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Electronic and vibronic states of the acceptor—bound-exciton complex (A^0,X) in CdS

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High-density excitation spectroscopy of the acceptor—bound-exciton emission I_1 in CdS results in series of new resonance states, situated on the high-energy side of the I_1. For polarized laser light $\vec{E}\perp c$ the series I_1^1 to I_1^5 appears, and is superimposed by another series of resonance maxima V_1 to V_7 at highest excitation intensities. For $\vec{E}||c$, excitation of the I_1 via a couple of doublets in the spectral region of the known absorption lines I_{1B} and $I_{1B'}$ is observed for the first time. They are interpreted as electronic ground-state levels of the (A^0,X_B) complex with one of its holes originating from the B valence band. The splitting off of the ground state by electron-hole and hole-hole exchange interactions is discussed in a simple fine-structure model of the (A^0,X) complex. The series I_1^1 to I_1^5 is thus attributed to ground- and excited-electronic-state levels of (A^0,X_A). Molecular analogous rotation or vibration modes of the (A^0,X) complex are discussed as origins of the series V_1 to V_7.

I. INTRODUCTION

In CdS emission lines due to the radiative recombination of excitons bound to impurities or defects are known as I_1 lines if the excitons are bound to neutral acceptors [(A^0,X) complex], I_2 lines if the excitons are bound to neutral donors (D^0,X), and I_3 lines for excitons bound at ionized donors (D^+,X).[1–3] Recently a number of investigations had been performed to clarify the formation mechanisms of bound-exciton complexes in semiconductors.[4–7] Beside the capture of free excitons by impurities or defects the direct formation of bound-exciton complexes in their electronic ground or excited states is also of interest.[5,6] In CdS excitation spectroscopy using high-pressure lamps[5] and tunable dye lasers[6] as light sources improved the possibilities to identify excited states of the (D^0,X) complex. Its ground-state recombination corresponds to the emission line I_2. In contrast to the case of the (D^0,X) complex no excited states of the (A^0,X) complex in CdS had been reported for a long time. After detecting a number of new emission lines called I_1^1 to I_1^6 lying on the high-energy side of the I_1 in some selected crystals, we reported corresponding Raman resonances in a preceding paper.[8] Performing excitation spectroscopy of the (A^0,X) ground state (emission line I_1) we recently found resonances[9] which correspond in energy to the I_1^1 and I_1^2 emission lines. In this paper we report additional excitation resonances I_1^3 to I_1^5, together with further new resonances V_1 to V_7 which are only excited at highest excitation intensities. Their temperature and intensity dependences differ substantially from that of I_1^1 to I_1^5. All these resonances occur only by irradiation with light of polarization $\vec{E}\perp c$. On the other hand, when irradiating with laser light of polarization $\vec{E}||c$ new doublet structures appear in the excitation spectra of the I_1 at the energy positions of the known absorption lines I_{1B} and $I_{1B'}$.[1] The experimental results are described in Sec. III. In Sec. IV we interpret our excitation resonances as electronic and vibronic excited states of the (A^0,X) complex.

II. EXPERIMENTAL TECHNIQUES

The samples used for the measurements were high-quality platelets of undoped CdS with a thickness of 30 to 450 μm. For the excitation spectra we employed a tunable dye laser (model FL-1000, Lambda Physik) pumped by a N_2 laser (Model 100-AS, Lambda Physik). A peak power of about 20 kW within 2.5 ns pulse duration and a spectral halfwidth of about 0.15 meV of the laser emission line were reached. By exciting the samples with polarization $\vec{E}||c$ and $\vec{E}\perp c$, respectively, the luminescence was observed in forward and backward direction. The optical spectra were recorded with a double-grating spectrometer (Spex 0.75 m) followed by a photomultiplier or an optical multichannel analyzer (OSA 500, B&M), alternatively. The OSA system is set up for emission-spectra measurements at fixed excitation wavelength of the laser. We used the OSA system to observe the crystal's luminescence within a spectral region of 5 nm. It enabled us to identify and exclude misleading indirect excitation of the I_1. For example the radiative recombination of possibly excited biexcitons in CdS results in photons of an energy identical to an excitation maximum of the I_1 transition which yield an indirect enhancement of this transition. The excitation spectra given in this paper were recorded by a photomultiplier as detector while tuning the dye-laser's wavelength.

III. EXPERIMENTAL RESULTS

In a first series of measurements with laser light of polarization $\vec{E}\perp c$ the excitation spectra of the I_1 emission line were detected in forward and backward configuration. The $\vec{E}$ vector of the I_1 emission line was completely polarized perpendicular to the c axis in agreement with the given optical transition probability in CdS.[1] Figure 1 shows excitation spectra in the backward arrangement for three typical excitation intensities. The resonance $I_1 + \mathrm{TA}$ dominates only at low intensities [spectrum 1(a)]. This simultaneous creation of an (A^0,X) complex and a TA phonon had been analyzed in our previous paper.[9] The very weak resonances I_1^1 to I_1^5 of spectrum 1(a) increase rapidly with growing excitation intensities as indicated in spectrum 1(b). In our preceding measurements[9] at lower excitation intensities only I_1^1 and I_1^2 could be detected. In spectrum 1(b) new resonance maxima V_1 to V_6 appear, which are partially or totally superimposed to $I_1 + \mathrm{TA}$ and the I_1^i states. Further increase of the excitation intensity yields spectrum 1(c) which is dominated by the resonances V_i. Table I lists the energies of I_1^i resonance states, Table III those of the V_i states. In contrast to $I_1 + \mathrm{TA}$, the intensity of the resonance lines I_1^1 to I_1^5 increase superlinearly in excitation. V_1 to V_6 show even a faster increase and are saturated at much higher intensities compared to I_1^1 to I_1^5. The excitability of the I_1 via the resonances V_1 to V_6 disappears at temperatures higher than 12 K, see Fig. 4. This is equal to the behavior of the I_1 exciting via the resonance $I_1 + \mathrm{TA}$.[9] Therefore, at higher temperatures it is possible to observe the pure excitation via I_1^1 to I_1^5 without superposition by the other resonances. A set of spectra for different temperatures is shown in Fig. 2. At 30 K these excitation processes disappear, too. This is to be expected because the I_1 emission itself does not remain at temperatures higher than 30 K as a result of the ionization of the neutral impurity.[10]

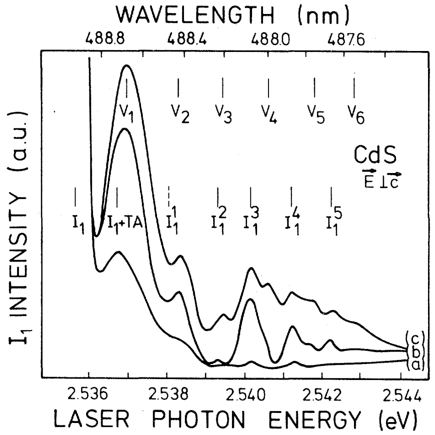

FIG. 1. Excitation spectra of the I_1 emission line by exciting with light of polarization $\vec{E}\perp\vec{c}$ and of intensities (a) 30 $\mathrm{kW\,cm^{-2}}$, (b) 55 $\mathrm{kW\,cm^{-2}}$, and (c) 75 $\mathrm{kW\,cm^{-2}}$. The He bath temperature is 1.3 K.

TABLE I. I_1 electronic excitation resonances using $\vec{E}\perp\vec{c}$ polarized incident laser light in comparison to the corresponding emission lines and LO Raman resonances reported in Ref. 8. The second column lists the absolute energy values of the excitation resonances, the further columns show the relative distances ΔE of the excitation resonances, emission lines, and LO Raman resonances, to the I_1 or I_1-LO emission lines, respectively.

Line	E (eV) I_1 excitation	ΔE (meV) I_1 excitation	ΔE (meV) Emission[a]	ΔE (meV) LO/2LO scattering[a]
I_1	2.5356			
$I_1 + \mathrm{TA}$	2.5367	1.1		
I_1^1	2.5381	2.5	2.5	2.6
I_1^2	2.5393	3.7	3.8	3.5
I_1^3	2.5402	4.6	4.7	4.7
I_1^4	2.5412	5.6	6.1	6.5
I_1^5	2.5422	6.6	7.0	7.2
I_1^6			8.3	

[a] Reference 8.

Some crystals show a particularly strong excitabil-

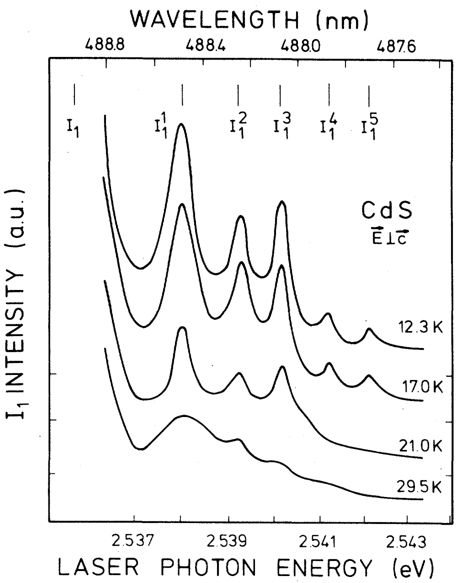

FIG. 2. Excitation spectra of the I_1, $\vec{E}\perp\vec{c}$, at different temperatures between 12.3 and 29.5 K. The resonances $I_1+\mathrm{TA}$ and V_i noticeable at 1.3 K in Fig. 1 are not observable at temperatures above 12 K.

ity via the resonances V_i probably submerging the resonances I_1^1 to I_1^5. Figure 3 shows the excitation spectra of such a crystal at different excitation intensities. These structures only occur at higher excitation intensities, in contrast to the resonance $I_1+\mathrm{TA}$. No further resonance lines are observable higher in energy than the resonance labeled V_7. Figure 4 shows the temperature dependences of V_1 to V_7 in comparison to the resonances I_1^1 to I_1^5 measured at other samples.

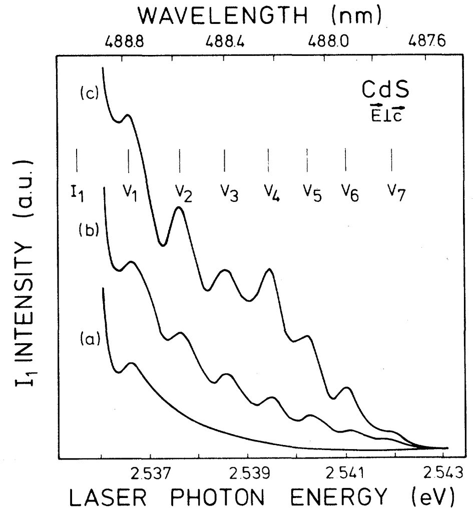

FIG. 3. Excitation spectra of the I_1, $\vec{E}\perp\vec{c}$, of a sample that shows strong vibronic resonances V_i at 1.3 K. The different excitation intensities amount to (a) 105 kW cm^{-2}, (b) 325 kW cm^{-2}, and (c) 390 kW cm^{-2}.

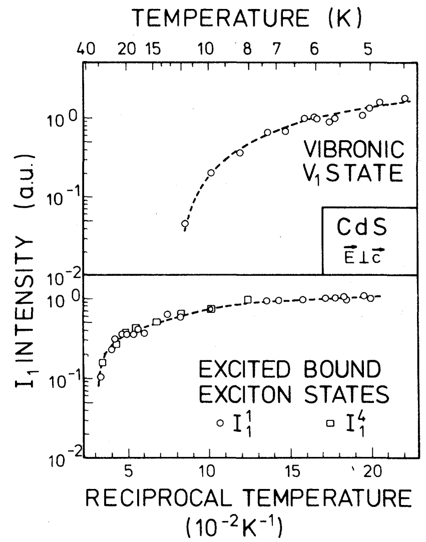

FIG. 4. Temperature dependent I_1 intensity exciting via the vibronic state V_1 (upper part), and via the electronic bound-exciton states I_1^1 and I_1^4 (lower part), given representatively for the states V_i, $i=1,\ldots,7$, and I_1^i, $i=1,\ldots,5$, respectively.

With a polarization $\vec{E}\|c$ of the incident laser light we detected a line quartet of resonances in the region of the known absorption lines I_{1B} and $I_{1B'}$ of the (A^0,X_B) complex.[1] Our excitation spectrum is shown in Fig. 5. In addition, the known resonance states of the free $1S\Gamma_6(A_F)$ triplet exciton and the $\Gamma_{5L}(A_L)$ longitudinal exciton[9] occur. The quartet

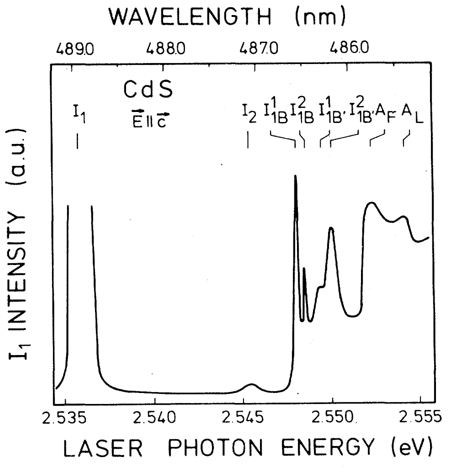

FIG. 5. I_1 excitation spectrum exciting with light polarized $\vec{E}\|\vec{c}$ at 1.3 K.

consists of two very sharp lines called I_{1B}^1 and I_{1B}^2 (0.2-meV half-width) at distances 12.3 and 12.9 meV from the I_1, and of two broader resonance maxima called $I_{1B'}^1$ and $I_{1B'}^2$ (0.5-meV half-width) at 13.8 and 14.4 meV on the high-energy side of the I_1, i.e., two doublet structures, one pair of sharp lines and the other a pair of broad lines. The energies are listed in Table II. The energy spacing in each of the doublets is 0.6 meV indicating the similar nature of the two pairs. Malm and Haering[5] reported steady-state excitation of the I_1 via I_{1B} and $I_{1B'}$, but could not observe the doublet structure in their low-intensity excitation measurements. However, we point out that our crystals show the two intermediate resonances I_{1B}^2 and $I_{1B'}^1$ with various strengths and resolutions. Spectrum Fig. 5 shows a well-resolved line quartet, but there exist also crystals yielding spectra in which some of these lines occur very weak. In $\vec{E}\parallel c$, no excitation maximum is to be seen in the spectral region between I_1 and I_2, not even at the highest laser intensities, see Fig. 5.

IV. DISCUSSION

Figure 1 shows three selected spectra which illustrate the conditions for the appearance of the different excitation processes. Firstly, one has to separate the resonance $I_1 + \mathrm{TA}$, observable already at low excitation intensities, from the resonances I_1^1 to I_1^5 which become stronger at higher intensities. Secondly, the resonances V_1 to V_7 become increasingly dominant in the spectrum when the excitation intensity further increases. The intensity and temperature dependence is different regarding the excitation maxima I_1^1 to I_1^5 on the one hand, V_1 to V_7 on the other hand, and $I_1 + \mathrm{TA}$. This demands the discussion of diverse processes being responsible for their appearance.

A. Electronic states

The similarity of line shape and narrowness of the I_1^i resonance transitions to the I_1 line itself encourages us to discuss excited electronic states of the (A^0,X) complex as adjoined levels. In the following we develop a theoretical explanation of these states making use of recent theoretical and experimental results.[7,11–13] The theoretical treatments include the hole-hole and electron-hole exchange interaction in the calculation of the energy values for the electronic ground state of the (A^0,X) complex in a crystal field. These interactions split off the electronic ground state, and the coupling rules of the electron's spins and angular momenta are considered to be valid by analogy to the diatomic molecule. The application of the theoretical considerations in the (A^0,X) complex in CdS with the point symmetry group C_{6v}^+ leads to the following results: We consider that in the electronic ground state of the (A^0,X) all complex particles remain in their lowest atomic

TABLE II. I_1 excitation resonances using $\vec{E}\parallel\vec{c}$ polarized incident laser light in comparison to emission and absorption lines given in Refs. 1 and 4. The left part of the table shows the I_1 excitation resonances with their absolute values E and their relative distances ΔE to the I_1 line. The right part of the table gives the corresponding emission or absorption lines with polarization and relative distances ΔE to the I_1 line.

Excitation resonance	E (eV)	ΔE (meV)	Emission and/or absorption line	E (eV) [λ (Å)]	Polarization	ΔE (meV)
I_2	2.5455	9.9	I_2	2.5467[a] (486.715 nm)	$\vec{E}\perp\vec{c}$	11.1
I_{1B}^1	2.5479	12.3	I_3	2.5479[b] (486.61 nm)		
I_{1B}^2	2.5485	12.9	I_{1B}	2.5485[a] (486.37 nm)	$\vec{E}\parallel\vec{c}$	12.9
			I_{1B}	2.5488[a] (486.32 nm)	$\vec{E}\perp\vec{c}$	13.2
$I_{1B'}^1$	2.5494	13.8	I_3	2.5495[a] (486.17 nm)	$\vec{E}\perp\vec{c}$	13.9
$I_{1B'}^2$	2.5500	14.4	$I_{1B'}$	2.5500[a] (486.08 nm)	$\vec{E}\parallel\vec{c}$	14.4
A_F	2.5522	16.6				
A_L	2.5542	18.6				

[a] Reference 1.

[b] Reference 4.

energy levels. In C_{6v}^{+}, the z components $M_J^z=\pm3,\pm2,\pm1,0$ of the momentum values $J=3,2,1,0$ of the coupled holes (each with $j_h=\frac{3}{2}$) are to be replaced by the crystal-symmetry quantum numbers μ which are related to the sixfold crystallographic c axis ($p=6$). M_J^z and μ are related by $M_J^z=\mu+zp$, $z=0,\pm1,\pm2,\ldots$. The corresponding product representation of the two holes with momentum $\frac{3}{2}$ and the two possible components $\frac{1}{2}$ and $\frac{3}{2}$ in the direction of the c axis is $(\Gamma_7+\Gamma_9)\times(\Gamma_7+\Gamma_9)$. The product includes three possible complexes: (1) (A^0,X_A) has both holes from the upper A valence band with symmetry Γ_9 and known transition line I_1; (2) In (A^0,X_B) one hole stems from the A, the other from the second B valence band (Γ_7), corresponding to the known transition lines I_{1B} and $I_{1B'}$; (3) Lines dues to (A_B^0,X_B) with two holes of the B valence band have never been observed. The possible momenta combinations in these complexes show that the (A^0,X_A) can have a resulting z component of hole spins $\mu=3$ and 0, the (A^0,X_B) $\mu=\pm1$ and ±2, and (A_B^0,X_B) $\mu=0$ and ±1. Although the hole momentum combination $\mu=3$ (spin parallelism) in the (A^0,X_A) complex is Pauli forbidden assuming two like holes, the validity of the Pauli prohibition is questionable in the (A^0,X_A) case because it requires the total equality of the wave functions of the two like particles, while in the (A^0,X_A) one hole belongs to the acceptor and the other to the exciton. Therefore we treat the complex including the $\mu=3$ combination. The product of the coupled hole momentum representations in C_{6v}^{+} and the electron representation Γ_7 attached to its spin $\frac{1}{2}$ gives

$$(\Gamma_7+\Gamma_9)\times(\Gamma_7+\Gamma_9)\times\Gamma_7 = 7\Gamma_7+4\Gamma_8 + 5\Gamma_9 \tag{1}$$

This set of states represents a comprehensive term scheme for the (A^0,X) complex which encompasses the term scheme of this complex developed by Thomas and Hopfield.[1] The attachment of these levels, involving the values of angular momenta, to the three possible (A^0,X) complexes requires the additional consideration of the representation products of the electrons and holes of the specific complex structures. The product representation corresponding to the (A^0,X_A) complex with two A holes is

$$(\Gamma_9\times\Gamma_9)\times\Gamma_7=2\Gamma_7+2\Gamma_8\ , \tag{2}$$

while the (A^0,X_B) complex is represented by

$$(\Gamma_9\times\Gamma_7)\times\Gamma_7=\Gamma_7+\Gamma_8+2\Gamma_9\ . \tag{3}$$

Including the representation Γ_9 of the A^0 we obtain the term schemes Figs. 6(a) and 6(b) for the (A^0,X_A) and (A^0,X_B) complex, respectively. The term schemes give also the intermediate results obtained by combining only the two holes. The energy sequence and separation of the terms are not available by group theoretical treatment. Together with the dipole selection rules and the Hund's rules, known from molecular physics, the observed polarization of the resonance maxima lead to a plausible term sequence. In the (A^0,X_A) term scheme [Fig. 6(a)] the sequence of the two Γ_7 levels which originate from the $\mu=0$ component of the hole momenta sum, and the two Γ_8 levels due to $\mu=3$, is opposite to the case of molecules. This seems to be a consequence of central cell corrections in the crystal.[12] Moreover, the two Γ_7 states only differ in the orientation of the identical total-momentum component $\mu=\frac{1}{2}$.

The dipole selection rules in CdS (Ref. 1) show that transitions from the crystal ground state into the (A^0,X_A) levels ($\Gamma_7,\Gamma_7,\Gamma_8,\Gamma_8$) are dipole allowed exclusively in the polarization $\vec{E}\perp c$. Transitions into the two Γ_9 levels of the (A^0,X_B) complex are possible with polarization $\vec{E}\|c$. Transitions into the Γ_7 and Γ_8 levels are allowed only in $\vec{E}\perp c$. Concerning the lowest excited electronic states of the complex in which one of the complex particles is in a higher electronic level theoretical treatments are more complicated because of the additional interactions of

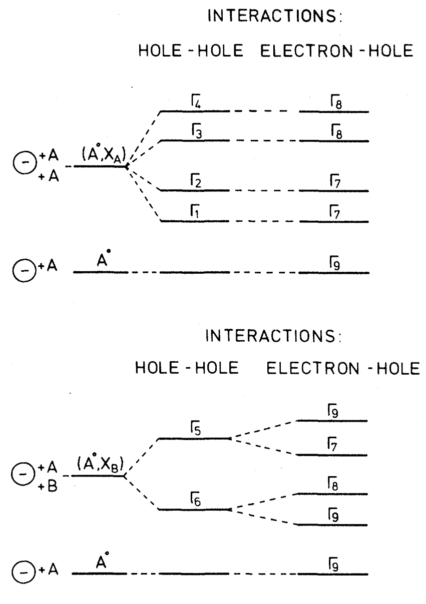

FIG. 6. Term scheme of the (A^0,X) and A^0 electronic ground-state levels taking into account the hole-hole and electron-hole interactions and the crystal-field symmetry C_{6v}^{+} of CdS. The upper scheme gives the splitting of the (A^0,X_A) complex with both holes stemming from the A valence band. The lower scheme shows the (A^0,X_B) complex with one hole stemming from the B valence band.

spins and angular momenta. A manifold splitting is expected to occur but no profound theoretical treatment is known up to now. Taking, for example, an excited level with $1=1$ angular momentum of the electron and therefore of the whole complex the envelope wave function should be P-like. Hence in CdS, the dipole transitions between the P-like acceptor and this excited (A^0,X) complex are parity forbidden because a dipole transition with its odd parity dipole operator between two states with p-like, and therefore odd wave functions, violates parity conservation. The parity selection rule, of course, might not be very strong in an uniaxial crystal like CdS where parity is an applicable but not a very good quantum number.[7] Taking into account the occurrence of the transitions I_1^1 to I_1^6 as emission lines in some selected, probably disturbed crystals, and the respective Raman resonances in undisturbed crystals,[8] the following interpretation of the excitation resonances I_1^1 to I_1^5 can be given:

(1) I_1^1 and I_1^2 are attached to transitions into the upper two Γ_8 levels of the (A^0,X_A) electronic ground state, while the upper Γ_7 level might be situated unresolvably near to the lower Γ_7 state which is the I_1 transition level. The subsequent relaxation from the Γ_8 levels into the lowest Γ_7 ground-state level is followed by the bound exciton recombination emitting an I_1 photon. The Pauli prohibition of the upper Γ_8 levels of the complex ground state is questionable, as has been argued before. Dissimilarities of the hole wave functions might enable the I_1^1 and I_1^2 transitions when high intensities are used for the excitation measurements and the Raman spectra, or when the crystal symmetry is heavily disturbed, e.g., in those samples which show the I_1^1 and I_1^2 emission lines. The theoretical calculations of the hole-hole and electron-hole exchange interactions in an (A^0,X) complex[11,13] indicate that the measurable distances of 2.5 and 3.7 meV of the I_1^1 and the I_1^2 from the I_1, respectively, are relatively large but possible exchange splitting energies of such a complex. This is supported by Zeeman measurements of the I_1^2 emission line.[14] In this measurements the I_1^2 showed a twofold splitting for $\vec{H}\|c$ and $\vec{H}\perp c$ and a fourfold splitting at any other angle between $\vec{H}$ and c. The analysis of these results yielded g-factor values $g_h=2.50$ of the hole belonging to the transition's final state A^0 and $g_e=1.77$ of the initial state (A^0,X) with an S-like wave function. The g value of the initial state is equal to that resulting from the I_1 splitting itself[1] representing the unpaired electron in the (A^0,X) complex. The S-like wave function establishes the affiliated level as an electronic ground-state level of the (A^0,X_A) complex. In terms of the given interpretation it is understandable that the resonances I_1^1 and I_1^2 are not seen below a lower limit of excitation intensity, in contrast to the $I_1 +$ TA maximum (see Fig. 1). The polarization $\vec{E}\perp c$ of the I_1^1 and I_1^2 emission lines[8] and of the excitation resonances reported here is in agreement with the theory, and the identical temperature and intensity dependences of the I_1 emission excited via I_1^1 to I_1^2 suggest that they are due to similar processes. The saturation of I_1 shows that the levels which are assigned to the resonances underly the same limiting factor like the I_1 emission line itself, i.e., the limited number of impurities. The disappearance of the I_1 emission at 30 K excited resonantly via I_1^1 and I_1^2 coincides with the temperature behavior of the I_1 emission under band-to-band excitation. The superlinear increase in the region of higher excitation intensities is due to the fact that the (A^0,X) decay is an induced emission process.[2]

(2) The transitions I_1^3 to I_1^5 are attached to excited electronic states of the (A^0,X_A) for the following reasons: The Zeeman splittings of the emission lines I_1^3 and I_1^4 indicate a P-like nature of the associated (A^0,X) wave functions.[14] Both lines I_1^3 and I_1^4 show a threefold splitting for $\vec{H}\perp c$, a twofold one for $\vec{H}\|c$, and a sixfold splitting for arbitrary other angles. The determined g values for the I_1^3 transition are $g_e=1.74$ for the excited (A^0,X) state due to the unpaired electron, and $g_h=2.62$ for the hole in the final state A^0. The I_1^4 transition yields the values $g_e=1.72$ and $g_h=2.64$. For the excited (A^0,X) levels with a P-like wave function[14] the dipole transitions to the A^0 level are in the first order parity forbidden. This prohibition is lifted by LO phonon participation or by symmetry disturbance or by high excitation intensities leading to an appreciable appearance of quadrupole transitions with equal parity. Temperature and intensity dependences completely agree with those of the excitation resonances I_1^1 and I_1^2. This supports the identification as excited electronic states of the same (A^0,X) complex.

The resonances I_1^2 and I_1^3 coincide fairly with I_1 emission lines obtained after doping CdS crystals with phosphorus.[3,15] An explanation of these two resonances in terms of an exciton bound to a P acceptor, however, seems to be very unlikely. No I_1 emission lines due to P are observable in our crystals. Therefore, it is not understandable that (P^0,X) complexes should strongly enhance the I_1 emission at 2.5356 eV due to excitons bound to a Li or Na acceptor which is observed in our undoped crystals.

The excitation spectra with polarization $\vec{E}\|c$ of the incident light can be interpreted in terms of the same model. The exchange splitting of the (A^0,X_B) complex leads to a couple of levels lying lower in energy with the two hole spins parallel [Γ_9 and Γ_8, see

Fig. 6(b)] and to a couple of levels with antiparallel hole spins and representations Γ_7 and Γ_9. Thomas and Hopfield[1] had shown that the $I_{1B'}$ absorption line due to the (A^0,X_B) complex with antiparallel hole spins is lifetime broadened because of the very fast relaxation of the B hole into an A hole. In the case of the I_{1B} transition the relaxation process is not directly possible because of the Pauli-forbidden spin parallelism in the (A^0,X_A) relaxation final state. Therefore we regard the two broader resonances $I^1_{1B'}$ and $I^2_{1B'}$ as transitions into the two (A^0,X_B) levels Γ_7 and Γ_9 with antiparallel hole spins and the two sharp resonances I^1_{1B} and I^2_{1B} as those into the lower levels Γ_9 and Γ_8 with parallel hole spins followed by the relaxation into the (A^0,X_A) ground state and the exciton's recombination. The narrow resonance I^1_{1B} and the broader resonance $I^2_{1B'}$, both relatively strong, correspond to the known absorption lines I_{1B} and $I_{1B'}$ with polarization $\vec{E}\|c$. The other two weaker resonances I^2_{1B} and $I^1_{1B'}$ are due to transitions into the levels Γ_7 and Γ_8, which are in first order allowed only in $\vec{E}\perp c$. Nevertheless, they occur in the excitation spectra $\vec{E}\|c$ because of the high excitation intensity which allows quadrupole transitions. Thomas and Hopfield[1] reported an absorption line "I_{1B}" in the polarization $\vec{E}\perp c$ shifted 0.3 meV to higher energies compared to the line I_{1B} in $\vec{E}\|c$. In spite of a smaller splitting energy, the trend of their observation is consistent with our results. Investigations of this spectral region in $\vec{E}\perp c$ excitation spectroscopy had no satisfactory results because of the strong absorption of the band edge of the crystals.

B. Vibronic-rotational states

The totally different experimental results concerning the temperature and intensity behavior of the resonances V_i occurring at higher excitation intensities make other explanations indispensable. Because of the decreasing distances of the resonances V_1 to V_7 interference phenomena can be excluded. Moreover, some crystals of different thickness show exactly the same energetic distances of these lines.

Multiphonon participation is excluded because theory of multiphonon TA processes[16] supplies no distinct maxima in a phonon wing. Therefore we investigate possible rotational and vibrational modes of the four-particle complex (A^0,X) by analogy to a diatomic molecule. A direct numerical analogy of the bound-exciton complex to the diatomic molecule cannot be expected since the mass ratios in the (A^0,X) system are more complicated. Further theoretical and experimental results[17] indicate that a mechanical model treatment of the (A^0,X) as an electron moving around an acceptor-hole-hole complex approaches best to the real situation. Therefore a vibration or rotation of the two holes against each other is conceivable. Two ways are practicable to describe a vibration: Firstly, one can use the semiempirical formula of an anharmonic oscillation including fitting parameters determined by the experimental data. The formula is given by[18]

$$\begin{aligned}E(v)=E_0+\hbar\omega_e(v+\tfrac{1}{2})-X_e\hbar\omega_e(v+\tfrac{1}{2})^2\\+Y_e\hbar\omega_e(v+\tfrac{1}{2})^3\\-Z_e\hbar\omega_e(v+\tfrac{1}{2})^4\pm\cdots\,,\end{aligned}\tag{4}$$

with v as vibrational quantum number, ω_e as vibration fundamental frequency, E_0 as pure electronic energy value, and X_e,Y_e,Z_e as fitting parameters. Table III gives the calculated values using $\hbar\omega_e=1.551\times10^{-3}$ eV, $E_0=2.53473$ eV, $X_e=0.1198$, $Y_e=0.01465$, $Z_e=0.000701$. Secondly, especially for molecular systems with rather dif-

TABLE III. I_1 vibronic excitation resonances using $\vec{E}\perp\vec{c}$ polarized incident laser light in comparison with the calculated values. The first two columns give the absolute experimental values of the resonances. ΔE marks the distances of the resonances to the I_1 emission line, δE the mutual distances $V_{i+1}-V_i$. This is valid for the columns showing the theoretical values, too.

Excitation resonance	E (eV) Sample 1	E (eV) Samples 2/3	ΔE (meV) Sample 1	ΔE (meV) Sample 2/3	δE (meV) Sample 1	δE (meV) Sample 2/3	δE (meV) Semiemp. theory vibronic states	δE (meV) Kratzer vibronic states	δE (meV) Kratzer rotational states
$V_0(I_1)$	2.5356	2.5355							
V_1	2.5370	2.5366	1.4	1.1	1.4	1.1	1.25	1.17	1.14
V_2	2.5383	2.5377	2.7	2.2	1.3	1.1	1.05	0.24	0.26
V_3	2.5394	2.5386	3.8	3.1	1.2	0.9	0.94		
V_4	2.5406	2.5395	5.0	4.0	1.2	0.9	0.88		
V_5	2.5418	2.5403	6.2	4.8	1.2	0.8	0.85		
V_6	2.5428	2.5410	7.2	5.5	1.0	0.7	0.84		
V_7		(2.5419)		6.4		(0.9)	0.71		

ferent masses, there exist approximate model potentials including rotational states. One of them which was applied to a similar problem in InP (Ref. 19) is the Kratzer potential.[20] Theory predicts that in moleculelike systems with mass ratios as in the (A^0,X) complex the energy values of rotational modes (quantum number J) and vibrational modes (v) must be of similar order of magnitude,[1] in contrast to molecules of equal parts like H_2. The Kratzer potential which complies with this condition in consequence cannot be distributed in one part giving the vibrational energies and another part due to the rotational energies. An advantage of this model potential is that no fitting parameters are necessary. The formula is given by[20]

$$E(v,J)=E_\infty-\frac{(2ma^2/\hbar^2)D^2}{\{(v+\frac{1}{2})+[(J+\frac{1}{2})^2+(2ma^2/\hbar^2)D]^{1/2}\}^2}\,, \tag{5}$$

with m as the reduced effective mass of the oscillating particles, a as the particle distance, D as the binding energy of the bound exciton, and rotational quantum number J. E_∞ gives the energy of the complex for $v\rightarrow\infty$ and/or $J\rightarrow\infty$. The energy of the I_1 line therefore is $E(I_1)=E(0,0)$. Both models were applied to the resonance structures of the I_1 line. Table III shows the theoretical values compared with the experimental data using $m=0.35m_0$, (m_h from Ref. 1), D=16.4 meV (using the free A exciton energy $E=2.5520$ eV from Ref. 21), $a=9$ Å (Ref. 22), and m_0 as the free-electron mass.

The semiempirical formula gives a good agreement with the experimental values. However, its disadvantage is the application of fitting parameters, which are not well physically established. Possible rotational levels are not included. On the other hand, the Kratzer potential immediately furnishes a result for the distances between the first two energy states, which agrees well with the experimental value. Moreover, Table III shows the similarity of the energy distances using the Kratzer formula for growing vibrational quantum numbers on the one hand and growing rotational quantum numbers on the other hand. Therefore the experimental energy values due to the (A^0,X) complex in principle do not help to decide whether vibrations or rotations are the origin of our resonances. However, for higher states the agreement is not good because the theoretical energy values converge too fast. This might be a consequence of the fact that the Kratzer formula does not take into account the increasing distance between exciton and impurity with growing vibrational or rotational quantum number which one can expect in such a weakly bound system.[18] The temperature-dependent measurements renew the discussion why the excitability of the I_1 via the phonon and vibration processes disappears at about 12 to 15 K. These temperatures are equivalent to energies of about 1.0 to 1.3 meV. These values are equal to the TA phonon and vibrational or rotational level energies. Therefore, at these temperatures the rapid dissipation of the TA phonon energy does not remain. This prevents the strong I_1 emission at higher temperatures when exciting via the vibrational or rotational levels of the (A^0,X) complex. As no resonances are observable with quantum numbers greater than 7, one must assume that the (A^0,X) complex is destroyed as a result of such high vibrational or rotational energies, or the Urbach tail absorption[23] takes away too much excitation intensity.

V. SUMMARY

In performing high-intensity excitation spectroscopy of the I_1 transition of an exciton bound to a neutral acceptor in CdS, we found series of new resonances in both polarizations. In $\vec{E}\perp c$ one group of excitation maxima called I_1^1 to I_1^5 agrees in energy with recently reported emission and LO Raman lines.[8] Beside a resonance $I_1+\text{TA}$, also reported in a previous paper,[9] a series of new resonances V_1 to V_7 appears and increasingly dominates the spectra as the excitation intensity grows. Exciting with light $\vec{E}\parallel c$ we observe two new doublet structures at the energies of the known absorption lines I_{1B} and $I_{1B'}$. The temperature behavior of the I_1 and its disappearance at 30 K by exciting via the resonance states I_1^1 to I_1^5 is in agreement with the results known from emission and absorption experiments. Assuming ground and excited electronic levels of the (A^0,X) complex split off by hole-hole and electron-hole interactions, we developed a theoretical model of the (A^0,X) states. We ascribe I_1^1 and I_1^2 to two Γ_8 electronic ground-state levels of the (A^0,X_A), I_1^3 to I_1^5 to excited electronic states. Both groups of transitions are first-order forbidden but made possible by the high intensities used in our measurements inducing higher-order transitions. The resonances V_1 to V_7 build a regulated orderly series with decreasing energy distances. Taking into account their intensity dependence being different from I_1^1 to I_1^5 and their temperature behavior being similar to the $I_1+\text{TA}$ excitation process with TA phonon buildup we assumed vibration or rotation modes of the complex. The calculation of energy values using molecular analogous models gives a satisfactory agreement with our experimental data.

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