Two-photon absorption of P excitons in ZnP_2

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The fine structure of the P excitons in β-ZnP_2 is studied by two-photon absorption. Due to the anisotropy of the crystal a giant energy splitting of the $2P$ exciton states of up to 7 meV is observed. This splitting allows the determination of the reduced masses without an external field. The following values are obtained: $\mu_a = 0.47m_0$, $\mu_b = 0.53m_0$, and $\mu_c = 0.088m_0$.

I. INTRODUCTION

The study of the excitonic structure in semiconductors by linear and nonlinear optical methods is of great interest, since fundamental band parameters can be deduced from these data. In cubic II-VI and III-V semiconductors the simple effective-mass theory has to be modified to include complications due to the degeneracy of the valence bands. As shown by Luttinger and Kohn[1] and by Baldereschi and Lipari,[2] the inclusion of nondiagonal terms in the effective-mass Hamiltonian is of considerable importance for the $J = \frac{3}{2}$ component of the spin-orbit doublet (Γ_8 in cubic crystals). P excitons exhibit a pronounced fine structure due to these nondiagonal terms, which leads to an envelope-hole coupling. This was demonstrated for the P excitons in ZnSe by Sondergeld and Stafford.[3] P excitons in other II-VI and III-V semiconductors were studied by other authors.[4–6] If valence and conduction band results from atomic orbitals of different parity, S excitons are one-photon allowed, whereas P excitons can be detected by two-photon absorption (TPA). In the classic exciton system of Cu_2O it is the other way around, since the valence band (Γ_7^+ symmetry) and the conduction band (Γ_6^+ symmetry) have the same parity. In this case S, D excitons were resolved up to $n = 5$ by TPA.[7] In crystals with lower than cubic symmetry (e.g., wurzite, C_{6v}) there is an additional anisotropy for P excitons, since the P_0 state (P envelope parallel to c axis) is split from the $P_{\pm1}$ states (P envelope perpendicular to c axis). This was indeed observed in AgI by Dinges *et al.*[8] They observed a splitting of about 2 meV between the $2P_0$ and $2P_{\pm1}$ excitons of the A series in AgI. Gerlach and Pollmann[9] have developed a theory for uniaxial crystals by introducing anisotropy parameters. This theory was successfully applied for AgI (Ref. 8) and PbI_2.[10] In the cases treated so far (uniaxial crystals), there was still a degeneracy for the P states perpendicular to the c axis.

In this contribution we report, to our knowledge, the first observation of P excitons in biaxial crystal. We have chosen β-ZnP_2, which has a monoclinic structure with space group symmetry C_{2h}^5. In this structure the b axis is perpendicular to the a and c axes, whereas the angle between the a and c axes is 102.3°.[11] Since S excitons have been observed in reflectivity measurements[12] and are well resolved up to $n = 7$ in one-photon absorption (OPA),[13] we expect that P excitons should be detectable by TPA. Due to the large crystal field anisotropy the P excitons should exhibit a large splitting into three components. We are indeed able to observe P_a, P_b, and P_c excitons with a maximum splitting of $\Delta E = E(2P_c) - E(2P_b) = 7$ meV. Because of the special orientation of the crystals available a magnetic field had to be applied in order to observe the P_a excitons. It will be shown that the detailed analysis of the P exciton spectra yields reliable values for the anisotropic reduced masses.

After a theoretical analysis in Sec. II the experimental setup is described in Sec. III. In Sec. IV we show the experimental results and compare them with the theoretical calculations.

II. THEORY

For the theoretical description it is assumed that the a axis (x) is perpendicular to the b axis (z) and c axis (y), despite the fact that there is an angle of 102.3° between the a axis and the bc plane. Because of the monoclinic structure of ZnP_2, the reduced mass and the dielectric constant are tensors. Thus, for the study of Wannier excitons in ZnP_2 one has to take into account the anisotropy of the crystal. The Hamiltonian of the Wannier exciton in effective-mass approximation is given by[14]

$$H_{ex} = -\frac{\hbar^2}{2}\left(\frac{1}{\mu_x}\frac{\partial^2}{\partial x^2} + \frac{1}{\mu_y}\frac{\partial^2}{\partial y^2} + \frac{1}{\mu_z}\frac{\partial^2}{\partial z^2}\right) - \frac{e^2}{4\pi\epsilon_0\sqrt{\epsilon_y\epsilon_z x^2 + \epsilon_x\epsilon_z y^2 + \epsilon_x\epsilon_y z^2}}. \quad (1)$$

With a transformation from x, y, and z to new coordinates $\xi = (\mu_x/\mu)^{1/2}x$, $\eta = (\mu_y/\mu)^{1/2}y$, and $\zeta = (\mu_z/\mu)^{1/2}z$ the Hamiltonian can be rewritten as

$$H_{ex} = H_0 + H_1, \quad (2)$$

where

$$H_0 = -\frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial\xi^2}+\frac{\partial^2}{\partial\eta^2}+\frac{\partial^2}{\partial\zeta^2}\right) - \frac{e^2}{4\pi\epsilon_0\epsilon\sqrt{\xi^2+\eta^2+\zeta^2}} \tag{3}$$

and

$$H_1 = \frac{e^2}{4\pi\epsilon_0\epsilon}\left(\frac{1}{\sqrt{\xi^2+\eta^2+\zeta^2}} - \frac{1}{\sqrt{A\xi^2+B\eta^2+C\zeta^2}}\right). \tag{4}$$

A, B, and C are the anisotropy parameters

$$A = \frac{\mu}{\mu_x}\frac{\epsilon_y\epsilon_z}{\epsilon^2}\ , \quad B = \frac{\mu}{\mu_y}\frac{\epsilon_z\epsilon_x}{\epsilon^2}\ , \quad C = \frac{\mu}{\mu_z}\frac{\epsilon_x\epsilon_y}{\epsilon^2}. \tag{5}$$

The average dielectric constant ϵ and reduced mass μ are given by

$$\epsilon = (\epsilon_x\epsilon_y\epsilon_z)^{1/3}\ , \quad \frac{1}{\mu} = \frac{\epsilon}{3}\left(\frac{1}{\epsilon_x\mu_x}+\frac{1}{\epsilon_y\mu_y}+\frac{1}{\epsilon_z\mu_z}\right). \tag{6}$$

H_0 is the unperturbed Hamiltonian, which describes the hydrogenlike exciton series with the eigenvalues[15]

$$E_n^{(0)} = -\frac{e^4\mu}{2\,(4\pi\epsilon_0\epsilon)^2\,\hbar^2}\frac{1}{n^2}, \tag{7}$$

where n is the main quantum number. The perturbation H_1 can be written in spherical coordinates

$$H_1 = \frac{e^2}{4\pi\epsilon_0\epsilon r}\left[1-g\,(\varphi,\vartheta)\right], \tag{8}$$

where $g\,(\varphi,\vartheta)$ is given by

$$g\,(\varphi,\vartheta) = \frac{1}{\sqrt{(A\cos^2\varphi + B\sin^2\varphi)\sin^2\vartheta + C\cos^2\vartheta}}. \tag{9}$$

This Hamiltonian does not mix states with different main quantum numbers n. Because of the large anisotropy of the crystal the eigenfunctions of the P excitons are chosen as follows:[16]

$$|\,P_x\rangle = \frac{1}{\sqrt{2}}\left(|\,P_{-1}\rangle - |\,P_1\rangle\right),$$

$$|\,P_y\rangle = \frac{i}{\sqrt{2}}\left(|\,P_{-1}\rangle + |\,P_1\rangle\right), \quad |\,P_z\rangle = |\,P_0\rangle, \tag{10}$$

where $|\,P_0\rangle$ and $|\,P_{\pm1}\rangle$ are the eigenfunctions due to the magnetic quantum numbers $m = 0, \pm1$. For these eigenstates the perturbation is diagonal. The total energy of the P excitons is given by

$$E_{n,i}^{(1)} = (f_i - 1)\,E_n^{(0)} \quad ; \qquad i = \xi,\eta,\zeta, \tag{11}$$

where

$$f_\xi = \frac{3}{4\pi}\int_0^{2\pi}\int_0^{\pi}\sin^3\vartheta\,[1+\cos(2\varphi)]\,g\,(\varphi,\vartheta)\,d\vartheta d\varphi, \tag{12a}$$

$$f_\eta = \frac{3}{4\pi}\int_0^{2\pi}\int_0^{\pi}\sin^3\vartheta\,[1-\cos(2\varphi)]\,g\,(\varphi,\vartheta)\,d\vartheta d\varphi, \tag{12b}$$

$$f_\zeta = \frac{3}{2\pi}\int_0^{2\pi}\int_0^{\pi}\sin\vartheta\cos^2\vartheta\;g\,(\varphi,\vartheta)\,d\vartheta d\varphi. \tag{12c}$$

In an external magnetic field the envelope Zeeman Hamiltonian[5] leads to a mixing of the P exciton states perpendicular to the magnetic field. Thus for $B\|b$ and $B\|c$ the P_a exciton can be observed.

III. EXPERIMENT

The two-photon absorption measurements are performed with a single-mode CO_2 laser (0.117 eV, model PL 4 from Edinburgh Instruments) with a CdTe Pockels cell as a Q switch (repetition rate: 150 Hz) and a Ti:sapphire laser as a tunable light source (model 3900 from spectra physics, pumped by an argon ion laser). The experimental setup is shown in Fig. 1. The CO_2

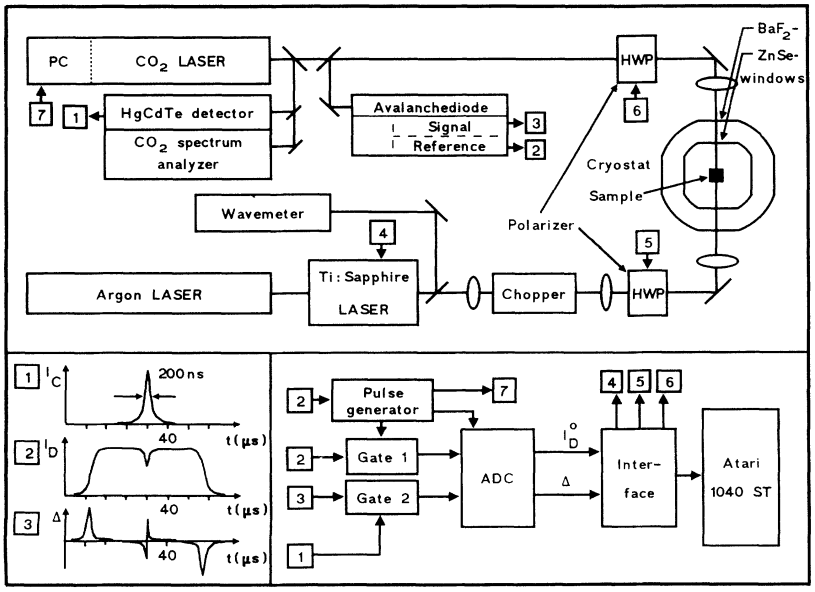

FIG. 1. Schematic diagram of the experimental setup. ADC: analog to digital converter; HWP: half-wave plate; PC: Pockels cell; I_D^0: intensity of the Ti:sapphire laser; I_D: transmitted signal; and Δ: change of the transmitted signal.

laser has a pulse length of 200 ns and a maximum peak power of 2 kW. The polarization directions of the two laser beams are adjustable in the (b,c) plane by half-wave plates. The beam directions of the lasers are antiparallel. The short pulse of the two-photon signal (200 ns) is separated from the long Ti:sapphire-laser pulse (40 μs) by electronic means. The spectral resolution is determined by the bandwidth of the Ti:sapphire laser, which is better than 150 μeV. The absolute wavelength of the Ti:sapphire laser is measured with a wave meter. Single crystals of monoclinic ZnP_2 were grown from the vapor phase.[12] The crystals have optically flat surfaces (bc plane [100]). The beam directions are always perpendicular to the bc plane while the magnetic-field directions are chosen parallel to the b and c axes (Voigt configuration $[k\perp B]$) and perpendicular to the bc plane (Faraday configuration $[k\|B]$). For the measurements in Faraday and Voigt configuration a 7 T split-coil magnet is used. The crystal is immersed in liquid helium.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

In Fig. 2 we show the two-photon absorption spectra for two different CO_2-laser polarizations. The two-photon data can be interpreted in a two-band model,[17] because the energy of the Ti:sapphire laser of about 1.5 eV is very close to a strong $1S$ transition (polarization parallel to the c axis). The CO_2 laser (with a photon energy of about 0.1 eV) induces the transition from the $1S$ exciton to nP excitons. Since the k vectors are perpendicular to the bc plane, nP_b and nP_c excitons are excited by polarization directions of the CO_2 laser parallel to the b and c axes, respectively. In Table I the symmetries of the S and P exciton states and the dipole operator are given for the point group C_{2h}. Only for a Ti:sapphire-laser polarization parallel to the c axis the nP excitons can be excited via the $1S$ exciton of Γ_2^- symmetry (singlet) as an intermediate state. Note that in our experiments the k vector is always perpendicular to the bc plane of the crystal. For the CO_2-laser polarization parallel to the c axis (Γ_2^-) nP_c excitons (Γ_1^+) are allowed, while for a CO_2-laser polarization parallel to the b axis (Γ_1^-) one can only excite nP_b excitons (Γ_2^+) (Fig. 2). Due to the anisotropy of the crystal there is a large splitting between the $2P_b$ and the $2P_c$ exciton state of about 7 meV. The nP_b and nP_c excitons can be observed for n up to 5 and 4, respectively. The parameters $\epsilon_x\mu_x$, $\epsilon_y\mu_y$, and $\epsilon_z\mu_z$ are determined with the use of Eqs. (7)–(12) as a best fit to the experimental results. With the values for the dielectric constants $\epsilon_x = (7.8 \pm 0.2)$, $\epsilon_y = (9.7 \pm 0.2)$, and $\epsilon_z = (10.0 \pm 0.2)$ from Ref. 14, we get $\mu_x = (0.47 \pm 0.03)\, m_0$, $\mu_y = (0.088 \pm 0.005)\, m_0$ and $\mu_z = (0.53 \pm 0.03)\, m_0$.

TABLE I. Irreducible representations of the valence and conduction band, the S and P excitons, the polarization vector, and the product representation of two polarization vectors.

Valence band	Γ_2^-
Conduction band	Γ_1^+
S exciton	$\Gamma_2^- \otimes \Gamma_1^+ \otimes \Gamma_1^+ = \Gamma_2^-$
$P_{a,c}$ exciton	$\Gamma_2^- \otimes \Gamma_1^+ \otimes \Gamma_2^- = \Gamma_1^+$
P_b exciton	$\Gamma_2^- \otimes \Gamma_1^+ \otimes \Gamma_1^- = \Gamma_2^+$
Dipole operator	Γ_2^- ($\|a,c$), Γ_1^- ($\|b$)
Two-photon symmetry	$\Gamma_2^- \otimes \Gamma_2^- = \Gamma_1^+$, $\Gamma_2^- \otimes \Gamma_1^- = \Gamma_2^+$

Our results differ slightly from one-photon measurements of Taguchi *et al.*,[14] who got $\mu_x = (0.39 \pm 0.03)\, m_0$, $\mu_y = (0.15 \pm 0.01)\, m_0$, and $\mu_z = (0.45 \pm 0.03)\, m_0$. The authors derive these values from absorption measurements of the $2S$ exciton in an external magnetic field up to 14 T.

Figure 3 shows the P exciton spectra at 6 T ($B\|c$-axis) for two CO_2-laser polarizations in Voigt configuration. There is a magnetic-field induced admixture of the $2P_b$ exciton to the $2P_a$ exciton, which leads to a new resonance at 1.5912 eV. Its energy position is nearly independent of the magnetic field. This is expected since the Zeeman term is a small perturbation in comparison to the term due to the large anisotropy of the crystal. The diamagnetic shift is also negligible. Besides the exciton states, which can be observed without a magnetic field

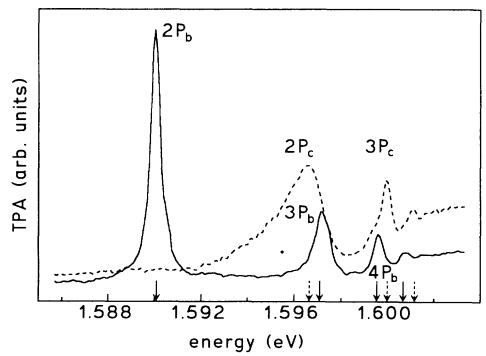

FIG. 2. TPA spectra of β-ZnP_2 at 1.5 K. The k vector is perpendicular to the bc plane. Full and dashed lines refer to the CO_2 laser polarized parallel to the b and c axes, respectively. Full and dashed arrows mark the corresponding theoretical resonances.

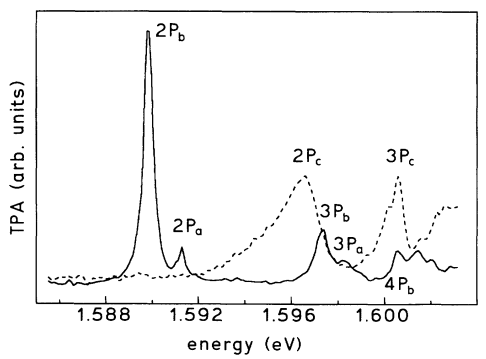

FIG. 3. TPA spectra of β-ZnP_2 at 1.5 K in a magnetic field of 6 T. The k vector is perpendicular to the bc plane. Full and dashed lines refer to the CO_2 laser polarized parallel to the b and c axes, respectively.

(nP_b and nP_c excitons), the energy value of the $2P_a$ exciton is also used to determine the values of the reduced masses.

It would certainly be of great interest to study in detail the behavior of the P excitons in a magnetic field. It is expected that Landau levels can also be observed by TPA for photon energies beyond the band gap. Since the selection rules for Landau transitions are different in TPA as compared to OPA one expects further information on band masses from TPA experiments. For GaAs-$Al_xGa_{1-x}As$ multiple quantum wells it was shown[18] that two-photon spectroscopy of Landau levels allows us to determine conduction and valence band masses separately, whereas from one-photon data one can only deduce the reduced mass. The band masses can be directly determined from two-photon magneto-optical data. The knowledge of the dielectric constants is not necessary. In combination with the TPA measurements of the P excitons, as reported in this paper, one should be able to derive a consistent set of ϵ and μ parameters.

In conclusion we have shown that the method of TPA allows us to determine all components of the P excitons in anisotropic crystals. These data yield reliable values for the reduced masses.

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