CHAPTER 5
NONLINEAR LUMINESCENCE STUDIES IN CdI₂ AND ZnSe

5.1 Introduction

The existence of high intensity lasers has made multiphoton spectroscopy an important tool in the study of the electronic structure of solids. Multiphoton processes may directly affect the power limit of lasers, the laser induced mechanism of damage to transparent materials and have various spectroscopic applications. Particularly, two photon spectroscopy has become an outstanding technique for analysing the band structure of crystals. For processes involving more than two photons, the required sensitivity may be achieved only by indirect methods such as NLP and NLL. In recent years, three photon spectroscopy has been the subject of extensive theoretical and experimental investigations. In quantitative studies, photoluminescence technique has been widely used.

Catalano et al. [1] have determined the three photon absorption (3PA) coefficient of CdS and PbI₂ by the comparative luminescence measurements of two and three photon absorption. The 3PA coefficient value at a fixed excitation energy and its frequency dependence in a large energy range have been measured in Rbi, CsI and NaI by Catalano et al. [2] using the comparative NLL technique. CdI₂ is an ionic crystal of layered structure in which each cadmium sheet is sandwiched by two iodine ion sheets. The crystal structure was given by Matsumoto et al. [3]. The most common polytype of CdI₂ is the hexagonal 4H type with a layer
arrangement, which is most suitable for multiphoton processes. The electronic structure of 4 H polytype of the layered compound CdI$_2$ was investigated by Coehoorn et al. [4] using angle resolved ultraviolet photoelectron spectroscopy (ARUPS). A detailed band structure calculation of CdI$_2$ have been done by Robertson [5] by tight-binding method. The result he obtained was in close agreement with the experimental results and previous pseudopotential calculations. Wright et al. [6] have made the photoconductivity measurements on single crystals of CdI$_2$ for illumination over a wide range of photon energies. Optical absorption measurements on single crystals of CdI$_2$ were made by Nakagawa et al. [7] in the region near the absorption edge.

These workers observed stimulated emission in CdI$_2$ and suggested that the amplification is due to the formation of self trapped bi-excitations. A lot of investigations have been done on the non-linear photoconductivity mechanisms and optoelectronic behaviour of CdI$_2$ under laser excitation [8,9]. Baldssarre et al. [10] have measured the photoacoustic spectra in this samples of CdI$_2$ layer semiconductor in the region of energies near the fundamental energy gap. By this technique they obtained the spectrum of the low values of the absorption coefficient in the range between 3.12 and 3.26 eV, where the absorption coefficient varied from 5 to 100 cm$^{-1}$. The photoconducting properties of CdI$_2$ as an indirect band gap crystal have been studied using fundamental and frequency doubled Nd:YAG laser by Singh et al. [11]. They also calculated the two and three photon absorption cross-sections with the help of experimental results. Catalano et al. [12] have made the Raman spectroscopy measurements and the experiments of optical amplification of CdI$_2$ under one and two photon excitation and of second harmonic generation. Ajithkumar et al. [13] have studied the emission spectra of CdI$_2$ and have calculated the emission parameters for various emission components.
ZnSe is a semiconductor with zinc blende structure, the detailed band structure of which has been calculated using the pseudopotential method by Cohen et al. [14]. Arsenev et al. [15] have studied the nonlinear absorption of the emission of a ruby laser in ZnSe and have measured the 2PA coefficient of this compound. Singh et al. [16] have studied qualitatively the photoconductivity of ZnSe crystal using pulsed N₂-laser and Nd-YAG laser. Lepore et al. [17] have experimentally investigated the 3PA spectra of ZnSe in a large excitation energy range above the optical gap. However, their spectral studies are based on the arbitrary values of 3PA coefficient.

Here we have investigated experimentally the 3PA processes in compounds CdI₂ and ZnSe by using the NLL technique. The 2PA coefficients of these compounds are determined by NLT technique. A comparative two and three photon luminescence measurements carried out using a ruby and neodymium laser enables us to obtain directly the 3PA coefficients. The experimental values are compared with the existing theories. In addition to these studies, the 3PA spectra have been experimentally investigated near and above the optical gap for CdI₂. In particular, absolute values of 3PA coefficient for ZnSe have been measured and its spectral behaviour has been studied. We have assumed a linear $k \cdot \pi$ - dependence approximation for the matrix elements in order to correctly describe the 3PA coefficient line shapes and to compare the experimental and theoretical line shapes.

5.2. Theory for nonlinear luminescence

In nonlinear luminescence experiments, the density of conduction electrons produced by the multiphoton processes is inferred from the luminescent radiation produced as a result of the subsequent recombination of the generated electrons and holes.
The luminescence intensity at the frequency $\omega_1$, induced by two or three photon excitation, is proportional to the number of absorbed photons, i.e.,

$$I_2 = K_2 \beta I_{Rb}^2 L \tag{1}$$

$$I_3 = K_3 \gamma I_{Nd}^3 L \tag{2}$$

where $I_{Rb}$ and $I_{Nd}$ are the two photon exciting flux at $h\omega_{Rb}$ and three photon exciting flux at $h\omega_{Nd}$ energies respectively; $\beta$ is the two photon absorption coefficient at the $\omega_{Rb}$ frequency; $\gamma$ is the 3PA coefficient at the $\omega_{Nd}$ frequency; $L$ is the sample thickness; $K_i = C_i \eta_i$ ($i = 2, 3$) where $C_i$ is the calibrating constant relative to the experimental configuration used in detecting the luminescence, and $\eta_i$ is the quantum efficiency relative to two and three photon absorption. It has already been established that in the context of higher order absorption processes accompanied by a one photon absorption process, the latter can be neglected [1]. Thus for all practical purposes the above equations are valid and one can modify the above equations as follows [1].

$$I_2 = K_2 \beta I_{Rb}^2 L (1-\alpha L) (1-\frac{1}{2}\alpha L) \tag{3}$$

$$I_3 = K_3 \gamma I_{Nd}^3 L (1-\frac{1}{2}\alpha L) \tag{4}$$

However, when the photon energies of the two excitation fluxes $I_{Rb}$ and $I_{Nd}$ are such that $2h\omega_{Rb} \approx 3h\omega_{Nd}$, the same quantum efficiency $\eta_1 = \eta_2 = \eta_3$ can be assumed in both absorption processes. In fact, the two or three photon absorption gives interband optical transitions having final states at almost the same energy. Therefore, the thermalisation process towards the band bottoms may be assumed to be similar in both cases.

By arranging an appropriate experimental configuration (Figure 5.1), it is possible to obtain $C_2 = C_3$, so that $\gamma$ can be obtained directly by the ratio $I_3/I_2$,

$$\gamma = \frac{I_3}{I_2} \frac{I_{Rb}^2}{I_{Nd}^3} \beta (1-\alpha L) \tag{5}$$
Figure 5.1. Experimental configuration for nonlinear luminescence measurements: \( I_{\text{Nd}} \), \( I_{\text{rub}} \) neodymium and ruby excitation beams. \( S_1 \), \( S_2 \): mirrors. BS: beam splitter. PD: photodiode. S: sample. L: lens. F: filter. M: monochromator. PM: photomultiplier.

5.3 Experimental details

Highly pure good quality single crystals of CdI\(_2\) were grown from melt by using the similar procedure as described for the PbI\(_2\) single crystal in the previous chapter. The crystals grown from the melt are found to be predominantly of the 4H type. Figure 5.2 shows the photograph of the CdI\(_2\) crystal grown from the melt. High quality samples (8 x 6 x 3 mm\(^3\)) were selected to use the maximum possible available power density for the excitation. The NLT and NLL measurements were carried out at liquid nitrogen temperature (80 K). For the stimulated luminescence measurements on orthogonal excitation collection geometry has been adopted. For the measurement of 3PA coefficient the experimental arrangement shown in Figure 5.1 was adopted. In order to study the optical amplification from ionic crystals a good candidate is CdI\(_2\), a layered compound that shows a broad emission [13] from self trapped excitations (STE) (Ajithkumar et al.). Its energy gap (3.5 eV at 80 K) is approximately in resonance with the two photon of ruby laser \((2hv = 3.56 \text{ eV})\).
5.4 Results and discussion

5.4.1 Nonlinear studies in CdI₂

Under two photon pumping by means of ruby laser the stimulated emission spectrum of CdI₂ at 80 K (Figure 5.3) shows a broad band with its maximum at about 523 nm (2.37 eV). The dependence of the emission intensity at the maximum wavelength $\lambda_{\text{max}} = 523$ nm on the excitation intensity of ruby laser is reported in Figure 5.4. Above the threshold of about 7 MW/cm² the slope becomes superquadratic and the emission shows lasing features, up to the saturation threshold of about 25 MW/cm². This means that also under two photon pumping, the optical amplification processes due to selftrapped excitation works properly. This result is quite analogous to the optical amplification process under one photon pumping using a nitrogen laser [13].

![Figure 5.3. Stimulated emission spectrum of CdI₂ at LNT](image)
Single crystals of ZnSe were obtained from CVD Inc. Woburn, USA. The sample size used in the present study was $5 \times 4 \times 3\,\text{mm}^3$. Nonlinear transmittance and luminescence experiments were carried out at the room temperature (Energy gap at 300 K; $E_g = 2.58\,\text{eV}$). The two and three photon luminescence was excited by a Q-switched ruby laser ($2\hbar \omega = 3.56\,\text{eV}$, peak power = 90 MW/cm$^2$) and an Nd:YAG laser ($3\hbar \omega = 3.51\,\text{eV}$, peak power = 60 MW/cm$^2$) respectively. Both lasers (IMPULSPHYSK) have 7 ns pulse duration. The intensity of the lasers were changed using neutral density filters. The 3PA line shapes have been obtained following the experimental procedure outlined in Chapter 4.
The nonlinear transmittance technique gives directly the two photon absorption coefficient $\beta$ by measuring the attenuation ratio $I_T/I_0$ (Similar procedure described for PbI$_2$ in Chapter 4). The two photon reciprocal transmittance formula is

\[
\frac{I_0}{I_T} = e^{\alpha t} + \frac{2\beta I_0}{\alpha} (e^{\alpha t} - 1)
\]

(6)

The $I_0/I_T$ vs. $I_0$ plot is shown in Figure 5.5. The one photon absorption coefficient obtained is 5.5 cm$^{-1}$. From the slope of the curve, the $\beta$ value is calculated to be $3.8 \times 10^{-2}$ cm/MW.

A combination of nonlinear transmittance and nonlinear luminescence method allows the quantitative determination of 3PA coefficient (Section 5.2) using the expression (5). At $\lambda = 523$ nm, the CdI$_2$ luminescence emission dependence on the exciting intensities $I_{Rb}$ and $I_{Nd}$ to the ruby and neodymium laser beam respectively is shown in Figure 5.6. Each experimental point is obtained by averaging over several measurements. In the neodymium excitation case, the straight line causing the experimental points has a slope around 3, which is constant with the three photon absorption process. On the other hand, the slope of 2 obtained for ruby excitation shows a two photon process.
Figure 5.5. Reciprocal transmittance vs. incident power

Figure 5.6. Luminiscence intensity vs. laser input power: (a) Ruby laser, (b) Neodymium laser
From the data in Figure 5.6 and from equation (5) and by knowing the two photon absorption coefficient at the ruby frequency, the 3PA coefficient at neodymium frequency can be deduced.

\[ \gamma = 4.6 \times 10^{-2} \text{ cm}^3/\text{GW}^2 \]

We have compared the experimental values with the predictions of the existing theories [18,19]. In the case of perturbative method, the theoretical 2PA value is more in line with the experimental one. While the 3PA value underestimate the experimental one, only by an order of magnitude. The nonperturbative method [20] greatly underestimates the TPA coefficients. This can be said that multiphoton process will become more competitive at high photon densities and that it is possible by means of two and three photon comparative photoluminescence measurements to determine quantitatively the 3PA coefficient. It should also be noted that an appropriate choice of the laser intensities is crucial in the experimental evaluation of the absorption coefficients. Moreover, the result of the stimulated emission of CdI$_2$ in particular has a relevant practical interest as a tuneable laser material at least in the low temperature region.

<table>
<thead>
<tr>
<th>Table 5.1. Theoretical and experimental values of 2PA ($\beta$) and 3PA ($\gamma$) coefficients for CdI$_2$.</th>
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<tbody>
<tr>
<td>Absorption coefficient</td>
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<tr>
<td>------------------------</td>
</tr>
<tr>
<td>$\beta$</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>$\gamma$</td>
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</tbody>
</table>
5.4.2 Nonlinear studies in ZnSe

The fundamental direct energy gap of ZnSe is 2.58 eV at 300 K and consequently two photon interband direct absorption can be observed by the ruby laser. The NLT technique gives directly the 2PA coefficient $\beta$ by measuring the attenuation ratio $\frac{I_0}{I_T}$ (Equation 6).

The plot $\frac{I_0}{I_T}$ vs. $I_0$ is shown in Figure 5.7, which is a straight line that intercepts the ordinate axis at $e^{\alpha d}$, and the one photon absorption coefficient obtained was 0.32 cm$^{-1}$. From the slope, $\beta$ can be calculated and its value obtained was $4.4 \times 10^{-2}$ cm/MW. Figure 5.8 shows the stimulated emission spectrum of ZnSe under ruby laser excitation. The emission peak is centred at 489 nm (2.54 eV) and shows a long wavelength tail. Its half width is 8 meV. The peak intensity of the 489 nm has a quadratic dependence on the laser intensity followed by saturation effect (Figure 5.9). This clearly establishes the fact that the emission is essentially a spontaneous one below the pump intensity of $\approx 7$ MW/cm$^2$. Above this threshold, the slope becomes superquadratic and the emission shows lasing features, up to the saturation threshold of about 25 MW/cm$^2$. This clearly substantiates the results obtained under one photon pumping [15].

At $\lambda = 489$ nm, the ZnSe luminescence emission depends on the exciting intensities $I_{Rh}$ and $I_{Nd}$. Figure 5.10 shows such a dependence corresponding to the ruby and neodymium laser beam intensities. Each experimental point was obtained by averaging over several measurements. In the Nd-excitation case, the straight line has a slope of 3, which is in consistent with the three photon absorption process. The slope 2 obtained for ruby laser case shows a two photon absorption. From the data in Figure 5.10 and from equation (5) and by knowing the 2PA coefficient at the ruby frequency, the 3PA coefficient at Nd-frequency was estimated to be $7.0 \times 10^{-2}$ cm$^3$/GW$^2$. 

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Figure 5.7. Reciprocal transmittance vs. incident power

Figure 5.8. Stimulated emission spectrum of ZnSe at 300 K
Figure 5.9. Stimulated emission intensity vs. two photon pumping power

Figure 5.10. Luminescence intensity vs. laser input power.
The $\beta$ and $\gamma$ coefficients obtained during the present study have been compared with the theoretical predictions. Theoretically, the absorption coefficients have been evaluated following the perturbative approach with due allowance for anisotropy [18,19] which yields better estimates and the nonperturbative approach [20]. The agreement between the $\beta$ and $\gamma$ values obtained from the perturbative method and the experimental ones may be considered quite good. While the $\beta$ and $\gamma$ values calculated by nonperturbative method underestimates the experimental one by an order of two and five respectively. The inconsistency of the values of the coefficients in the case of the nonperturbative model with experimental one is a direct consequence of the two band model adopted in this case. While, the perturbative approach assumes a three band model and a four band model for the 2PA and 3PA cases respectively. The study confirms the usefulness of the nonlinear technique for the analysis of nonlinear process of order higher than two. Thus it can be said that multiphoton process will become more competitive at high photon densities and that it is possible by means of two and three photon comparative photoluminescence measurements to determine quantitatively the 3PA coefficient. It should also be noted that an appropriate choice of the laser intensities is crucial in the experimental evaluation of the absorption coefficient.

**Table 5.2.** Theoretical and experimental values of $\beta$ and $\gamma$ for ZnSe.

<table>
<thead>
<tr>
<th>Absorption coefficient</th>
<th>Peturbative method</th>
<th>Nonperturbative method</th>
<th>Experimental results</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>$2.8 \times 10^{-2}$ cm/MW</td>
<td>$7.5 \times 10^{-4}$ cm/MW</td>
<td>$4.4 \times 10^{-2}$ cm/MW (Present work)</td>
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<td></td>
<td></td>
<td></td>
<td>$4.0 \times 10^{-2}$ cm/MW (Present work) [15]</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>$1.2 \times 10^{-1}$ cm$^3$/GW$^2$</td>
<td>$1.4 \times 10^{-2}$ cm$^3$/GW$^2$</td>
<td>$7.0 \times 10^{-2}$ cm$^3$/GW$^2$ (Present work)</td>
</tr>
</tbody>
</table>
5.4.3 Spectral behaviour of 3PA coefficients in CdI₂ and ZnSe

Figure 5.11 shows the spectral behaviour of 3PA coefficient in CdI₂. As already stated in Chapter 4, the experimental data can be fitted with the parametric formula

\[ \gamma = \sum_{n=0}^{3} C_n (3 \hbar \omega - E_g)^{n-1} \]  

The agreement is good as shown by the \( \chi^2 \) value = 0.32 and by the fit probability \( P(=0.992) \).

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Figure 5.11. Three photon absorption coefficients vs. \( (3 \hbar \omega - E_g) \) for CdI₂. The solid line is the best fit curve. Dots indicate experimental results.
All the four terms contribute to the 3PA spectral dependence which proves to be actually mixed. In fact, the interaction matrix elements corresponding to the four different transitions can be expanded in terms of $\tilde{k}$, assuming the general form

$$\tilde{P}_{ij}(\tilde{k}) = \tilde{P}_{ij}(0) + \tilde{k} \cdot \tilde{V} \cdot \tilde{P}_{ij} + \ldots$$  \hspace{1cm} (8)

When the transition is between bands of opposite parity (a allowed transitions) the first term is the dominant one and the $\tilde{k}$ linear term is neglected. The second term corresponds to transition between bands of the same parity (f forbidden transitions) when $\tilde{P}_{ij} = 0$ and $\tilde{k} = 0$. Thus all the four absorption mechanisms have been included in the parametric formula. The $C_n$ coefficients obtained following the fitting of the experimental data are given in Table 5.3.

\begin{table}
\centering
\caption{Values of the parameter formula $C_n$ coefficients for CdI$_2$. $C_n$ dimensions are $\text{cm}^3 \text{GW}^{-2} \text{meV}^{(n-1)}$ for $n = 0, 1, 2, 3$.}
\begin{tabular}{|c|c|c|c|}
\hline
$C_0$ & $C_1$ & $C_2$ & $C_3$
\hline
$1.5 \times 10^{-2}$ & $3.2 \times 10^{-4}$ & $2.5 \times 10^{-6}$ & $1.5 \times 10^{-8}$
\hline
\end{tabular}
\end{table}

A quantitative comparison of the experimental line shape with the theoretical ones has been shown in Figure 5.12. It is clear that only a satisfactory qualitative agreement is obtained between the $\gamma$ experimental line shape and the perturbative one for $(3h\omega - Eg)$ ranging between 50 meV and 70 meV. In the higher energy side there is no agreement at all. The nonperturbative treatment greatly underestimates the experimental line shape. It should be noted that even the inclusion of nonparabolicity and anisotropy has not improved the situation.
Figure 5.12. Quantitative comparison between the $\gamma$ experimental (dots) and theoretical (solid lines) line shapes for CdI$_2$. Solid lines A and B correspond to perturbative and nonperturbative models.
The $(3\hbar\omega - E_g)$ versus 3PA coefficient (absolute values) curve for ZnSe has been reported in Figure 5.13. In this case the experimental line shape is initially increasing ($50 \text{ meV} \leq (3\hbar\omega - E_g) \leq 700 \text{ meV}$) and then tends to be constant ($(3\hbar\omega - E_g) > 700 \text{ meV}$). This is quite analogous to the results obtained earlier [17] where the 3PA coefficients were measured in arbitrary units. The fitting results are good only for the three terms characterised by $1/2$, $3/2$ and $5/2$ exponents in the parametric formula. The $C_n$ coefficients have been summarized in Table 5.4. The $\chi^2$ value and the fit probability are found to be 0.25 and 0.952 respectively. For ZnSe the $\gamma$ behaviour for $(3\hbar\omega - E_g) > 700 \text{ meV}$ can be ascribed to a small joint density of states. Thus the ZnSe line shape points to different band curvatures causing different density of states available for three photon transition. As in the case of CdI$_2$, for ZnSe also there is only qualitative agreement between the perturbative treatment and the experimental results near the energy gap and the nonperturbative results are eight orders less than the experimental ones (Figure 5.14). This inadequacy may be ascribed to the linear approximation for the matrix elements and to the limited number of intermediate states considered.

In conclusion, one notes that the complete $\gamma$ spectral behaviour can be described by the parametric formula for CdI$_2$ while for ZnSe only the three mechanisms are contributing. These features have been tentatively ascribed to the different contribution of joint density of states. In these large gap semiconductors the comparison between the experimental and theoretical results has shown that the available theoretical models are inadequate to describe the dispersion curve throughout the whole energy range used. In fact, each of these just predicts a good frequency dependence near the direct energy gap. To sum up one finds that 3PA experiments together with other relevant experimental or theoretical observation can give information about the band structure and transitions not readily obtained from linear techniques.
Figure 5.13. Three photon absorption coefficients vs. $(3 \hbar \omega - E_g)$ for ZnSe. The solid line is the best fit curve. Dots indicate experimental results.

Table 5.4. Values of the parameter formula $C_n$ coefficients for ZnSe. $C_n$ dimensions are $\text{cm}^3 \text{GW}^{-2} \text{meV}^{(n+1)/2}$ for $n = 0, 1, 2, 3$.

<table>
<thead>
<tr>
<th>$C_0$</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2.2 \times 10^{-4}$</td>
<td>$5.6 \times 10^{-7}$</td>
<td>$2.0 \times 10^{-9}$</td>
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</tbody>
</table>
Figure 5.14. Quantitative comparison between the $\gamma$ experimental (dots) and theoretical (solid lines) line shapes for ZnSe. Solid lines A and B correspond to perturbative and nonperturbative models.
References