotropies has been performed in $Zn_{1-x}Cd_xSe$/ZnSe MWQs. Substantial differences both in the line shape and in the selection rules have been found for the polarization along the growth axis ($\hat{\varepsilon} \parallel \hat{z}$) or in the layer planes ($\hat{\varepsilon} \perp \hat{z}$). In particular, the polarization allowed the first distinct detection of excited light-hole excitons which are only weakly bound in the investigated heterostructures.

Finally we compared our experimental results with the two-photon transition rates calculated by the model of [6], finding a satisfactory overall agreement.

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