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Forbidden Luminescence and Resonance Raman Scattering of Bound Exciton States in CdS

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A series of six energy levels is found at energy distances 2.5, 3.8, 4.7, 6.1, 7.0, and 8.3 meV on the high energy side of the neutral-acceptor bound exciton I_1 in CdS. They appear in the emission and absorption spectra of some freshly grown virgin crystals and of some crystals damaged by laser-irradiation. Resonance Raman scattering (RRS) establishes the new levels as intermediate states in every high quality crystal. These levels are interpreted as excited states of the bound exciton I_1. The direct radiative recombination is forbidden due to parity selection rules. These selection rules are removed in symmetry disturbed crystals, at high excitation intensities, or by recombination with phonon participation. In consequence they are detected as forbidden luminescence, as LO phonon replica, or as 1-LO- and 2-LO-Raman lines. The 2-LO scattering cross section of the energy region of bound excitons in CdS is determined.

Auf der hochenergetischen Seite des an einen neutralen Akzeptor gebundenen Exzitons I_1 in CdS werden sechs neue Zustände in einem energetischen Abstand von 2,5; 3,8; 4,7; 6,1; 7,0 und 8,3 meV zur I_1 gefunden. Sie erscheinen sowohl in Emissions- als auch in Absorptionsspektren von einigen frisch gezüchteten und einigen durch Laserbestrahlung stark geschädigten CdS-Kristallen. Resonante Raman-Streuung erzeugt diese neuen Niveaus als Zwischenzustände in beliebigen, ungestörten CdS-Kristallen. Sie werden interpretiert als angeregte Zustände des gebundenen Exzitons I_1. Der strahlende Zerfall des Exzitons in diesen Zuständen ist aufgrund von Paritätsauswahlregeln verboten. Diese Auswahlregeln werden aufgehoben in symmetriegestörten Kristallen, durch hohe Anregungsintensitäten und durch Phononenbeteiligung. Daher werden die Niveaus sichtbar als verbotene Lumineszenz sowie als LO-Phononenreplika bzw. 1-LO- und 2-LO-Ramanlinien. Im Energiebereich der gebundenen Exzitonen in CdS werden die 2-LO Ramanstreuquerschnitte bestimmt.

1. Introduction

In CdS the I_1 emission line corresponds to the radiative recombination of an exciton X_A with a hole from the A valence band bound to a neutral acceptor A^0 [1]. A series of six sharp lines, named I_1^1 to I_1^6, has been observed on the high energy side of I_1 and below the neutral-donor bound exciton I_2 in emission as well as in absorption [2]. They appeared in some undoped freshly grown crystals which showed strong band edge emission, but disappeared after a few optical measurements at liquid helium temperature. In contrast some strong ruby laser excited and thus damaged crystals showed them permanently. The lines are weakened, however, by excitation with intense cw-laser light. Magnetic field dependent measurements were carried out which showed S- and P-like envelope wave functions [3]. Though an initial idea of excited bound exciton states was pursued, a consistent explanation for these observations could not yet been found. Additional bound exciton states have never been found in this energy region except when the samples were doped definitely with phosphorus or iodine [4, 5] and silver [6].

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In a recent paper [7], two excitation maxima of the I_1 complex lying on the same energy position as the I_1^1 and I_1^2 emission lines had been interpreted as excited bound exciton states. Their radiative decay to the neutral acceptor state and vice versa their direct excitation are dipole forbidden due to parity arguments (Laporte rule). In the case of very strong laser light irradiation this restriction is apparently lifted by higher-order transitions.

To obtain further informations about excited bound exciton states, resonance Raman scattering (RRS) experiments with high quality undoped crystals were performed. The strong coupling of LO phonons and excitons in wurtzite-type semiconductors gives rise to Raman scattering lines as well as to phonon replica of excitonic recombinations. Various authors [8 to 15] interpreted their resulting enhancement of the 1-LO Raman cross-section by free or bound exciton intermediate states. Only free exciton state resonances had been reported in the case of 2-LO phonon scattering [8, 14, 15]. No resonance states could be detected between the acceptor- and donor-bound excitons I_1 and I_2, respectively, by these authors. In this paper we present examples of the forbidden luminescence lines I_1^1 to I_1^6 together with their phonon replica, their absorption spectra and their 1-LO and 2-LO Raman lines. Two of these Raman lines and phonon replicas coincide in energy with two small peaks on the high energy side of the I_1-LO line. They had been interpreted by Reynolds et al. [16] as so-called bound 1-LO-phonon quasiparticles (BPQ). One of their essential arguments was the lack of any zero-phonon line just in the region of the I_1^1 and I_1^6 structure. In consequence of our results their interpretation now becomes questionable.

2. Experimental Techniques

Steady-state low excitation spectroscopy was performed with a mercury high pressure lamp (Osram, HBO 2000) as light source. The photon energy of the transmitted or emitted light was analysed using a double grating spectrometer (Spex) followed by an optical multi-channel analyser (B & M, OSA 500). The very early spectra [2] reproduced in Fig. 2 were taken photographically at the exit-slit plane of a high resolution grating spectrometer.

The experimental set-up in our RRS experiments consisted of the following components. A N_2-laser pumped dye laser system (Lambda Physik) served as a wavelength tunable light source. The dye laser emitted light pulses of 2.5 ns temporal and 0.3 meV spectral half-width with a peak power up to 200 kW. An excitation density of 2 MW/cm^2 was reached by focusing the laser beam on the crystal. The crystal was immersed in liquid helium within a conventional cryostat. A cooled multiplier (EMI, bialcaline cathode) detected the scattered light behind a double monochromator. The electrical signal was fed in a box-car integrator (PAR, model 162).

The wavelength selecting gratings of both the dye laser and the spectrometer were equipped with stepmotor drives. By this the photon energy of the dye laser and of the spectrometer were tunable simultaneously.

Crystal platelets of CdS and a rod-shaped crystal with two surfaces perpendicular to each other were used as samples. The wave vector of the incident light was adjusted to be normal to the first surface. The scattered light was collected from the second surface and from one side surface of the platelets in the direction of its normal. Thus a scattering angle of 90° was formed. Both wave vectors were oriented perpendicular to the crystallographic c-axis. The incoming and outgoing light waves were polarized according to the optical selection rules of the Raman transitions under consideration. In the following the $x(y, x)\,y$ and $x(y, z)\,y$ scattering configurations (notation following Damen et al. [17]) were used. In this way RRS of CdS via excitonic states activates the LO phonon mode E_1 [18].

3. Experimental Results

In Fig. 1 the emission spectra of two disturbed crystals (dotted and dashed curves) in comparison with an undisturbed one (solid curve) are shown. The intensity of each spectrum is normalized to have the same I_1 intensity. The typical spectra of undisturbed crystals show only the two strong emission lines which are due to excitons bound to a neutral acceptor (I_1, 2.5363 eV) and to a neutral donor (I_2, 2.5470 eV). All spectra are taken under the condition of band-to-band steady-state excitation.

The disturbed crystals show six additional sharp lines designated as I_1^1 to I_1^6. Their relative intensities vary strongly for different crystals. Generally I_1^2, I_1^3, and I_1^4 are more intense than I_1^1, I_1^5, and I_1^6. The I_1^3 emission line is often the strongest one, and for one sample even stronger than the I_1 bound exciton. The energy position of the bound exciton I_1 itself and of the lines I_1^1 to I_1^6 vary only very little for different crystals, indicating different types of shallow acceptors. It is important to note that their relative energy distances remain constant. Without any exception all lines show the 1-LO phonon replica with an energy spacing of 37.8 meV (Fig. 2). This energy corresponds to the well-known E_1 mode of the LO phonon in CdS [18]. In addition small but narrow minima can be detected as forbidden lines in the transmission spectrum for $\boldsymbol{E} \parallel \boldsymbol{c}$.

In Fig. 3 the 2-LO Raman scattering spectra are shown for various incident laser photon energies. The actual wavelength is given on the right side of each spectrum. The 2-LO Raman line is labelled with an arrow. To demonstrate an identical stepwise change in the photon energy of the laser and the 2-LO Raman line two equal scalings, E_{exc} and $E_{\text{exc}} - 2\text{-LO}$, are drawn in the figure. Their energy spacing amounts to 75.6 meV which is twice the LO phonon energy. The 2-LO phonon replica of the free A-exciton, the bound excitons I_1 and I_2, the state I_1^2, and the transverse acoustic (TA) phonon wing I_1-TA of the I_1 bound exciton always occur in the 2-LO Raman

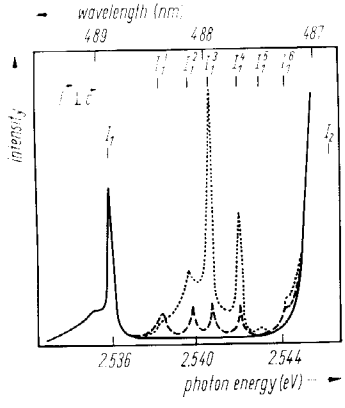

Fig. 1

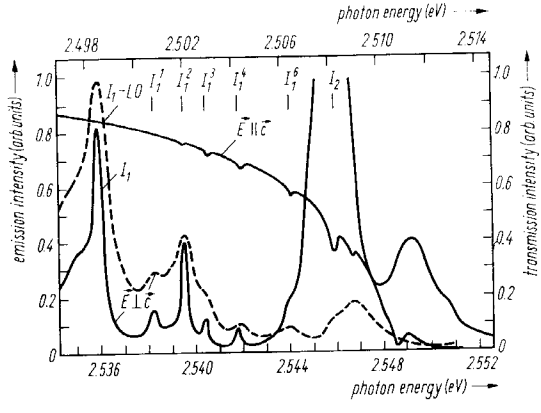

Fig. 2

Fig. 1. Emission spectra of two disturbed CdS crystals (dotted and dashed curves) in comparison with an undisturbed one (solid curve). The intensities are normalized to the I_1-line. The energy scales of all figures are not corrected by the air refractive index. $T = 4.2$ K

Fig. 2. Transmission (polarization $\boldsymbol{E} \parallel \boldsymbol{c}$) and emission (polarization $\boldsymbol{E} \perp \boldsymbol{c}$) spectra (solid curves) of a disturbed crystal in comparison with the luminescence spectrum of their 1-LO phonon replica (dashed curve). The lower energy scale belongs to the solid curves, while the upper scale relates to the dashed curve

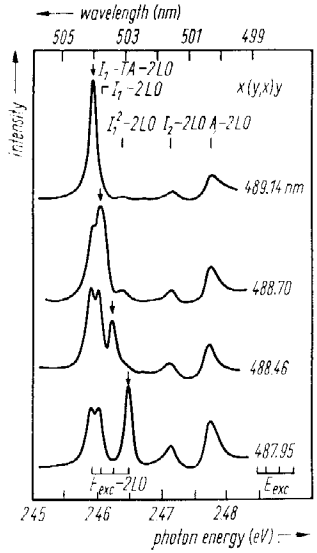

Fig. 3. 2-LO scattering spectra for various incident laser photon energies. The excitation wavelength of each spectrum is given on the right hand side. The arrows indicate the actual 2-LO Raman line

spectra. Their intensities are independent of the resonant 2-LO scattering. Two-photon absorption is presumably responsible for the excitation of these free and bound exciton lines and their phonon replica. The 2-LO Raman line intensity dominates in all spectra. A variation of the 2-LO line intensity corresponds to a partial or total resonance with intermediate exciton states.

To find the resonance states of the 2-LO RRS, the scattered light intensity versus the laser photon energy must be considered. A direct measurement is performed by tuning simultaneously the photon energy of the dye laser and of the spectrometer. Both instruments are calibrated to the energy difference of the 2-LO phonon energy. The resulting 2-LO scattering spectrum given in Fig. 4 shows a great number of distinct resonance states. Four of them coincide in energy with the emission lines I_1^2 to I_1^5. On the low-energy side of I_1 its TA-phonon wing I_1-TA and another new state I_1^A show a 2-LO Raman resonance.

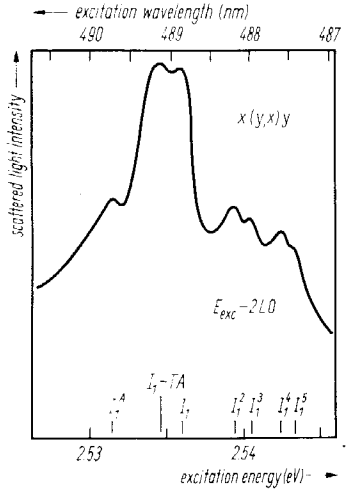

Fig. 4

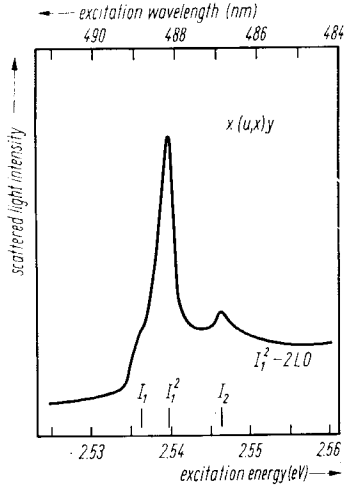

Fig. 5

Fig. 4. Excitation spectrum of the 2-LO Raman line in the configuration x $(y, x)y$. $T = 1.3$ K

Fig. 5. Excitation spectrum of the I_1^2-2-LO line in the configuration $x(u, x)$ y (u unpolarized). $T = 1.3$ K

The occurrence of phonon replica of non-emitting zero-phonon states allows us to measure indirectly the excitation spectrum of the zero-phonon lines. The intensity of the phonon replica under consideration is detected as a function of the exciting photon energy. Then the spectrometer is set to the wavelength of the phonon replica while the laser photon energy is varied. As an example, the excitation spectrum of the state I_1^2 is shown in Fig. 5. I_1^2-2-LO, i.e. I_1^2 indirectly, is always excitable with photons of higher energy than the state itself. At the donor-bound exciton I_2 an excitation maximum is superimposed. A weak anti-Stokes excitation via the I_1-bound exciton occurs at lower energies. This behaviour is shared by all other I_1^i states ($i = 2$ to 5).

Generally the results of 2-LO and 1-LO RRS are identical except for the higher scattering cross-section and the broader linewidth of the 2-LO scattering. The 1-LO and 2-LO phonon replica are equal in intensity. The very intense I_1-LO phonon line is known to be exceptionally strong. Each excitation spectrum of the I_1^i-LO phonon replica ($i = 1$ to 4) shows two resonance states. Beside I_2, the immediate high energy neighbour I_1^{i+1} ($i = 1$ to 4) acts as an excitation maximum.

Table 1

Listing of the observed exciton emission and Raman lines in comparison with the relevant results of other authors. The table gives the energy distances ΔE (meV) of the observed lines to the I_1 (or I_1-LO or I_1-2 LO) line

line	emission LO-replica	LO-scattering	2-LO-scattering	excitation [7]	BPQ [16]	P/I-doped [4]	P/Ne-doped [5]	Ag-doped [6]
I_1^1	2.5	2.6	—	2.5	2.7	—	—	—
I_1^2	3.8	3.5	3.4	3.7	3.3	4.0	3.9	—
I_1^3	4.7	4.7	4.5	—		4.7	4.7	4.6
I_1^4	6.1	6.5	6.4	—		—	—	5.7
I_1^5	7.0	—	7.2	—	—	—	—	—
I_1^6	8.3	—	—	—		—	—	—
I_1-TA	-1.2	—	—1.3	—	—	—	—	—
I_1^A	—	—	—4.6	—	—	—	—	—

In Table 1 the energies of all the measured states are listed together with the relevant results of other authors. Two of the BPQ lines given by Reynolds et al. [16] coincide with the I_1^1-LO and I_1^2-LO line, respectively. The lowest BPQ line could not be found. In CdS crystals doped with phosphorus or iodine Henry et al. [4] and Shiraki et al. [5] found a doublet of emission lines near the states $I_1^{2,3}$. In Ag-doped crystals Colbow et al. [6] observed two lines near $I_1^{3,4}$. Excitation spectroscopy of the I_1-complex [21] recently resulted in five excitation maxima whose energy positions are identical to those of I_1^1 to I_1^5.

4. Discussion

In this paper we focus our attention on transitions from the ground and excited states of the neutral-acceptor exciton complex (A^0, X_A) to the ground state of the crystal. Recent theoretical treatments of the (A^0, X) ground state in zincblende structured direct-gap semiconductors resulted in fine structures [19, 20], when hole-hole and electron-hole exchange interactions had been included in the calculations of the

ground state of (A^0, X) in a crystal field. A variety of four ground state levels of the (A^0, X_A) complex in wurtzite-type CdS has been deduced in a similar way [21]. Thereby the upper two levels originate from a parallel hole spin (the lower two ones from an antiparallel hole spin) combination of the two holes from the A-valence band. The parallel spin combination is forbidden due to Pauli's exclusion principle.

The possible lowest excited configuration of (A^0, X_A) is claimed to be a symmetric spin state of the two holes h_A [21]. One of them belongs to an excited 2p and the other to the ground 1s configuration. A manifold splitting is expected due to additional interactions of spins and angular momenta. The $l = 1$ angular momentum of the excited 2p hole leads to a P-like envelope wavefunction of the excited state itself.

The electric dipole operator and P-like wavefunctions show odd parity. The S-like wavefunctions, in consequence, are ascribed to even parity. The parity selection for electric dipole transitions thus yields the parities of the initial and final states to be unequal. For this reason the transitions from the upper three levels of the complex ground state (S-wavefunction) to the groundstate A^0 of the crystal (P-wavefunction) are parity-allowed. However, these states themselves are Pauli-forbidden. On the other hand transitions from the excited complex state to the A^0 final state turned out to be parity-forbidden. In detail the measured Zeeman splitting of the emission lines I_1^2 to I_1^5 in laser damaged crystals [3] shows an S-like wavefunction for I_1^2 and a P-like one for I_1^3 and I_1^4. We attribute I_1^2 (and the energetically lower lying level I_1^1) to one of the higher levels of the complex ground state. In contrast to Pauli's exclusion principle they may exist because of the following reasons. One hole is bound to a negative acceptor and the other one to a quasi-free electron. The wavefunctions of the two holes h_A are then expected to be slightly changed. The Pauli principle is valid only for identical wavefunctions. The existence of such levels seems to be the more probable the stronger the crystal symmetry is distorted, otherwise the observed emission lines in disturbed crystals would not be explainable. On the other hand, we conclude from the P-like wavefunctions of I_1^3 and I_1^4 that they belong to the split-off excited state of the complex (A^0, X_A). The parity prohibition of their transition to the crystal ground state is weakened by symmetry distortions in disturbed crystals or removed by LO phonon participation at high laser intensities.

We calculated the 2-LO RRS cross-section $\sigma(\omega_i, I_0)$ for our scattering configuration from the measured Raman and absorption spectra. The Raman line intensity $I(\omega_s)$ can be expressed by the following equation [22]:

$$I(\omega_s) = \frac{1 - \exp\left(\alpha(\omega_i, I_0)\, d\right)}{\alpha(\omega_i, I_0)} \sigma(I_0, \omega_i)\, I_0(\omega_i)\,. \tag{1}$$

$\alpha(\omega_i, I_0)$ represents the absorption coefficient for a given incident light intensity $I_0(\omega_i)$ at a photon energy ω_i, and d the crystal thickness along the laser beam. An excitation-intensity dependent band-gap shift has been established leading to an I_0-dependent absorption coefficient [7]. The 2-LO Raman cross-section of Γ_1 in CdS amounts to $6.3 \times 10^3\ \mathrm{cm}^{-1}$ at an excitation intensity of $2\ \mathrm{MW/cm^2}$. I_1^2 to I_1^5 show Raman cross-sections in the same order of magnitude. With increasing power the 2-LO cross-sections of all lines enhance linearly. For the 2-LO RRS many authors [8, 13 to 15] found a monotonic increase of the 2-LO Raman cross-section with increasing photon energy. Oka and Kushida [14] described the 2-LO scattering process as a successive scattering of a virtually created $\Gamma_5(A)$ exciton by two phonons. In the energy region around 2.5470 eV we get a cross-section three times greater than that observed by Oka and Kushida [14]. We explain this result by our excitation intensity being enhanced by the same factor. In contrast to [14] the 2-LO cross-section is enhanced by a factor of ten in the vicinity of bound excitons and their excited

states. The cross-section ratio between the 2-LO and 1-LO scatterings in the allowed configuration $x(y, x)\,y$ amounts to 30 in the bound exciton region. The forbidden configuration $x(z, z)\,y$ [23] yields a 1-LO cross-section ten times greater than the allowed one.

In the used high quality crystals the excited states I_1^1 to I_1^5 and I_1^A were not detectable as emission or absorption lines. Therefore an explanation as (A^0, X) bound exciton lines formed with other acceptor elements [4, 5, 6] can be excluded. Based on our RRS measurements and the detection of the zero-phonon lines in disturbed crystals an interpretation as bound phonon quasi-particle [16] is unlikely.

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