Three-photon-absorption spectroscopy in an indirect-gap material: CdI_2

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The three-photon absorption (3PA) spectrum of an indirect-gap material (CdI_2) has been measured at 10 K by monitoring the resulting self-trapped-exciton emission. The contribution of excitonic transitions has been evidenced for excitation energies near the indirect gap, while the contribution of allowed and forbidden indirect transitions has been shown for excitation energies far from the gap. The spectral behavior of the 3PA coefficient has been described by parametric formulas, which are analogous to the ones successfully applied for 3PA in direct-gap materials.

In recent years three-photon spectroscopy has become a powerful tool to investigate electronic and excitonic properties in insulators and semiconductors. From a theoretical point of view a detailed symmetry analysis has been performed to determine the polarization dependence of multiphoton transitions to excitonic states in solids.[1] From the experimental side, **k**-space spectroscopy of polaritons and longitudinal excitons has been performed in alkali halides.[2] For the same materials and for some II-VI compounds, three-photon absorption (3PA) spectroscopy has also been performed in a wide energy range.[3]

However, it must be noted that all the 3PA theoretical investigations and spectroscopic studies have considered direct-gap materials even though some fixed-frequency 3PA measurements have been performed on indirect-gap semiconductors. The scarcity of experimental investigations on 3PA processes in indirect-gap materials has been due to the difficulties in achieving high power density in the spectral region of interest for this kind of material. Nowadays the development of laser sources with enough power in the suitable frequency region allows the experimental investigation of some indirect-gap materials.

Hence, the aim of this paper is to investigate experimentally the three-photon-absorption process in an indirect-gap material with particular attention paid to the possible excitonic contribution and the nature of valence to conduction-band transitions.

The 3PA line-shape measurements have been carried out on a CdI_2 sample, which is characterized by a noncentrosymmetric structure and an indirect gap (E_{gi}) that has been evaluated to be at 3.538 eV at 10 K from Ref. 4. CdI_2 is especially well suited for our studies because (a) its strong luminescence emission[5] at low-temperature allows us to study the 3PA indirect process by using a nanosecond laser source, and (b) its relatively large gap enables us to use highly efficient dyes to pump the Raman cell providing the frequency down conversion in the near-infrared region. High-quality crystal was selected in order to avoid dependence on the degree of crystal purity. The spectral dependence in CdI_2 has been measured near and far from the indirect energy gap ($36 \leq 3\hbar\omega - E_{gi} \leq 500$ meV) at 10 K by means of the nonlinear luminescence technique. This consists of the detection of a luminescence signal excited by the simultaneous absorption of three identical photons at the energy of the intrinsic G emission ($\hbar\omega_L = 2.5$ eV) which is dominant below 20 K.[4] The detected luminescence signal at the frequency $\hbar\omega_L$ is given by

$$L = qf\alpha^{(3)} I_0^3 z(1 - \tfrac{1}{2}\alpha_L z) , \quad (1)$$

where q is the quantum efficiency for excitation at $3\hbar\omega$, f is the fraction of the collected luminescence, which is a function of the geometry, I_0 is the laser intensity, z is the sample thickness, and α_L is the linear absorption coefficient at $\hbar\omega_L$.

It is worth noting that this highly sensitive technique is the most suitable one for measuring the very small 3PA induced luminescence signals in indirect-gap materials when using a nanosecond dye laser source equipped with a Raman shifter. The experimental setup was similar to that in Ref. 3.

The 3PA spectrum was obtained by means of a Quantel Nd:YAG (yttrium aluminum garnet) laser whose second harmonic pumped a dye laser with 9-nsec pulse duration and 10-Hz repetition rate. The wavelength range obtained in the present experiment ($0.92 < \lambda < 1.05$ μm) was achieved by using a low-pressure H_2 Raman cell providing the frequency down conversion of the dye laser with its first- and second-order Stokes emission. In this range the power density is around some tens of MW/cm^2 after focalization. In particular, the second-order Stokes emission of a very efficient dye (Rod6G) was used together with the first-order Stokes emission of other two efficient dyes: LD700 and DCM. The emitted radiation was detected by a 60ER response photomultiplier tube, while the incident beam was monitored by a fast response germanium photodiode. Both signals were stored and processed by a computer data acquisition system. To reduce the effects of fluctuations in the input beam intensity, a ratio of the photomultiplier signal to the third power of the monitor signal was used. Moreover, the cubic behavior of the detected luminescence signal versus excitation intensity was checked at each experimental point and, for each of them, different measurement runs were carried out. In Fig. 1 the CdI_2 luminescence intensity versus laser input peak power has been reported for the $3\hbar\omega = 3.670$ eV excitation energy. The experimental accuracy was within the 20% for each run. The 3PA spec-

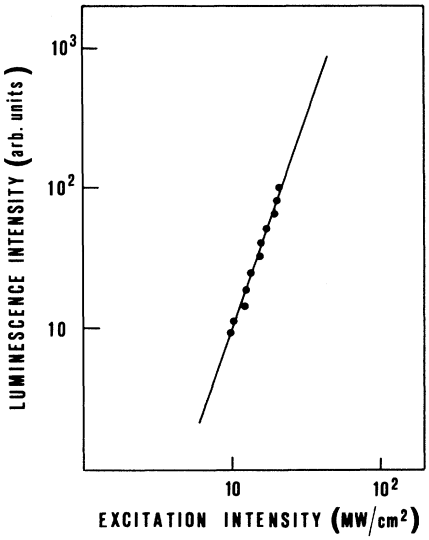

FIG. 1. Logarithimic plot of the intensity dependence of the photoluminescence induced by three-photon absorption at the energy $3\hbar\omega = 3.670$ eV. The straight lines are the best-fit cubic regression curves to the experimental points. The curve fits all data points, within ±5%.

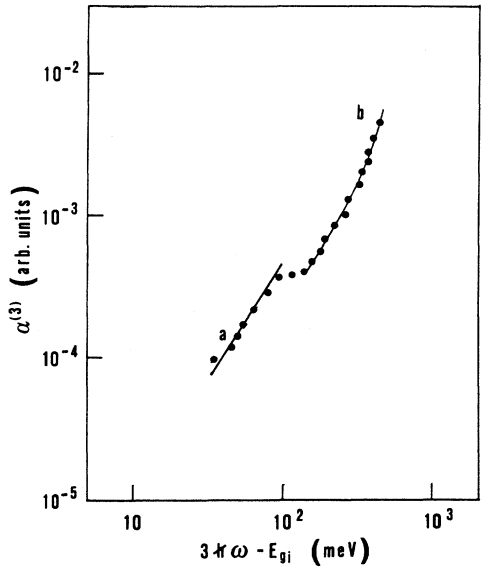

FIG. 2. Three-photon-absorption coefficient vs $(3\hbar\omega - E_{gi})$ for the CdI_2 crystal. The dots indicate experimental results. The solid lines *a* is the best-fit curve obtained by means of Eq. (6) by considering the experimental data in the range $36 \leq 3\hbar\omega - E_{gi} \leq 100$ meV. (The χ^2 value for a degree of freedom if 0.27 and the fit probability is 0.93.) The solid line *b* is the best-fit curve obtained by means of Eq. (7) by considering the experimental data in the range $150 \leq 3\hbar\omega - E_{gi} \leq 500$ meV. (The χ^2 value for a degree of freedom is 0.20 and the fit probability is 0.97.)

trum reported here has been obtained by measuring $\alpha^{(3)}$ every 20 meV on average with more data points in the region near the band gap.

The 3PA line shapes (dots) of CdI_2 vs $3\hbar\omega - E_{gi}$ is reported in Fig. 2. The experimental results clearly show that in this indirect-gap material $\alpha^{(3)}$ is augmented when the difference $3\hbar\omega - E_{gi}$ increases. The energy region very near E_{gi} has not been investigated due to the low luminescence signal induced by the 3PA process. For the same reason also the energy range below E_{gi} in which interesting excitonic effects should be present has not been examined.

In order to give an interpretation of these experimental results it could be very useful to remember the perturbative theory predictions about indirect-gap one-photon transitions.[6]

The theory of these indirect optical transitions can be developed by considering the electron-lattice perturbation Hamiltonian and using the results of second-order time-dependent perturbation theory. Using standard procedure one can obtain the following expression for allowed indirect one-photon transitions (allowed transition generally indicates a transition for which the matrix element of dipole is kept as a constant):

$$\alpha \propto (\hbar\omega \pm E_p - E_{gi})^2 , \tag{2}$$

where α is the one-photon-absorption coefficient, E_p indicates the phonon energy, and the plus and minus terms represent the contribution of phonon absorption and emission, respectively. Just as for the case of direct transitions, the indirect absorption can be the result of forbidden transitions (namely, transitions for which the matrix element of dipole is **k** dependent). Under this condition the main energy dependence of the absorption curve can be shown to be of the form

$$\alpha \propto (\hbar\omega \pm E_p - E_{gi})^3 . \tag{3}$$

For photon energy $3\hbar\omega$ very near the indirect energy gap we need to take into account the Coulomb interaction between the excited electron-hole pairs. In doing this it must be remembered that indirect transitions to exciton states give rise to a continuous absorption since phonons may be found to give transitions to all values of wave vector **k**. This continuous absorption resulting from the first exciton band starts at $\hbar\omega = E_{gi} \pm E_p - R$, where R is the exciton binding energy and shows an energy dependence of the form

$$\alpha \propto (\hbar\omega \pm E_p - E_{gi} + R)^{1/2} . \tag{4}$$

When the contribution of other exciton bands occurs it is more difficult to write down a valid analytical expression because at least one of the bands in an indirect-gap semiconductor will have an anisotropic E vs **k** relationship. However, for $\hbar\omega \geq E_{gi} \pm E_p$ the absorption starts to be roughly proportional to

$$\alpha \propto (\hbar\omega - E_{gi} \pm E_p)^{3/2} . \tag{5}$$

For $\hbar\omega \gg E_{gi} \pm E_p + R$ exciton effects are very much reduced and the absorption coefficient gains the usual forms for indirect interband transition.

In order to employ these general results to attempt a preliminary interpretation of our experimental data, a

fitting procedure similar to the one already used for 3PA in direct-gap materials[3] and 2PA in direct- and indirect-gap samples[7] has been employed. In particular, these results have shown that 3PA and 2PA absorption coefficient line shapes can be fully described by parametric equations containing several terms related to different transition mechanisms. Their energy dependence has been predicted on the ground of parity selection rules regarding the interaction matrix elements which couple the valence, the conduction band, and the intermediate states among them.[8] It is useful to note that the different terms are just the extension of the time-dependent perturbative theory results for one-photon absorption process to higher-order ones. For example, in the case of indirect 2PA process, two different transition mechanisms have been theoretically predicted and experimentally observed: *a-a* and *a-f* [where *a* (*f*) stands for allowed (forbidden)]. In the former mechanism, only **k**-independent transition-matrix elements have been used for electron-photon interaction, giving a 2PA absorption coefficient ($\alpha^{(2)}$) frequency dependence equal to $(2\hbar\omega \pm E_p - E_{gi})^2$. Instead in the latter mechanism k-dependent dipole matrix elements are also taken into account and an $\alpha^{(2)}$ proportional to $(2\hbar\omega \pm E_p - E_{gi})^3$ has been obtained. In the present case, the fitting procedures will be obtained by extending the results of indirect one- and two-photon absorption to indirect 3PA processes. In particular, a parametric formula containing the contribution of *a-a-a* and *a-a-f* interband transitions will be considered; while for the excitonic part of the 3PA spectrum an expression similar to Eq. (5) will be employed. In Fig. 2 the experimental results provide evidence for the different slopes followed by the 3PA coefficient that allows us to distinguish two main parts in the spectrum: the former, in which the excitonic effect dominates, and the latter, in which the interband transition contribution is relevant. In fact, in Fig. 2 the $\alpha^{(3)}$ experimental points in the energy range $36 \leq 3\hbar\omega - E_{gi} \leq 100$ meV have been fitted by the following expression:

$$\alpha^{(3)} = C_1 (3\hbar\omega - E_{gi} \pm E_p + R)^{3/2} , \tag{6}$$

which is represented in Fig. 2 by a continuous line *a* and it is valid even for excitation energy well above E_{gi}, in agreement with the theory of indirect excitonic transitions.[9] Equation (6) takes into account the contribution of excitonic bands with an index higher than 1 in the indirect absorption continuum. The experimental results for $3\hbar\omega - E_{gi} \geq 150$ meV for which the excitonic contribution can be neglected have been fitted by the formula

$$\alpha^{(3)} = \sum_{i=2}^{3} C_i (3\hbar\omega - E_{gi} \pm E_p)^i , \tag{7}$$

which considers the contribution of *a-a-a* and *a-a-f* interband transitions, namely, transitions in which all the matrix elements are assumed **k** independent and transitions in which only one of them is assumed to be **k** dependent. Expression (7) is shown in Fig. 2 by the continuous curve *b*. The contribution of phonon energy has been neglected in the numerical evaluation because $3\hbar\omega - E_{gi} \gg E_p$. The agreement is good for both formulas, as shown by the values and by the fit probabilities reported in the figure caption. Even though these fitting procedures have not been very accurate regarding CdI_2 phonon properties, they have been good enough to show that all the terms of Eqs. (6) and (7) contribute to the 3PA spectral dependence which is actually mixed.

It must be noted that between the excitonic and interband contributions energy range there is a flat region ($100 < 3\hbar\omega - E_{gi} < 150$ meV) in which $\alpha^{(3)}$ does not increase with photon energy. This behavior can be ascribed to interference terms among the contributions from the different transition mechanisms. The analysis of the CdI_2 band structure allows us to exclude that the $\alpha^{(3)}$ dependences could be ascribed to other critical points or singularities in the joint density of states. Conversely, for $3\hbar\omega - E_{gi} > 500$ meV no experimental investigation has been performed because previous 2PA spectroscopy studies on this material have shown that the contribution of direct-gap transitions becomes evident in this region.[7] Without this contribution the occurrence of other transition mechanisms would be shown analogously to the direct 3PA process in which four different transition mechanisms have been observed.[3]

Unfortunately, in the case of CdI_2, it is not possible to improve the present interpretation by comparing our experimental results with theoretical predictions because no theoretical model is available for 3PA processes in indirect-gap materials, to our knowledge.

In conclusion, we have reported the 3PA spectrum in a wide excitation energy range for an indirect-gap material. The $\alpha^{(3)}$ dispersion curve has been tentatively described by two parametric formulas which take into account the contribution of excitonic transitions and of *a-a-a* and *a-a-f* interband ones. The results are analogous to the one already obtained for 3PA spectroscopy in direct-gap materials[3] and 2PA spectroscopy in direct- and indirect-gap ones.[7] These experimental results clearly show the need of further theoretical investigation on these processes.

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