

Exciton Fine Structure via Envelope-Hole Coupling in Cubic ZnSe

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For the first time there is experimental evidence for a distinct fine structure in the exciton spectrum of cubic semiconductors caused by envelope-hole coupling. As an example, we present measurements of the $2P$ exciton in cubic ZnSe by two-photon absorption. The highly resolved threefold energy splitting into $P_{1/2}$, $P_{3/2}$, and $P_{5/2}$ states is explained within a spherical model. We determine the spherical effective-mass parameter μ and give an upper limit for the cubic parameter δ .

Very recently, the complex nature of the exciton structure in cubic semiconductors resulting from the degeneracy and anisotropy of the bands has gained increasing interest.¹⁻³ The exciton spectrum is modified drastically by including the complex valence-band parameters of the hole. This results in a lowering of the hydrogenlike S -excitonic state whereas the P -excitonic states split into a maximum of four components. Although there has been developed the theoretical framework on S - and P -excitonic states in the case of degenerate valence bands,^{1,2} only S excitons have been investigated experimentally so far.⁴

Because of their characteristic behavior P excitons are especially qualified for studying the deviations from the hydrogenic model. In contrast to one-photon experiments the method of two-photon spectroscopy is a powerful tool to observe p -like states since the creation of P excitons is in most cases allowed by two-quantum processes. Hopfield and Worlock⁵ were the first to report on P -exciton contributions to the near-band-edge two-photon absorption spectrum in cubic crystals. Later, two-photon excited P states in cubic and axial crystals have been detected by many others.⁶ But up to now there is no experimental indication for the multiplet structure of exciton P states. From theoretical considerations² the II-VI compound ZnSe is expected to be one of the most favorable substances to observe fine structure. S excitons have been observed in this substance by many one-photon experiments^{7,8} but until now no P excitons could be resolved.

We now report the first measurements of P -excitonic states in cubic ZnSe by two-photon absorption. We want to demonstrate the experimental evidence for the $2P$ -exciton energy splitting. For the experiments we used a Chromatix tunable dye oscillator (rhodamine 6G) pumped by

a Chromatix yttrium aluminum garnet laser (second harmonic of 1.064 μm) and a high-power Q -switched yttrium aluminum garnet laser with a Raman-shifted line at 1.909 μm . Both superimposed collinear laser beams were directed simultaneously into the crystal to induce a two-photon absorption effect. A detailed description of the apparatus has been given in a previous paper.⁹ The spectral resolution is mainly limited by the linewidth of the tunable dye oscillator. We were able to improve the resolution from 0.3 to 0.1 meV which allowed fine tuning of the spectrum.

Figure 1 shows the fine structure of the $2P$ ex-

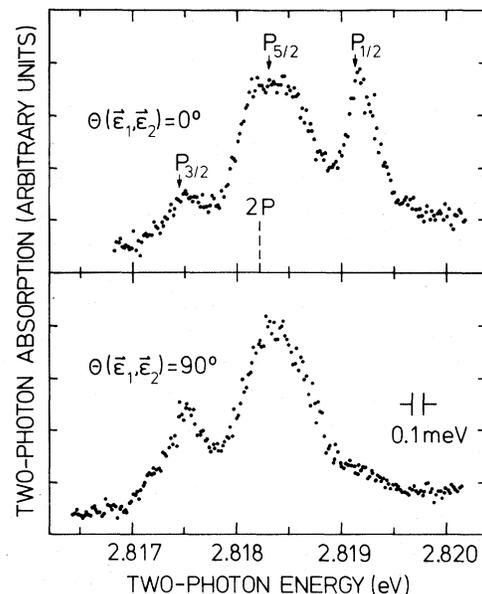


FIG. 1. Two-photon absorption spectrum of the $2P$ -exciton states $P_{1/2}$, $P_{3/2}$, and $P_{5/2}$ in cubic ZnSe (polycrystalline sample) at 1.6 K. The dashed line denotes the unperturbed $2P$ energy level. The polarization vectors $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ refer to the high-power yttrium aluminum garnet laser and the tunable Chromatix laser, respectively. $\Theta(\vec{\epsilon}_1, \vec{\epsilon}_2)$ is the angle between $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$.

citon at low temperature (1.6 K). In the upper curve the polarization vectors $\vec{\epsilon}_1$ and $\vec{\epsilon}_2$ of the two laser beams are chosen parallel to each other, i.e., $\Theta(\vec{\epsilon}_1, \vec{\epsilon}_2) = 0^\circ$. The lower curve was obtained with $\Theta(\vec{\epsilon}_1, \vec{\epsilon}_2) = 90^\circ$. The spectrum consists of three peaks with different line strengths and half-widths. The high-energy peak denoted by $P_{1/2}$ shows a striking polarization dependence. It gains maximum strength for parallel polarization and nearly vanishes for perpendicular polarization of both beams. The $P_{3/2}$ peak shows opposite behavior and the $P_{5/2}$ peak remains nearly unaffected by the change of relative polarization. The dashed line marks the unperturbed $2P$ energy level in the case of nondegenerate valence bands. The experimental results demonstrate that the simple hydrogenic model cannot be applied to the interpretation of these states. The observed energy levels may be well explained by use of the theory of Lipari and Baldereschi² as will be shown in the following.

The exciton Hamiltonian for the relative motion can be written in the form^{1,2}

$$H_{\text{ex}} = H_s + H_d, \quad (1)$$

where the s -like term H_s describes the unperturbed problem with hydrogenlike eigenvalues and the mean value μ_0 of the reduced mass. The d -like term,

$$H_d = H_d(\text{sph}) + H_d(\text{cub}), \quad (2)$$

consists of a spherical and a cubic part¹⁰ represented by the spherical parameter μ and the cubic parameter δ , respectively.² In principle there exists also a p -like H_p term in Eq. (1) if the crystal lacks inversion symmetry. (Cubic ZnSe belongs to the crystallographic point group T_d .) It has been neglected since it yields only a small contribution to the total exciton energy.¹ In most cases the parameter δ is much smaller than μ . Calculations within a two-band model give a rough estimate of $\mu = 0.25$ and $\delta = 0$. This means that the cubic term in Eq. (2) is only generated by higher-band contributions. The H_d term represents a spin-orbit-type interaction because it effects a coupling between the envelope angular momentum \vec{L} and the total hole spin \vec{J} . Thus the exciton states may be described in the LJ -coupling scheme. With use of the notations of the full rotation group, the symmetries of the new P -excitonic states composed of the $D_{3/2}(\Gamma_8)$ valence band and the p -like $D_1(\Gamma_5)$ envelope are classified by

$$D_{3/2} \times D_1 = D_{1/2}(\Gamma_6) + D_{3/2}(\Gamma_8) + D_{5/2}(\Gamma_7 + \Gamma_8).$$

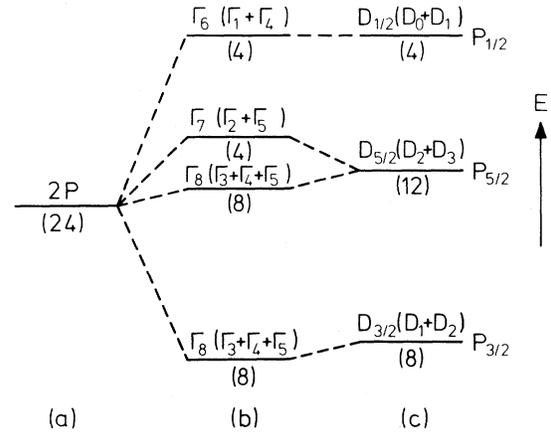


FIG. 2. Energy splitting of P -exciton states by envelope-hole coupling for the unperturbed case ($\mu = 0, \delta = 0$); (b) for the most general case, i.e. with spherical and cubic H_d contributions ($\mu \neq 0, \delta \neq 0$); and (c) for the spherical case ($\mu \neq 0, \delta = 0$). The numbers in parentheses denote the remaining degeneracy of the levels. The irreducible representations given in parentheses refer to the total symmetries of the exciton states including the electron spin of the Γ_6 conduction band.

The equivalent symmetries of the cubic point group T_d are given in parentheses. Figure 2 shows the energy splitting of a P -excitonic state with and without the spherical and cubic H_d contributions. The 24-fold degeneracy of the P exciton is partially lifted. The total symmetries of the exciton states as given in Fig. 2 include the electron spin $\frac{1}{2}$ of the Γ_6 conduction band. It does not cause any additional splitting of the energy levels but only doubles the degeneracy. The fourfold $\Gamma_7 \times \Gamma_6$ and one of the eightfold $\Gamma_8 \times \Gamma_6$ states are degenerate in the spherical limit.

The threefold energy splitting of the $2P$ state (Fig. 1) shows clearly that in a good approximation the excitons may be described in the spherical model. The cubic H_d term in the exciton Hamiltonian makes very small contributions to the exciton energies since it produces only a slight broadening of the $P_{5/2}$ peak. This is explained by assuming *nearly* degenerate Γ_7 and Γ_8 states (see Fig. 2). From the experimental energy splitting we calculate the spherical parameter μ . The broadening of the $P_{5/2}$ line allows us to estimate an upper limit for the cubic parameter δ . Theoretical values and our experimental results are given in Table I. The experimental value of the parameter R_0 of the effective Rydberg energy is taken from the $2P$ - $3P$ energy splitting gained from a two-photon absorption spectrum

TABLE I. Comparison between experimental and theoretical parameters of the H_s and H_d terms. All quantities are defined in the text. For the determination of μ_0/m_0 from R_0 we used $\epsilon_0=8.7$ for the static dielectric constant (see Ref. 6). m_0 is the free electron mass.

ZnSe	R_0 (meV)	μ_0/m_0	μ	δ	Ref.
Theor.	22.43	0.125	0.126	0.055	a
	23.67	0.132	0.339	0.019	b
	16.46	0.092	0.275	0.040	c
Expt.	19.9 ± 0.7	0.111 ± 0.004	0.184 ± 0.006	$\lesssim 0.026$	d

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^dThis work.

which is not shown here. The uncertainty of the given values is mainly caused by the uncertainty of R_0 .

The angular dependence of the two-photon transition probability W_F of an exciton P_F state in the spherical limit is given by¹¹

$$W_F \propto d_0^F A_1(\vec{\epsilon}_1, \vec{\epsilon}_2) + d_1^F T_1(\vec{\epsilon}_1, \vec{\epsilon}_2) + d_2^F [T_2(\vec{\epsilon}_1, \vec{\epsilon}_2) + \frac{4}{3}E(\vec{\epsilon}_1, \vec{\epsilon}_2)]. \quad (3)$$

The coefficients d_i^F denote the different symmetry contributions of the representations D_i . By symmetry arguments it follows that $d_0^{3/2}$, $d_0^{5/2}$, $d_1^{5/2}$, and $d_2^{1/2}$ are equal to zero (Fig. 2). From the observed polarization behavior (Fig. 1) we find $d_2^{3/2} = 0.93d_1^{3/2}$ and $d_1^{1/2} \sim 0.03d_0^{1/2}$. The rather small D_1 contribution of the $P_{1/2}$ state with respect to D_0 is quite obvious because $d_1^{1/2}$ represents the antisymmetrical part of the two-photon operator¹¹ whereas $d_0^{1/2}$ belongs to the symmetrical part. The polarization ratio $W_{5/2}(\Theta=0^\circ)/W_{5/2}(\Theta=90^\circ)$ of the $P_{5/2}$ state is determined by experiment as 1.44 and is in good agreement with the value of 1.33 expected from Eq. (3), thus proving the proper identification of the exciton P_F states. The relative and absolute values of the d_i^F 's cannot be explained solely by the final P -state splitting. The reason is that the hole kinetic energy is nondiagonal (H_d term) which, in contrast to the simple two-band model,¹² leads to spin-dependent two-photon transition matrix elements.¹³

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