Second harmonic generation spectroscopy of excitons in ZnO

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Nonlinear optics of semiconductors is an important field of fundamental and applied research, but surprisingly the role of excitons in the coherent processes leading to harmonics generation has remained essentially unexplored. Here we report results of a comprehensive experimental and theoretical study of the three-photon process of optical second harmonic generation (SHG) involving the exciton resonances of the noncentrosymmetric hexagonal wide-band-gap semiconductor ZnO in the photon energy range of 3.2–3.5 eV. Resonant crystallographic SHG is observed for the 1s(A, B), 2s(A, B), 2p(A, B), and 1s(C) excitons. We show that strong SHG signals at these exciton resonances are induced by the application of a magnetic field when the incident and the SHG light wave vectors are along the crystal z-axis where the crystallographic SHG response vanishes. A microscopic theory of SHG generation through excitons is developed, which shows that the nonlinear interaction of coherent light with excitons has to be considered beyond the electric-dipole approximation. Depending on the particular symmetry of the exciton states SHG can originate from the electric- and magnetic-field-induced perturbations of the excitons due to the Stark effect, the spin as well as orbital Zeeman effects, or the magneto-Stark effect. The importance of each mechanism is analyzed and discussed by confronting experimental data and theoretical results for the dependencies of the SHG signals on photon energy, magnetic field, electric field, crystal temperature, and light polarization. Good agreement is obtained between experiment and theory proving the validity of our approach to the complex problem of nonlinear interaction of light with ZnO excitons. This general approach can be applied also to other semiconductors.

PACS numbers: 71.35.Ji, 42.65.Ky, 78.20.Ls

I. INTRODUCTION

Nonlinear optics has opened multifaceted possibilities for studying and tailoring light-matter interaction. Nowadays nonlinear optical phenomena and materials are a broad basis for fundamental and applied research. In linear optics, propagation, absorption, and emission of light are essentially single-photon processes. In contrast, in nonlinear optics the interaction of light with a medium is governed by multi-photon processes. Obviously the light-matter interaction becomes more intricate thereby. Linear and nonlinear optical experiments address different types of optical susceptibilities, still they all are determined by the features of the crystal structure of the material under study as well as the resulting charge and spin properties. Therefore they open versatile opportunities for in-depth analysis from different perspectives. In this sense, linear and nonlinear optics may be regarded as independent and simultaneously complementary to each other in material investigations.

In nonlinear optics, frequency conversion processes such as second, third, and higher order harmonics generation as well as the sum and difference frequency generation play a particularly important role. Among these phenomena, most prominent is the simplest three-photon process (ω, ω, −2ω) of optical second harmonic generation (SHG): first, the parity selection rules for the optical transitions between the contributing electronic states radically differ from those in linear optics and also from other, more complicated nonlinear phenomena; second, besides the parity selection rules, the time-reversal symmetry operation is a principally important factor in harmonics generation when the spin system becomes involved in applied magnetic fields or in magnetically ordered materials.

From the beginning of nonlinear optics, optical generation of second and higher order harmonics has been subject of active research in various semiconductors. However, the majority of these studies, typically performed on bulk crystals or thin films, were limited to fixed excitation wavelengths when the fundamental and harmonics photon frequencies were in the transparency region, below the fundamental band gap. This approach is motivated by avoiding any absorption in the medium which would impede potential applications. There are only few examples where the SHG spectroscopic studies of semiconductors covered broad spectral ranges. Absolute values of the SHG coefficients for bulk zinc-blende ZnTe, ZnSe, and ZnS were measured at room temperature in the SHG spectral range 1.8–4.8 eV. Spectroscopic SHG in bulk GaAs was reported in the range 2–5 eV, covering several electronic transitions at critical points. The SHG spectral features found for these materials were in reasonable agreement with theoretical calculations and experimental data acquired by other techniques. For hexagonal ZnO, the material selected for the present study, SHG was reported for selected wavelengths below the band gap in numerous publications, see e.g. Further, also spectroscopic SHG studies in the range 2.25–3.44 eV were reported for ZnO micro-
crystallite thin films\textsuperscript{20}. The SHG output was found to increase significantly in the vicinity of the direct band gap. SHG over broad infrared spectral ranges was also applied to various chalcopyrites, semiconductors of practical importance, see e.g.\textsuperscript{21,22} and references therein.

In semiconductors the optical properties in close vicinity of the band gap are largely determined by excitons, bound complexes of an electron and a hole. The exciton energy levels including their spin properties have been intensely studied using both linear and nonlinear optical methods such as absorption, reflection, photoluminescence, two-photon absorption, four-wave mixing, etc.\textsuperscript{9,10} Surprisingly, the contributions of excitons to harmonics generation have remained essentially unexplored. Typically studies lack a microscopic theoretical explanation, with scarce exceptions.\textsuperscript{11–13} Experimental observations were reported for forbidden SHG in resonance with the $2p$ Wannier exciton in ZnSe thin films,\textsuperscript{24–27} resonant SHG at the $1s$ orthoexciton level in Cu$_2$O,\textsuperscript{28} and second and third harmonic spectroscopy of excitons in a homoepitaxial GaN layer.\textsuperscript{29} An early attempt to detect SHG signals in the spectral region of the $C$ exciton in ZnO and the $1s$ excitons in CuCl was undertaken in Refs.\textsuperscript{30–32}. The concept of Wannier excitons was used in the SHG study of CuCl, whereas Frenkel excitons were explored in SHG studies of a C$_60$ molecular crystal\textsuperscript{33–34}.

Detail insight into the role of excitons in harmonics generation can be taken if the studies are performed at low temperatures with high spectral resolution. External magnetic and electric fields can perturb and mix charge and spin states, providing novel mechanisms for nonlinear harmonics generation. For example, in diamagnetic materials GaAs and CdTe the orbital quantization is the origin of magnetic-field-induced SHG.\textsuperscript{35–37} In diluted magnetic semiconductors (Cd,Mn)Te, on the other hand, the giant Zeeman spin splitting was shown to be the source of magnetic-field-induced SHG. Even for the centrosymmetric magnetic semiconductors EuTe and EuSe a magnetic field was found to induce SHG with high efficiency.\textsuperscript{38–40}

This rudimentary state of the exciton SHG problem has motivated our spectroscopic research of SHG as the simplest frequency conversion process in the wide-band-gap semiconductor ZnO, characterized by a large exciton binding energy of 60 meV and a rich exciton level structure.\textsuperscript{41–43} This material has recently gained substantial renewed interest, partly because the large exciton binding energy could lead to lasing by exciton recombination even at room temperature. This and other potential ZnO applications are discussed in the comprehensive review by Ozgür et al.\textsuperscript{44}. In order to get deeper insight, our study of SHG at excitons is performed in applied magnetic and electric fields. In conjunction with a detailed theoretical analysis we show that SHG spectroscopy allows us to work out the underlying microscopic mechanisms of the nonlinear process of simultaneous coherent two-photon excitation and subsequent one-photon emission involving excitons. Magnetic and electric fields can perturb the exciton states through the Stark, the magneto-Stark, and the Zeeman effects and may act therefore as sources of SHG carrying characteristic signatures for the chosen field geometry. Our findings open new opportunities for studying exciton complexes in detail and involving them in frequency conversion processes.

The paper is organized as follows. In Sec. \textsuperscript{2} we describe the crystallographic and electronic structures as well as the optical and magneto-optical properties of hexagonal ZnO. Also a symmetry analysis of the SHG polarization selection rules is given. The details of the experiment are presented in Sec. \textsuperscript{II} followed by Sec. \textsuperscript{IV} where the experimental data are shown. In Sec. \textsuperscript{V} the microscopic theory of the SHG is introduced and several mechanisms involving exciton states are suggested. The comparison of experiment and theory in Sec. \textsuperscript{VII} allows assignment of particular signals in the SHG to a specific mechanism, which to our knowledge has been mission so far. The developed understanding can be applied also to other semiconductor materials.

\section{SECOND HARMONIC GENERATION IN ZnO}

\subsection{Symmetry of electronic states, excitons and polaritons}

ZnO crystallizes preferably in the wurtzite-type structure,\textsuperscript{37,45} see Fig. 1(a), characterized by two interconnected sublattices of Zn$^{2+}$ and O$^{2−}$ ions with a strong ionic binding. The lattice constants of ZnO are $a_0 = 3.2495$ Å and $c_0 = 5.2069$ Å.\textsuperscript{46} The unit cell is formed by two Zn$^{2+}$ and two O$^{2−}$ ions ($Z = 2$) each of them being tetrahedrally surrounded by four ions of the other species. Wurtzite ZnO has a hexagonal crystal lattice, belonging to the point group 6$mm$ and space group $P6_3mc$.\textsuperscript{47} The $z$-direction of the used Cartesian $xyz$-system is chosen parallel to the polar hexagonal [0001]-axis, the so-called $c$-axis, which subsequently will be referred to as $z$-axis following the Birs notation, [0001] $|$ $z$ and [1T00] $|$ $c$. From the optical point of view ZnO is a uniaxial material with the optical axis directed along the crystallographic $z$-axis.

The electronic band structure of wurtzite ZnO is shown in Fig. 1(b). The valence band is formed by the $2p^3$ orbitals of the O$^{2−}$ ions and the conduction band is formed by the 4$s$ orbitals of the Zn$^{2+}$ ions. The $2p$-levels (and the antibonding $sp^3$ orbitals) are split by the hexagonal crystal field into two $Γ_5$ and $Γ_1$ subbands. Including the spin through the spin-orbit interaction leads to a further splitting into three twofold degenerate valence band states ($Γ_1$ $+$ $Γ_3$) $⊕$ $Γ_7 = Γ_5$ $⊕$ $Γ_0$ $⊕$ $Γ_7$. In all wurtzite-type semiconductors these bands are usually labeled from higher to lower energies as $A$ ($Γ_0$), $B$ ($Γ_7$) and $C$ ($Γ_7$) bands. However, ZnO has an inverted valence band ordering $A$ ($Γ_7$), $B$ ($Γ_0$) and $C$ ($Γ_7$).\textsuperscript{48} The selection
rules for transitions from the upper valence bands $A$ ($\Gamma_7$) and $B$ ($\Gamma_9$) to the conduction band ($\Gamma_7$) are essentially the same, because the admixture of the $|z\rangle$ character to the Bloch wave functions of the $A$ ($\Gamma_7$) valence band is small. As a result, these transitions are allowed for $E^\omega \perp z$, where $E^\omega$ is the electric field of the fundamental light wave. Transitions from the $C$ ($\Gamma_7$) valence band to the conduction band ($\Gamma_7$) are allowed for $E^\omega \parallel z$.

Correspondingly, three exciton series are formed in ZnO by a $\Gamma_7$ electron and a hole from one of the $A$ ($\Gamma_7$), $B$ ($\Gamma_9$), or $C$ ($\Gamma_7$) valence bands. These excitons have approximately the same binding energy of $\approx 60$ meV and a Bohr radius of $\approx 1.8$ nm. The exciton symmetry results from the direct product of the envelope function symmetry and the symmetry of conduction and valence band Bloch states, see e.g., Ref. 39. The energies of the resulting exciton states are split by the short-range exchange interaction. For the $s$-symmetry excitons of the $A$ and $B$ series, the strongest state has $\Gamma_5$ symmetry. It is twofold degenerate and polarized perpendicular to the $z$-axis, while for the $C$ exciton it has $\Gamma_1$ symmetry and is polarized parallel to the $z$-axis. As a result, for light propagating along the $z$-axis ($k \parallel z$) both $\Gamma_5$ excitons are transversal, while the $\Gamma_1$ exciton is longitudinal and cannot be excited. For light with $k \perp z$, one of the $\Gamma_5$ exciton states is transverse and the other is longitudinal, while the $\Gamma_1$ exciton is transversal. The resonances of the longitudinal excitons are shifted to higher energies by the long-range exchange interaction.

The strong light-matter interaction in ZnO leads to the formation of exciton-polaritons and their symmetries depend on the direction of the light propagation. The interaction of the transverse excitons with photons leads to the formation of two transverse, lower (LPB) and upper (UPB), polariton branches. Their dispersion relations can be obtained from the condition $\varepsilon_{\perp}^{}(\omega,k) = (\mathbf{k}c/\omega)^2$ for the $\Gamma_5$ excitons and $\varepsilon_{\parallel}^{}(\omega,k) = (\mathbf{k}c/\omega)^2$ for the $\Gamma_1$ excitons. Here $c$ is the speed of light and $\omega$ is the photon frequency. $\varepsilon_{\perp}^{}$ and $\varepsilon_{\parallel}^{}$ are the dielectric functions for the electric field of light polarized perpendicular and parallel to the $z$-axis, respectively, including contributions of exciton resonances with energies close to $\hbar \omega$. The energies of the UPB at $k = 0$ coincide with the energies of the longitudinal excitons determined from $\varepsilon_{\perp}^{}(\omega,k = 0) = 0$, while the energies of the LPB at $k \to \infty$ coincide with the energies of the transversal excitons. If $\mathbf{k}$ is not parallel or perpendicular to the crystal $z$-axis, one obtains the so called mixed-mode polaritons.

**B. Polarization selection rules for SHG**

Wurtzite ZnO belongs to the noncentrosymmetric point group $6mm$ and, consequently, the leading-order SHG is allowed in the electric-dipole (ED) approximation. The crystallographic SHG polarization $P^{2\omega}_{\text{eff}}$ can be written as

$$P^{2\omega}_{\text{eff}} = \epsilon_0 \chi_{ijl}^{\text{cryst}}(\omega, -2\omega) E_j^\omega E_l^\omega,$$

where $i, j, l$ are the Cartesian indices, $\epsilon_0$ is the vacuum permittivity, $\chi_{ijl}^{\text{cryst}}$ is the nonlinear optical susceptibility, $E_j^\omega$ are the components of the fundamental light electric field $E^\omega$. In the ED approximation and in absence of external fields a group theoretical analysis predicts the following nonzero components of the crystallographic nonlinear susceptibility for bulk ZnO

$$\chi_{zzz}^{\text{cryst}} = \chi_{xxz} = \chi_{yyy} = \chi_{xyz} = \chi_{xzy},$$

Note, that Eq. (1) accounts only for the ED contributions on- or off-resonant with electronic band transitions at the fundamental and SHG photon frequencies $\omega$ and $2\omega$. However, more generally the SHG process can involve also electric-quadrupole (EQ) and magnetic-dipole (MD) contributions. They become important when the outgoing SHG is resonant with the exciton energy $E_{\text{exc}}$, for example. Taking into account higher order contributions and the feasibility of a resonance, the incoming fundamental electric field $E^\omega(\mathbf{r}, t) = |E^\omega e^{i[\mathbf{k}\mathbf{r} - \omega t]}|$ generates an effective polarization inside the semiconductor at the double frequency as

$$P^{2\omega}_{\text{eff}}(E_{\text{exc}}) = \epsilon_0 \chi_{ijl}^{\text{cryst}}(E_{\text{exc}}, \mathbf{k}_{\text{exc}}) E_j^\omega E_l^\omega,$$

where the nonlinear optical susceptibility $\chi_{ijl}^{\text{cryst}}(E_{\text{exc}}, \mathbf{k}_{\text{exc}})$ describes the spatial-dispersion phenomena entering in the EQ and MD approximation. $\mathbf{k}_{\text{exc}} = 2n\mathbf{k}$ is the exciton wave vector, $n$ is the refractive index at the fundamental energy $\hbar \omega$, and $\mathbf{k}$ is the wave vector of the incoming light.

Additional information on the exciton energy levels including their spin structure, as well as on their wave functions can be obtained by applying external fields. The symmetries of exciton states may be modified by electric or magnetic fields, enabling mixing of states. This opens the way for novel SHG mechanisms induced by the
fields. In this case, the effective polarization inside the semiconductor can be written as

\[ P_{\text{eff},B,E,i}^{2\omega}(G) = \epsilon_0 \chi_{ijkl}(G, E, B) P_{j\omega}(B) E_{\omega} \],

(3)

where the nonlinear optical susceptibility \( \chi_{ijkl}(G, E, B) \) accounts for phenomena induced by the external magnetic \( B \) and electric \( E \) fields. The nonlinear polarizations in Eqs. (1)-(3) are the sources of the outgoing SHG electric field \( E_{2\omega}(r,t) \propto P_{2\omega} \exp[i(2k_{\omega}r - 2\omega t)] \) with SHG intensity \( I_{2\omega} \propto |P_{2\omega}|^2 \).

For a resonant SHG process, which involves the ground state of the unexcited crystal \( |G\rangle \) and an exciton state \( |\text{exc}\rangle \), the optical transition from \( |G\rangle \) to \( |\text{exc}\rangle \) should be allowed both for the two-photon excitation and the one-photon emission process. Fulfillment of this condition strongly depends on the crystal symmetry and experimental geometry. With including excitonic effects, this situation becomes richer due to the different symmetries of the exciton states with \( s \), \( p \) and \( d \) type of envelope wave functions.

Further, external perturbations such as stress, electric or magnetic field can mix the exciton states, thereby reducing their symmetry. For linear optical spectroscopy on ZnO (e.g. one-photon absorption or emission) only \( s \) exciton states are active, while \( p \) states cannot be seen. In order to study \( p \) exciton states, either nonlinear spectroscopy (e.g. two-photon absorption) or external perturbations, which mix \( s \) and \( p \) states have to be used. To study exciton states and their mixing, we performed detailed experimental and theoretical studies of ZnO, serving as a model system, by SHG spectroscopy with application of magnetic and electric fields.

III. EXPERIMENT

A hydrothermally grown hexagonal ZnO crystal of high optical quality with [0001] orientation and thickness of 500 \( \mu m \) was chosen for this study. The SHG technique used for exciton spectroscopy was described in Ref.[43]. The linearly polarized fundamental light with photon energy \( h\omega \) was provided by a laser system with an optical parametric oscillator tunable in the spectral range of interest \( (h\omega = 1.6-1.75 \text{ eV}) \) and generating optical pulses of 7 ns duration with energies up to 3 mJ per pulse. The experiments were performed in the transmission geometry with the light wave vector \( k \) either parallel or tilted to the \( z \)-axis of the ZnO sample. The SHG signal at photon energies \( 2h\omega \) was spectrally selected by a monochromator and detected by a cooled charge-coupled-device camera. The experimental geometry is shown in Fig. [2]. Here \( \theta \) is the angle between the light wave vector \( k \) and the \( z \)-axis which gives the sample tilting. \( \varphi \) is the azimuthal angle of the fundamental light polarization, where \( \varphi = 0^\circ \) coincides with the crystallographic \( y \)-axis. Magnetic fields \( B \) up to 10 T generated by a split-coil superconducting solenoid were applied in the Voigt geometry \( (B \parallel k) \) or the Faraday geometry \( (B \perp k) \). External electric fields \( E \) up to 550 V/cm were applied via contacts perpendicular both to the magnetic field and the propagation direction of the light \( E \parallel B \perp k \). The sample temperature \( T \) was varied in the range 1.6 – 125 K.

As we will show below in Secs. [V] and Sec. [V] decisive experiments for distinguishing different microscopic contributions to the SHG signal are measurements of the rotational anisotropy, i.e., the dependence of the SHG signal on the azimuthal angle. Such rotational anisotropies were measured for four different geometries:

1. \( I_{\theta B}^{2\omega} \rightarrow E_{2\omega} \parallel E_{\omega} \), fundamental and SHG light polarizations are rotated synchronously such that they are parallel to each other.
2. \( I_{\theta B}^{2\omega} \rightarrow E_{2\omega} \perp E_{\omega} \), fundamental and SHG light polarization are rotated synchronously, such that the SHG light polarization is perpendicular to the fundamental light.
3. \( I_{\varphi B}^{2\omega} \rightarrow E_{2\omega} \parallel B \), SHG light polarization is fixed parallel to the magnetic field direction while the fundamental light polarization is rotated around \( k \).
4. \( I_{\varphi B}^{2\omega} \rightarrow E_{2\omega} \perp B \), SHG light polarization is fixed perpendicular to the magnetic field direction while the fundamental light polarization is turned around \( k \).

The corresponding patterns of rotational anisotropies are modeled according to Eqs. (1-3). The results are discussed in Sec. [VI].

IV. EXPERIMENTAL RESULTS

A. Crystallographic SHG

It follows from the symmetry analysis of the selection rules in Sec. [13] that for laser light propagating along the hexagonal \( z \)-axis \( (k \parallel z) \) no ED crystallographic SHG is allowed. This geometry addresses solely components of the susceptibility without \( z \) index, which are all zero. Indeed, no SHG signals are found experimentally in the
vicinity of the ZnO band gap for zero tilting angle $\theta = 0^\circ$, see Fig. 3(b).

For tilted geometry, $k/z \neq 0$, SHG is provided by the nonzero $\chi^{(2)}$ components with $z$ index, see Eq. (1). For parallel orientation of the linear polarizations of fundamental and SHG light ($E^{2\omega} \parallel E^\omega$), strong SHG signals are found for $\varphi = 90^\circ$ (see Fig. 3). As one can see in Fig. 3(b), the SHG consists of a broad band in the spectral range below the exciton transitions. Further, several sharp lines show up in the exciton spectral range. Above the band gap the SHG signal vanishes. The SHG intensity shows pronounced rotational anisotropies summarized in Fig. 4. These anisotropies allow separation of the SHG signals from two-photon photoluminescence signals which are expected to be isotropic.

The exciton spectral range is shown in more detail in Fig. 3(a). Arrows mark the the reported energies of the different exciton states in hexagonal ZnO25. Letters T and L mark the transversal and longitudinal excitons, respectively. A feature at 3.407 eV has not been reported in literature so far. It will be referred to as the X-line and discussed in more detail in Sec. V. In the tilted geometry, both $s$ and $p$ exciton states are SHG-active. Using linear spectroscopy, only the $1s$ exciton states are observed in absorption and reflection spectra due to their strong oscillator strength. By contrast, the SHG intensity in the range of $1s$ states of $A$ and $B$ excitons is surprisingly much weaker than the intensity of their excited $2s$ and $2p$ states. This observation is a clear manifestation that nonlinear SHG spectroscopy addresses exciton properties inaccessible by linear spectroscopy.

Rotational anisotropy diagrams were measured for $E^{2\omega} \parallel E^\omega$ and $E^{2\omega} \perp E^\omega$ at the following spectral positions: 3.361, 3.379, 3.391, 3.400, 3.407, 3.413, 3.425, 3.430, 3.434, and 3.444 eV. Those anisotropies in Figs. 4(a) and 4(c) are representative for the off-resonant and $A, B$ exciton regions. Figs. 4(b) and 4(d) show rotational anisotropies specific for energies close to the $X$-line and the $1s_L(C)$ exciton. The strongest signal for $E^{2\omega} \parallel E^\omega$ is found for all energies in the $(yz)$-plane meaning that the shape is dominated by the $\chi^{(2)}$ component. Indeed, the fitting procedure gives an $\chi^{(2)}$ value which is an order of magnitude larger than the other components. For the crossed geometry $E^{2\omega} \perp E^\omega$, the fitting procedure gives the same ratio of nonlinear components. On the other hand, for energies close to the $1s_L(C)$ exciton and the $X$-line in Figs. 4(b) and 4(d), the SHG intensity $I^\perp_{2\omega}$ has a pronounced feature along the $y$-axis, which can be explained by a phase shift. The real and imagi-

![FIG. 3. (color online) Crystallographic SHG spectra of ZnO for $E^{2\omega} \parallel E^\omega$ and $\varphi = 90^\circ$ (compare with anisotropies in Fig. 4), measured at $T = 1.6$ K. (a) Close-up of the exciton spectral range 3.37 – 3.44 eV for $\theta = 49^\circ$. (b) Extended spectral range 3.2 – 3.5 eV for $\theta = 49^\circ$ and $0^\circ$. SHG signals vanish for $k \parallel z (\theta = 0^\circ)$.](image)

![FIG. 4. (color online) Angular dependencies of the crystallographic SHG measured at $\theta = 49^\circ$ for different energies. Filled (blue) and open (red) circles represent the geometries $E^{2\omega} \parallel E^\omega$ and $E^{2\omega} \perp E^\omega$, respectively. Lines and shaded areas show best fits according to Eq. (1). (a) Off-resonant signal at $2\hbar\omega = 3.361$ eV. (b) Unidentified $X$-line at $2\hbar\omega = 3.407$ eV. Signal is scaled down by a factor of 2. (c) $2p(\Pi)$ exciton line at $2\hbar\omega = 3.425$ eV. Signal is scaled up by a factor of 1.5. (d) $1s_L(C)$ exciton line at $2\hbar\omega = 3.434$ eV.](image)
nary parts of the nonlinear components change signs in these specific regions, leading to a strong distortion in the crossed geometry $\mathbf{E}^{2\omega} \perp \mathbf{E}^\omega$.

We note, that our experiments do not allow us to measure the absolute values of the nonlinear susceptibilities. Therefore, it is difficult to compare the relative nonlinearities for SHG signals which are widely separated on the photon energy scale. To measure the absolute values of the nonlinear susceptibilities one has to take into account the complex linear refraction indices for both the fundamental and the SHG photon energies.\(^\text{29}\) We also note, that the expected quadratic increase of the SHG intensity with the fundamental power has been confirmed for the off-resonant and on-resonant crystallographic SHG signals, as well as for the magnetic-field-induced SHG signals, described in the next subsection.

### B. Magnetic-field-induced SHG

For investigating magnetic-field-induced SHG (MFISH) we chose the experimental geometry with $\theta = 0^\circ$, where the crystallographic SHG signal vanishes. A magnetic field $B = 5$ T was applied perpendicular to the $z$-axis in the geometry $\mathbf{B} \perp \mathbf{k} \parallel z$. SHG signals are observed only in resonance with excitons, see Fig. 4. Two strong lines are seen in the spectral range of the $2s/2p(A,B)$ exciton states and three much weaker lines in the range of the $1s(A,B)$ excitons. Note, that this behavior differs from the observations in GaAs and CdTe, where the $1s$ exciton line always dominates in the MFISH spectrum.\(^\text{12,13}\) In ZnO, the weak SHG intensity observed at the $1s(A,B)$ excitons can be related to the strong absorption of SHG light due to the large absolute values of the complex dielectric function.\(^\text{33}\)

A magnetic field is an axial vector of even parity and, therefore, it is not supposed to mix wave functions of opposite parities. In spite of this restriction, a strong magnetic-field-induced contribution to SHG was found in ZnO. An in-depth analysis of the SHG microscopic mechanisms is required for understanding these experimental findings. Such analysis based on the theoretical model of Sec. \( \text{V} \) will be given in Sec. \( \text{VI} \).

#### 1. SHG on $1s(A,B)$ excitons

Let us consider the experimental observations in the $1s$ exciton region in magnetic field more thoroughly. The corresponding SHG spectra for different fields up to 10 T are shown in Fig. 6(a). Three lines corresponding to the $1s(A)$ paraexciton, the $1s(A,B)$ middle polariton branch,\(^\text{40}\) and the $1s(B)$ paraexciton are clearly seen at the strongest field with the first line at 3.3754 eV being the most intense. The integrated intensity of the $1s(A,\Gamma_{1,2})$ line shows a $B^2$ dependence, see Fig. 7(a). Its temperature dependence measured at $B = 7$ T shows a rapid decrease; see Fig. 14(a). For excitons with strong binding energies it is expected that the diamagnetic shift of their $1s$ states for the magnetic field strengths used here is very small, as illustrated in Fig. 6(b).

Figure 6(c) shows the rotational anisotropies of the SHG intensities in a magnetic field of 5 T for the parallel $\mathbf{E}^{2\omega} \parallel \mathbf{E}^\omega$ and the perpendicular $\mathbf{E}^{2\omega} \perp \mathbf{E}^\omega$ detection geometries. The rotational anisotropies show twofold symmetry patterns, have the same amplitudes and are rotated relative to each other by 90°, where the strongest signal is found for $\varphi = 0^\circ$ in the parallel geometry. These patterns clearly differ from the crystallographic ones in Fig. 7 highlighting the difference of involved SHG mechanisms. The fits are done according to Eqs. (9) and (11) in Sec. \( \text{V} \).

#### 2. SHG at $2s/2p(A,B)$ excitons

Figure 8(a) shows the magnetic-field-induced SHG spectra at the $2s/2p(A,B)$ exciton photon energies. A double peak structure with lines at 3.425 and 3.431 eV appears with increasing magnetic field, corresponding to the energies of the $2p(A,B)$ excitons.\(^\text{47,48}\) In strong magnetic fields exceeding 7 T the doublet structure splits further into at least four peaks. In fact, more states can be distinguished in high magnetic fields when the signals in different polarization geometries are analyzed, see Fig. 8(b). The energy shifts of these lines are plotted as a fan chart diagram in Fig. 9 where the SHG peak intensities are represented by the symbol sizes.

The magnetic field dependence of the integrated SHG intensity of the $2s/2p$ states shows a quadratic increase.
FIG. 6. (color online) (a) Magnetic-field-induced SHG spectra in the range of the $1s(A, B)$ excitons in ZnO. (b) Magnetic field dependence of the peak energy of the SHG exciton lines from panel (a), dashed lines are calculated after Eq. (28). (c) Rotational anisotropy of SHG intensity measured for the strongest line at $B = 5$ T, detected for synchronous rotation of the linear polarizers for fundamental and SHG light: blue filled circles for $E^{2\omega} \parallel E^\omega$ and red open circles for $E^{2\omega} \perp E^\omega$. Black lines give best fits after Eqs. (9) and (11).

FIG. 7. (color online) (a) Integrated SHG intensity for the strongest $1s$ line at $2\omega = 3.3754$ eV [compare Fig. 6(a)] as function of magnetic field (symbols). Line is the best fit with $I_{2\omega} \propto B^2$. (b) Integrated SHG intensity in the spectral range of the $2s/2p(A, B)$ excitons at $2\omega = 3.420 - 3.439$ eV (compare Fig. 8 as function of magnetic field (symbols)). Line gives model calculation for $2\omega = 3.4254$ eV (the energy of the strongest peak in the SHG spectra) and $\Gamma = 1.2$ meV.

at low fields $B < 6$ T, similar to the $1s$ exciton, and then tends to saturate for $B > 6$ T, see Fig. 7(b). This behavior, which was not observed for the $1s$ states, gives a strong hint that the mechanisms responsible for the magnetic-field-induced SHG differ for the $1s$ and the $2s/2p$ excitons in ZnO. The temperature dependence of the $2s/2p$ SHG intensity in Fig. 14(a) shows a similar but slightly faster decrease than that of the $1s$ excitons.

SHG rotational anisotropies detected in different geometries at $B = 10$ T for the $2s/2p(A, B)$ states are shown in Figs. 10 and 11. They have different patterns depending on the exciton state involved, see, e.g., Figs. 10(b) and 11(c). The anisotropies differ strongly in the amplitude ratios for different geometries. In the perpendicular geometry $E^{2\omega} \perp E^\omega$ the shapes are quite different, compare Figs. 11(b) and 11(f), leading to the assumption that the responsible SHG mechanisms are different and vary with the photon energy.
FIG. 9. (color online) Fan chart diagram for the magnetic field dependencies of the 2s and 2p excited state energies of the A and B excitons. Symbols are experimental data with their size scaled by the observed peak intensity. Black and red circles are observed in the geometries $E^{2\omega} \parallel E^s \perp B$ and $E^{2\omega} \parallel B$ with $\varphi(E^s) = 45^\circ$, respectively. Solid lines give the energies of the coupled $2s/2p_{x}/2p_{y}$ and the $2p_z$ states according to the calculations in Sec. VII and after Eq. (30). Labels at low fields indicate the zero field exciton energies, while labels at high fields give the dominant component in the mixed exciton wave functions.

FIG. 10. Angular dependencies of the magnetic-field-induced SHG intensity at 3.424 eV for different energies at $B = 10$ T. Open circles represent measured data and lines show best fits following Eqs. (6)-(11). (a) $E^{2\omega} \parallel E^s$; fit according to Eq. (7); (b) $E^{2\omega} \perp E^s$; fit according to $I^{2\omega} \propto \left[ a \sin \varphi + b \sin \varphi \cos^2 \varphi \right]^2$ with $a/b = 1/2$; $a$ and $b$ represent the spin Zeeman contributions of 's-' and 'p'-type excitons, respectively, see Figs. 16(b) and 16(j). The ratio $I^{2\omega}_{s}/I^{2\omega}_{p}$ indicates the dominance of the magneto-Stark contribution compared to the spin Zeeman contribution. (a, b) $2\hbar \omega = 3.429$ eV; $I^{2\omega}_{s}/I^{2\omega}_{p} \approx 14/1$; $I^{2\omega}_{p}$ with $a/b = 1/1$. (c, d) $2\hbar \omega = 3.427$ eV; $I^{2\omega}_{s}/I^{2\omega}_{p} \approx 40/1$; $I^{2\omega}_{p}$ with $a/b = 3/4$. (e, f) $2\hbar \omega = 3.432$ eV; $I^{2\omega}_{s}/I^{2\omega}_{p} \approx 3/1$; $I^{2\omega}_{p}$ with $a/b = 2/1$.

3. Magnetic-field-induced versus crystallographic SHG

It is instructive to compare the intensities of the crystallographic and the magnetic-field-induced SHG signals. This comparison is presented in Fig. 12 where all four panels, recorded with the tilting angle $\theta \approx 45^\circ$, have the same intensity scale. In absence of magnetic field the strongest crystallographic SHG signal is found for $E^{2\omega} \parallel E^s$ and $\varphi(E^s) = 90^\circ$, while it vanishes for $E^{2\omega} \parallel E^s$ and $\varphi(E^s) = 0^\circ$; see Fig. 12(c). Fig. 12(a) demonstrates, that even for a tilted sample no signal is observed for $E^{2\omega} \parallel E^s$, $\varphi(E^s) = 90^\circ$, but in magnetic field strong signals appear for this configuration, see Figs. 10(a) and 10(b). Thus, for a tilted sample Fig. 12(b) shows the intensity of a pure MFISH signal for the $2s/2p(A, B)$ states, which is even more intense than the strongest crystallographic signal $I^{2\omega}_{s}$ in Fig. 12(c) ob-
FIG. 12. (color online) Crystallographic and magnetic-field-induced SHG in the spectral range of the 2s/2p(A, B) and 1sΓ(C) excitons measured for the tilted geometry with θ ≈ 45°. T = 1.6 K. (a) There is no crystallographic contribution to I\(2\omega\parallel E\) for \(E = 0^\circ\). (b) Pure magnetic-field-induced SHG signals at \(B = 4 T\) for \(I_{2\omega\perp}^\parallel\) and \(E = 0^\circ\) contributed by the 2s/2p(A, B) excitons. (c) and (d) \(I_{2\omega\perp}^\parallel\) for the 1sΓ(C) exciton does not change significantly from \(B = 0\) to 4 T.

served for the 1sΓ(C) with \(E_{2\omega\perp}^\parallel\) and \(E = 0^\circ\), see Fig. 4c. Consequently, we can conclude that the susceptibilities of MFISH and crystallographic SHG have comparable values. On the other hand, the 1sΓ(C) state is not strongly modified by the MFISH contributions, compare amplitudes in Figs. 12c and 12d.

C. Temperature dependence

Figure 13 compares the crystallographic SHG intensities \(I_{2\omega\parallel}^\parallel\) recorded at 1.6 K and 128 K. While the off-resonant contribution has comparable intensity, the exciton SHG signals strongly decrease with rising temperature. A closer look at the detailed evolutions of the peak intensities shows that all 1s state and the X-line intensities decrease slower with temperature than the 2p\(_{x,y}(A)\) states, compare the results shown in Fig. 14a. At the same time, the full width at half maximum (FWHM) of the 2p\(_{x,y}(A)\) line increases much faster than those of the 1sΓ(C) state and the X-line, see Fig. 14b. The magnetic field influences the temperature dependence only slightly: the magnetic-field-induced signals show a similar behavior as the crystallographic ones; the closed and open dots in Figure 14a give the temperature dependencies for zero field and \(B = 7 T\), respectively. We conclude that the signal decays are rather independent of the SHG generating mechanism. An explanation based on our theoretical model will be discussed in Sec. VI.

D. Joint action of magnetic and electric field

An applied electric field modifies the wave functions of the exciton states and, therefore, offers another promising option for SHG spectroscopy. The electric field is a polar vector of odd parity, in contrast to the even parity magnetic field, so that it can mix exciton wave functions of opposite parity.

The two spectra in Fig. 15b demonstrate the ef-
FIG. 15. (color online) (a) SHG spectra in the range of the 2s/2p(A, B) excitons in ZnO subject to magnetic field and combined electric and magnetic fields. An applied electric field of $E = \pm 550$ V/cm corresponds inside the crystal to the field $E/\epsilon^*$, where $\epsilon^* = 7.40$ is the static dielectric permittivity perpendicular to the hexagonal $z$-axis. Inset shows integrated intensity in the spectral range 3.417–3.438 eV as function of electric field for $B = +1$ and $-1$ T. Symbols are experimental data and lines give best fits according to $I^2 \propto (\pm B + \gamma E)^2$ with $\gamma = 2.5 \times 10^{-4}$. (b) SHG spectra without applied magnetic field. Black line shows residual crystallographic signal due to slight sample misalignment. Red line demonstrates electric field effect [intensity is increased by a factor of 4 compared to (a)]. (c) Measured resistivity of the sample at $B = 0$ T showing a strong drop by about three orders of magnitude when 2$\omega$ becomes close to that of the 2$p_{x,y}$ excitons. Inset shows a close-up ($\times 100$) of this region.

The effect of an applied electric field on SHG spectra for the 2s/2p($A, B$) excitons in ZnO at zero magnetic field. In the absence of electric field the residual SHG amplitude (about 1% of those previously discussed) originates from small strain caused by the sample holder with electrical contacts. Application of an electric field perpendicular to the $z$-axis $E \perp k \parallel z$ leads to an increase in the SHG signal. The electric field effect is much more pronounced in combination with an applied magnetic field $E \perp B$, see Fig. 15(a). Here the SHG amplitude is initially gained by applying a magnetic field of $+1$ T and then tuned by adding an electric field of $\pm 550$ V/cm. The SHG signal increases for positive electric fields and decreases for negative fields. The rotational anisotropies of these signals are not changed by the electric field. The variation of the integral SHG intensity with electric field strength is shown in the inset of Fig. 15(a). Such a behavior, that a weak effect (here induced by the electric field) is enhanced when combined with a stronger effect (by the magnetic field) is known in SHG spectroscopy when these effects interfere with each other, see e.g. Eq. (3) in Ref. [33].

Resistivity measurements have shown, that the incident laser beam reduces the sample resistivity enormously (by several orders of magnitude), when twice the fundamental photon energy $2\omega$ comes close to that of the 2$p$ exciton states, see Fig. 15(c). The resistivity is not instantaneously restored when the laser is switched off.

V. THEORY OF SHG AT EXCITON RESONANCES

A. General consideration

Theoretical studies of SHG were performed for many model semiconductors, see for example [39–40]. These publications analyze the generation of the second and higher harmonics by band theory or first-principle calculations, while exciton contributions have remained essentially unexplored. The complex experimentally observed exciton SHG signals for ZnO in external fields as reported here demands development of a corresponding microscopic theory.

In this section we focus on SHG effects in resonance with exciton states. This requires the analysis of the wave function symmetries for different exciton states and their modifications in external magnetic and electric fields. We present a theoretical analysis for the excitons in ZnO with wurtzite-type crystal structure. The developed theoretical approach, however, can be readily applied to other semiconductors. In particular, most of the suggested mechanisms of magnetic- and electric-field-induced SHG at the exciton resonances should prevail also in other materials.

To analyze SHG in close vicinity of an exciton resonance we write the nonlinear optical susceptibilities $\chi_{ijl}(\epsilon_{\text{exc}}, \mathbf{k}_{\text{exc}}, \mathbf{B}, \mathbf{E})$ introduced in Eq. (3) for each exciton energy $\epsilon_{\text{exc}} = 2\omega$ in general form as...
\[ \chi_{ij}(\mathbf{E}_{\text{exc}}, \mathbf{k}_{\text{exc}}, \mathbf{B}, E) \sim \sum_{\nu} \frac{\langle G | \tilde{V}_{\nu}^{2w} | \psi_{\text{exc}} \rangle \langle \psi_{\text{exc}} | \tilde{V}_{\nu}^{\omega} | \varphi \rangle \langle \varphi | \tilde{V}_{\nu}^{\omega} | G \rangle}{(\mathbf{E}_{\text{exc}} - 2\hbar \omega - i\Gamma_{\text{exc}})(\mathbf{E}_{\nu} - \hbar \omega)} \approx \frac{i}{\Gamma_{\text{exc}}} \langle G | \tilde{V}_{\nu}^{2w} | \psi_{\text{exc}} \rangle M_{\text{exc},G}^{2\text{ph}}. \quad (4) \]

Here \( |G\) denotes the unperturbed ground state with zero energy, \( |\varphi\rangle \) describes intermediate virtual states, \( |\psi_{\text{exc}}\rangle \) describes the exciton state, and \( \Gamma_{\text{exc}} \) is the exciton damping constant. The summation in Eq. (4) is carried out over all intermediate states satisfying the symmetry selection rules for the two-photon transition from the ground to the exciton state described by the matrix element \( M_{\text{exc},G}^{2\text{ph}} \).

To account for the effects of the external electric and magnetic fields we consider the geometry where the crystallographic SHG signals are suppressed, namely \( \mathbf{k}_{\text{exc}} \parallel \mathbf{z} \), \( \mathbf{B} \parallel \mathbf{x} \), and \( \mathbf{E} \parallel \mathbf{y} \). In this case the incoming field is described by \( \mathbf{E}^{\omega} = (E_x^{\omega}, E_y^{\omega}) \), so that the outgoing polarization can be written as \( \mathbf{P}_{\text{eff}}^{2w} = (P_{\text{eff},x}^{2w}, P_{\text{eff},y}^{2w}, 0) \).

The perturbation caused by the photon field \( \mathbf{E}^{\omega}(\mathbf{r}, t) \) is described by \( (ie/m_0\omega)\langle \mathbf{E}^{\omega}(\mathbf{r}, t) | \hat{\mathbf{p}} \rangle \), where \( e \) and \( m_0 \) are the charge and mass of free electron and \( \hat{\mathbf{p}} \) is the momentum operator. Then the perturbation \( \tilde{V}_{\nu}^{\omega}(\mathbf{r}) \) is given by

\[ \tilde{V}_{\nu}^{\omega}(\mathbf{r}) = \frac{ie}{m_0\omega} \hat{p}_x(\mathbf{r}) \exp(ik_z r_z) \approx \frac{ie}{m_0\omega} \hat{p}_x(\mathbf{r})(1 + ik_z r_z + \ldots) \]

where \( \hat{p}_x(\mathbf{r}) \) are the projections of the momentum operator \( \hat{\mathbf{p}} \) on the light polarization components, \( x \) or \( y \), respectively. For \( \tilde{V}_{\nu}^{\omega}(\mathbf{r}) \) one should substitute \( k_z \) by \( 2k_z \) in Eq. (5) and everywhere below, as well as \( \omega \) by \( 2\omega \). We are interested in the lowest order effects in \( k_z \), that is zero-order independent of \( k_z \), if it exists, or first-order, linear in \( k_z \). Therefore, we keep only two terms in the expansion of \( \exp(ik_z r_z) \) = \( 1 + ik_z r_z \) and consider the matrix elements of the form \( \tilde{V}_{\nu}^{\omega}(\mathbf{r}) = \tilde{D}_{\nu}^{\omega}(\mathbf{r}) + \tilde{Q}_{\nu}^{\omega}(\mathbf{r}) \).

The first term \( \tilde{D}_{\nu}^{\omega}(\mathbf{r}) = (ie/m_0\omega)\hat{p}_x(\mathbf{r}) \) corresponds to the electric-dipole (ED) approximation for which the matrix elements can be replaced by the matrix elements of the dipole operator \( e r z(\mathbf{r})/\hbar \). The operator \( \tilde{Q}_{\nu}^{\omega}(\mathbf{r}) = -(ek_z/m_0\omega)\hat{p}_x(\mathbf{r}) \) includes the electric-quadrupole (EQ) and the magnetic-dipole (MD) contributions where the matrix elements can be replaced by the sum of matrix elements of the electric-quadrupole operator \( Q_{\nu}^{\omega,q}(\mathbf{r}) = -(i e k_z/2m_0\omega)\hat{L}_y(\mathbf{r}) \) and the magnetic-dipole operator \( Q_{\nu}^{\omega,m}(\mathbf{r}) = \pm(e k_z/2m_0\omega)\hat{L}_y(\mathbf{r}) \). Here \( \hat{L} \) is the orbital momentum operator. Depending on the perturbation \( \tilde{V}^{\omega} \) and \( \tilde{V}^{2w} \) involved in the two-photon absorption and one-photon emission, respectively, we denote the resulting three-photon SHG process as \( X^{2w}Y^{\omega}Z^{\omega} \), where the \( X, Y, Z \) are either \( D \) (ED) or \( Q \) (EQ+MD). We emphasize, that the presence of EQ or MD transition for one of the steps either excitation or emission, leads to a linear dependence of the susceptibility on \( k_z \).

In ZnO, the direct ED transitions between the valence and conduction band states are allowed. The strongest one-photon process for \( K \parallel z \) are the excitation of the \((s \times \Gamma_5)\) states or the emission from them. The respective matrix elements can be written as \( D^{\omega,a} \) or \( D^{2\omega,a} \) where the index \( a \) denotes "allowed" transition within the ED approximation according to the notation of Elizalde. In contrast, the one-photon ED "forbidden" transitions to the 2p excitons in noncentrosymmetric wurtzite semiconductors like ZnO may occur because the valence and conduction band states do not have pure even or odd parities. These transitions are much weaker compared to the \( s \) exciton transitions and can be described by the matrix elements \( D^{\omega,f} \) or \( D^{2\omega,f} \), where the index \( f \) denotes the "forbidden" character within the ED approximation. The used geometry such "forbidden" transitions are possible only for the 2px, 2py states, and not for the 2pz state. Alternatively, the one-photon emission from all three 2px, 2py, and 2pz states may occur due to magnetic-dipole transitions described by the matrix element \( Q^{\omega,m} \).

The strongest two-photon process in ZnO is the excitation of the 2p exciton states. It is ED allowed, exploiting intermediate virtual states in the valence or conduction band. Such process involves a transition between valence and conduction band states and another transition between \( s \) and \( p \) envelopes in the same energy band. The relevant two-photon matrix element is \( M_{2\text{ph},G}^{2\text{ph}} \propto D^{\omega,a}D^{\omega,f} \). On the other hand, the direct two-photon absorption by the \( s \) exciton states in noncentrosymmetric semiconductors may occur within the ED approximation via the intermediate virtual states in remote band. In this case the two-photon matrix element is \( M_{s,G}^{2\text{ph}} \propto D^{\omega,a}D^{\omega,a} \). However, such processes are much weaker than those for the 2p excitons. Alternatively, the \( s \) states can be excited in the two-photon process when the first transition is a MD transition (or ED transition of "forbidden" character) to the \( 2px,py \) states and the second one is a ED transition of "forbidden" character between the \( s \) and \( p \) envelopes. In this case the two-photon matrix element is \( M_{s,G}^{2\text{ph}} \propto D^{\omega,f}Q^{\omega,m} \) or \( M_{s,G}^{2\text{ph}} \propto D^{\omega,a}D^{\omega,f} \).

Important information on the symmetry of the exciton states involved in the SHG process is provided by the SHG rotational anisotropies. According to Eq. (3) the SHG intensity is given by

\[ I_{\perp B}^{2w} \propto |\chi_{yzy} \cos^2 \varphi + \chi_{yxz} \sin^2 \varphi|^2, \quad (6) \]

if \( E^{2w} \perp B \), and by

\[ I_{|| B}^{2w} \propto |\chi_{xxy} \sin(2\varphi)|^2, \quad (7) \]

for the \( E^{2w} || B \) geometry. Here \( \varphi \) is the angle between \( E^{\omega} \) and the \( y \)-axis. Note that \( B \perp y \). For parallel polarization
\( \mathbf{E}_{2\omega} \parallel \mathbf{E}^\omega \) one obtains

\[ I_{||}^{2\omega} \propto \cos^2 \varphi |\chi_{yxy} \cos^2 \varphi + (\chi_{yzz} + 2\chi_{xxy}) \sin^2 \varphi|^2. \quad (8) \]

In a hexagonal 6\,mmm crystal the relation \( \chi_{yxy} = \chi_{yzz} + 2\chi_{xxy} \) is fulfilled\(^\text{[23]}\) so that

\[ I_{||}^{2\omega} \propto |\chi_{yxy} \cos \varphi|^2. \quad (9) \]

For perpendicular polarization \( \mathbf{E}_{2\omega} \perp \mathbf{E}^\omega \) one finds

\[ I_{\perp}^{2\omega} \propto \sin^2 \varphi |(\chi_{yxy} - 2\chi_{xxy}) \cos^2 \varphi + \chi_{yzz} \sin^2 \varphi|^2, \quad (10) \]

and if the relation \( \chi_{yxy} = \chi_{yzz} + 2\chi_{xxy} \) is fulfilled, then

\[ I_{\perp}^{2\omega} \propto |\chi_{yxy} \sin \varphi|^2. \quad (11) \]

Below we will show, that a magnetic field applied perpendicular to the hexagonal \( z \)-axis may reduce the symmetry of an exciton state and, consequently, it violates the relation \( \chi_{yxy} = \chi_{yzz} + 2\chi_{xxy} \).

In the following subsections we will proceed with the analysis of different specific mechanisms of the field-induced mixing of exciton states and derive the corresponding nonlinear optical susceptibilities. The results of this analysis are summarized in Table\(^\text{1}^\) Relating to the \( \chi_{yxy} \), \( \chi_{yzz} \), and \( \chi_{xxy} \) allow one to model the rotational anisotropies for each particular mechanism. We note that the admixture of exciton states in applied fields may lead to the dependence of the wave function \( \Psi_{\text{exc}} \) and the respective energy \( \mathcal{E}_{\text{exc}} \) on the exciton wave vector \( \mathbf{k}_{\text{exc}} \), as well as on \( B_z \) and \( E_y \). These complex perturbations may lead to a nonlinear dependence of the susceptibilities \( \chi_{ijkl}(\mathcal{E}_{\text{exc}}, \mathbf{k}_{\text{exc}}, B_z, E_y) \) on \( B_z \), \( E_y \) and \( k_z \), via \( k_{\text{exc}} = 2n k_z \). They act in addition to those arising from the second term in the expansion of \( \exp(ik_z z) \) according to Eq. (5).

### B. SHG and exciton Stark effect (\( \mathbf{E} \perp \mathbf{k} \))

Let us first consider the SHG signals induced by an external electric field \( E_y \) which mixes the \( 2s \) and \( 2p_y \) exciton states of opposite parity due to the Stark effect for the \( A \) and \( B \) excitons. However, it does not affect their spin states. Two polariton branches can be formed for each of the mixed \( 2s/2p \) exciton states. The new energies \( \mathcal{E}_{\text{exc}} = \mathcal{E}_{2s\perp 2p_y}^\pm \) for the transversal lower polariton branch (LPB) and \( \mathcal{E}_{\text{exc}} = \mathcal{E}_{2s\perp 2p_y}^\pm \) for the transverse upper polariton branch (UPB) are given in the Appendix. The resulting wave functions of the mixed states in Eq. (21) are constructed from the \( 2s \) and \( 2p_y \) components. In this process, all matrix elements for excitation and emission in Eq. (4) become allowed in the ED approximation \( \tilde{T}^{\omega}(x(y), y(x)) = \tilde{D}^{\omega}_z(x(y)) \). We denote the corresponding SHG as \( D^{2\omega} D^\omega \) as shown in the first row of Table\(^\text{I}^\). The corresponding SHG signals can be observed only when the incoming light has a nonzero component \( E_{2\omega}^y \) responsible for excitation of the \( 2p_y \) state. Therefore, for this process \( \chi_{yxy} = 0 \) and the resulting electric-field-induced susceptibilities \( \chi_{yxy} = 2\chi_{xxy} = 2\chi_{xxy} \) are proportional to the product of the wave function admixture coefficients in Eqs. (21) and (23). They can be written as

\[
\chi_{yxy}(\mathcal{E}_{2p_y}, \mathbf{k}_{\text{exc}}, 0, E_y) \propto C_{2s}(E_y)C_{2p_y}(E_y) = \frac{3\epsilon E_y a_B(D_{2p_y} - D_{2s/2p_y}^\pm)}{(3\epsilon E_y a_B)^2 + (D_{2p_y} - D_{2s/2p_y}^\pm)^2},
\]

where \( a_B \) is the exciton Bohr radius. One sees that these electric-field-induced susceptibilities do not depend on the absolute value of \( k_z \), however, the direction of \( \mathbf{k} \) parallel to the \( z \)-axis is important. If the electric field perturbation energy is much smaller than the zero-field splitting of the exciton states, \( |eE_y a_B| \ll |\mathcal{E}_{2p} - \mathcal{E}_{2p_L(x)}| \), then the susceptibilities depend linearly on \( E_y \). However, for larger fields a saturation is expected because for \( |eE_y a_B| \gg |\mathcal{E}_{2p} - \mathcal{E}_{2p_L(x)}| \) the susceptibilities become independent of \( E_y \).

### C. SHG and magnetic field effects on excitons (\( \mathbf{E} \perp \mathbf{k} \parallel \mathbf{z} \))

The effect of an applied magnetic field \( \mathbf{B} \) on excitons shows more facets than an electric field. We will discuss several mechanisms acting when the magnetic field is applied along the \( x \)-axis, \( \mathbf{B} = (B_z, 0, 0) \):

1. **The spin Zeeman effect**, which mixes the exciton spin states through a perturbation \( \propto (\sigma_x B_z) \), where \( \sigma_x \) is the corresponding Pauli matrix.
2. **The orbital Zeeman effect**, which affects the \( p \) states having nonzero envelope orbital momentum \( L = 1 \) and mixes the \( 2p \) and \( 2p_y \) states by a perturbation \( \propto (L_z B_z) \).
3. **The magneto-Stark effect**. This effect arises from the oppositely directed Lorentz forces acting on electron and hole in a magnetic field during the exciton center-of-mass motion. The resulting perturbation of the exciton wave function is equivalent to the effect of an effective electric field \( \mathbf{E}_{\text{eff}} \) acting on the exciton at rest:

\[
\mathbf{E}_{\text{eff}} = \frac{\hbar}{M_{\text{exc}}} (\mathbf{k}_{\text{exc}} \times \mathbf{B}),
\]

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\[
\mathbf{E}_{\text{eff}} = \frac{\hbar}{M_{\text{exc}}} (\mathbf{k}_{\text{exc}} \times \mathbf{B}),
\]
Here $M_{\text{exc}} = m_e + m_h$ denotes the exciton translational mass. In the given geometry the effective electron and hole masses for motion parallel to the hexagonal $z$-axis $k_{\text{exc}} \parallel z$ and $E_{\text{eff}} \parallel y$ have to be used: $m_e = m_e^\parallel$ and $m_h = m_h^\parallel$.

The diamagnetic shift of the exciton energy occurs for all states and is state-dependent. It does not directly lead to a state mixing, but can enhance mixing by other mechanisms due to favorable energy shifts, bringing states closer to each other.

It is important, that the external magnetic field $B_x$ can mix exciton states of different symmetry allowing two-photon resonant excitation and one-photon resonant emission at a given energy and thus leading to SHG signals. The Zeeman spin mixing may induce SHG signals for one particular envelope exciton state. The orbital Zeeman effect and the magneto-Stark effect mix states with different envelope functions. The strength of this mixing depends on the energy separation of these states at zero field. At a given exciton energy the SHG signal might be induced by several mixing mechanisms acting simultaneously. Below we analyze these mechanisms in detail for each particular exciton state.

1. Magnetic-field-induced SHG for s-type excitons due to spin Zeeman effect

The spin states of the s-type excitons depend on the symmetries of the conduction and valence bands. For excitons formed from the conduction band of $\Gamma_7$ symmetry and the valence band of $\Gamma_7$ symmetry the resulting exciton states are of $\Gamma_5$, $\Gamma_1$ and $\Gamma_2$ symmetry, split from each other by the electron-hole exchange interaction. Examples of such states are the $A$ and $C$ excitons in ZnO, or the $B$ and $C$ excitons in GaN. The dipole-allowed $\Gamma_5$ state can occur for a one-photon process and forms two polariton branches in the given geometry. The $\Gamma_1$ state can become excited by a two-photon process if one of the involved photons is due to the quadrupole perturbation or due to the involvement of intermediate virtual states in remote bands. As a result, the 1s exciton states of the $A$ and $C$ excitons might be observed in the SHG spectrum due to the Zeeman spin mixing of the $\Gamma_{5y}$ and $\Gamma_1$ states. The energies of the new mixed polariton states $\mathcal{E}_{\Gamma_{5y}/\Gamma_1}$ are given by Eq. (26) in the Appendix. The resulting wave functions of the mixed states described by Eq. (27) are constituted by both $\Gamma_5$ and $\Gamma_1$ components.

The two-photon excitation of the $s$ state might occur through an electric-dipole/electric-dipole ($D^\omega-aD^\omega-a$) or an electric-dipole/magnetic-dipole ($D^\omega Q^\omega-m$) process as discussed above. For the sake of clarity we consider the second case in detail. It is represented by the process $D^\omega D-a^\omega Q^\omega-m$ in the third row of Table I. Then the SHG process involves a matrix element for the two-photon excitation with $V_x^\omega = Q_x^\omega \chi_{xxy}$ for one of the photons and $V_y^\omega = D_y^\omega$ for the second photon. The subsequent one-photon ED emission with $V_{xy}^\omega = D_{xy}^\omega$ is allowed through the $s_{\Gamma_{5y}}$ part of the exciton wave function, so that $\chi_{xxy} = 0$. The resulting magnetic-field-induced nonzero susceptibilities $\chi_{yyzz} = \chi_{yyxx}$ are given by

$$\chi_{yyzz}(\mathcal{E}_{\Gamma_{5y}/\Gamma_1}, k_{\text{exc}}, B_x, 0) \propto C_{\Gamma_5}(B_x)C_{\Gamma_1}(B_x)(k_z a_0) = \frac{2\mu B g_{\text{exc}} B_x (\mathcal{E}_{\Gamma_5} - \mathcal{E}_{\Gamma_{5y}/\Gamma_1})(k_z a_0)}{\mu B g_{\text{exc}} B_x^2 + 4(\mathcal{E}_{\Gamma_5} - \mathcal{E}_{\Gamma_{5y}/\Gamma_1})^2}. \quad (14)$$

SHG signals of the same amplitude are predicted. Their anisotropies are described by $I^\omega_{\|} \propto |\chi_{yyzz}|^2 \cos^2 \varphi$ and $I^\omega_{\perp} \propto |\chi_{yyzz}|^2 \sin^2 \varphi$.

For excitons formed by the conduction band of $\Gamma_7$ symmetry and the valence band of $\Gamma_7$ symmetry the resulting exciton states are of $\Gamma_5$ and $\Gamma_6$ symmetry. Examples are the $B$ excitons in ZnO and the $A$ excitons in GaN. The Zeeman effect mixes the dipole-allowed $\Gamma_5$ states and the dark $\Gamma_6$ state. In addition, one has to take into account the exchange interaction between the $\Gamma_5$ components of the $A$ and $B$ excitons which may lead to SHG from the $\Gamma_{5y}/\Gamma_6$ exciton states with the same properties as described above for the $\Gamma_{5y}/\Gamma_1$ excitons. In addition, the $\Gamma_{5y}/\Gamma_6$ exciton states can be excited via the $D^\omega-aD^\omega-a$ process.
2. Magnetic-field-induced SHG for mixed 2s/2p excitons

Let us now consider the effect of the effective electric field $E_{\text{eff}} = \frac{h}{\hbar} \kappa_{\text{exc}} B_z$ on the exciton states. The mixing of 2s and 2p$_y$ states of opposite parity induced thereby is similar to that caused by the Stark effect due to an external electric field. Simultaneously, another type of mixing occurs due to the Zeeman orbital effect, but this mechanism mixes the 2p$_z$ and 2p$_y$ states of the same parity. The resulting energies $E_i^{2s/2p_z/2p_y}$ ($i = 1, 2, 3$) of the mixed 2s/2p$_z$/2p$_y$ polariton branches are listed in Eq. (34). The appropriate wave functions in Eq. (35) are constructed from all three contributing states with coefficients $C_{2s(2p_z, 2p_y)}(B_z)$ given by Eqs. (36-38). As a result, all mixed states can be excited by two photons with polarization having a nonzero field component $E_\omega \neq 0$ which excites the $\Psi_{2p_y}$ component. ED perturbations $\hat{V}_2^{\omega \omega} = \hat{D}_2^{\omega \omega}(z)$ are associated with the first photon and the $\hat{V}_2^{\omega \omega} = \hat{D}_2^{\omega \omega}(y)$ perturbation with the second photon. There are three possible mechanisms allowing observation of these mixed 2s/2p$_z$/2p$_y$ states in one-photon emission: (i) emission due to the $\Psi_{2s}$ component through the ED perturbation $\hat{V}_2^{\omega \omega}(x) = \hat{D}_2^{\omega \omega}(y)$; (ii) emission due to the $\Psi_{2p_y}$ component through the magnetic-dipole perturbation $\hat{V}_2^{\omega \omega}(z) = \hat{Q}_2^{\omega \omega}(y)$, and (iii) emission due to the $\Psi_{2p_y}$ component through the magnetic-dipole-perturbation $\hat{V}_2^{\omega \omega}(z) = \hat{Q}_2^{\omega \omega}(y)$ or through the electric-dipole-forbidden process $\hat{V}_2^{\omega \omega}(y) = \hat{D}_2^{\omega \omega}(y)$.

a. Magneto-Stark effect. In the first case (i) the mechanism responsible for the SHG signal is coupling of the 2s and 2p$_y$ states via the magneto-Stark effect and ED emission of the 2s state. The $D_2^{\omega \omega} D_2^{\omega \omega} D_2^{\omega \omega}$ process in the second row of Table I corresponds to this mechanism. The resulting magnetic-field-induced nonzero susceptibilities $\chi_{2kxy} = 2\chi_{xxy} = 2\chi_{xyy}$, $\chi_{2kz} = 2\chi_{zxx}$, and $\chi_{2kz} = 2\chi_{zxx}$ are proportional to the product of admixed components in the corresponding wave functions:

$$\chi_{2kxy}^{2s/2p_z}(c^{2s/2p_z/2p_y}, k_{\text{exc}}, B_z, 0) \propto C_k^{2s}(B_z) C_k^{2p_z}(B_z)$$

The susceptibilities depend both on the magnetic field and the wave vector value only via the dependence on the effective electric field $E_{\text{eff}} = \gamma \kappa_{\text{exc}} B_z$. This dependence is linear when the energy of the effective electric field is smaller than the zero field splitting of the states and it saturates in the opposite limit.

b. Orbital Zeeman effect. In the second case (ii) the mechanism responsible for the SHG signal is due to coupling of the 2p$_z$ and 2p$_y$ states via the orbital Zeeman effect and magnetic-dipole emission from the 2p$_z$ state. This is the $Q_2^{\omega \omega} D_2^{\omega \omega} D_2^{\omega \omega}$ process shown in the fifth row of Table I. This effect is expected to be much weaker than the magneto-Stark effect and not important at the energy where the 2s exciton is dominant. The resulting magnetic-field-induced nonzero susceptibilities $\chi_{yy} = 2\chi_{xxy} = 2\chi_{xyy}$ can be written as

$$\chi_{yy}^{2p_y}(c^{2s/2p_z/2p_y}, k_{\text{exc}}, B_z, 0) \propto k_{\text{exc}} C_k^{2s}(B_z) C_k^{2p_y}(B_z)$$

$$\chi_{yy}^{2p_y}(c^{2s/2p_z/2p_y}, k_{\text{exc}}, B_z, 0) \propto \frac{1}{2} k_{\text{exc}} C_k^{2s}(B_z) C_k^{2p_y}(B_z)$$

The linear dependence on $k_z$ comes from the matrix element of the magnetic-dipole perturbation $\hat{V}_2^{\omega \omega}(y) = \hat{Q}_2^{\omega \omega}(y)$, $\hat{Q}_2^{\omega \omega}(y)$, and $\hat{Q}_2^{\omega \omega}(y)$, $\hat{Q}_2^{\omega \omega}(y)$, or through the electric-dipole-forbidden process $\hat{V}_2^{\omega \omega}(y) = \hat{D}_2^{\omega \omega}(y)$.

Linear dependence of the $\chi$ on $B_z$ is expected only for weak magnetic fields.

The rotational anisotropy patterns of the SHG intensities for the processes induced by the magneto-Stark and the orbital Zeeman effect are similar. The main feature for both of them is disappearance of the signal in crossed geometry $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega}$ because $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \cos^2 \varphi$, while the signal polarized along the magnetic field direction varies as $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \sin^2(2\varphi)$. Since $\chi_{yy} = 0$, the signal polarized perpendicular to the magnetic field direction can be described by $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \cos^2 \varphi$.

3. SHG due to spin Zeeman effect on p states

a. The p$_y$ state. For the 2p$_y$ state the spin Zeeman effect provides only one nonzero susceptibility due to the process $Q_2^{\omega \omega} D_2^{\omega \omega} D_2^{\omega \omega}$ shown in the fourth row of Table I. This susceptibility can be written as

$$\chi_{yy}^{2p_y}(c^{2s/2p_z/2p_y}, k_{\text{exc}}, B_z, 0) \propto \frac{1}{2} k_{\text{exc}} C_k^{2s}(B_z) C_k^{2p_y}(B_z)$$

where the linear dependence on $k_z$ comes from the matrix element of the magnetic-dipole perturbation $\hat{V}_2^{\omega \omega}(y) = \hat{Q}_2^{\omega \omega}(y)$. We have neglected here the electron-hole spin exchange splitting of the p states. The magnetic field mixing of the 2s/2p$_z$/2p$_y$ envelopes reduces the SHG signal from the Zeeman effect.

The corresponding rotational anisotropy patterns for the 2p$_y$ states are: $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \cos^2 \varphi$, $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \cos^2 \varphi$, and $I_{\text{eff}}^{\omega \omega} \parallel E^{\omega \omega} \propto |\chi_{yy}^{2s}|^2 \cos^2 \varphi$. Note, that the relation $\chi_{yy} = \chi_{xy} + 2\chi_{xy}$ valid for 6mm crystals is broken because of the symmetry reduction by the magnetic field $B_z$. This field, directed perpendicular to the $z$-axis, lifts the degeneracy of the 2p$_z$ and 2p$_y$ states.

b. The p$_z$ state. A similar spin Zeeman mechanism is acting on the 2p$_z$($A$) exciton state, which is not mixed by the magnetic field with other $p$ or $s$ states. The $p_z$ state can be excited by two photons with a polarization with nonzero field component $E_{\omega} \neq 0$ via the dipole perturbations $\hat{V}_2^{\omega \omega}(y) = \hat{D}_2^{\omega \omega}(x)$ for the first photon and $\hat{V}_2^{\omega \omega}(y) = \hat{D}_2^{\omega \omega}(y)$ for the second photon or vice versa. Emission is due to the Zeeman mixing of the $\Gamma_5$ and $\Gamma_1$ spin states and the magnetic-dipole perturbation $\hat{V}_2^{\omega \omega}(y) = \hat{Q}_2^{\omega \omega}(y)$, the relevant process $Q_2^{\omega \omega} D_2^{\omega \omega} D_2^{\omega \omega}$ is shown in the fourth row of Table I.
In fact it corresponds to the very same Zeeman mixing of spin states as for the 1s states. Differences occur in the two-photon absorption and the one-photon emission for the s and p states. The nonzero susceptibility $\chi_{xxy} = \chi_{xyz}$ relevant to these processes can be written as

$$\chi_{xxy}(E_{2px}) \propto \frac{1}{2} k_z a_0.$$  \hspace{1cm} (18)

where the linear dependence on $k_z$ comes from the matrix element of the magnetic-dipole perturbation $V^{2\omega}_{x(x+y)z} = \hat{Q}_{x(y)z}^{z}$. 

There is no explicit dependence on the magnetic field in Eq. (18). However, a finite $B_z$ is required for mixing the $\Gamma_5$ and $\Gamma_1$ spin states because without magnetic field the effect vanishes. $B_z$ does not appear in Eq. (18) because we have neglected the exchange splitting of the mixed states, so that they have the same energy. However, even a very weak but finite magnetic field can mix them in equal strength. In other words, a kind of “phase transition” takes place, as there is no effect at $B = 0$ which then emerges instantaneously as soon as $B > 0$ with a finite magnitude independent of $B$. One may compare this case with Eq. (14), where there is a mixing of the $\Gamma_5$ and $\Gamma_1$ states that are split at $B = 0$. The magnetic field dependence in Eq. (17) comes only from the $B$-dependence of the contribution of the $2py$ component, given by $C_{2py}(B_z)$.

The SHG rotational anisotropy patterns for the $2px$ states via the spin Zeeman mixing are: $I_{x}^{2 \omega} \propto |\chi_{xxy}|^{2} \sin^{2}(2\varphi) \sin^{2} \varphi$, $I_{y}^{2 \omega} \propto |\chi_{xxy}|^{2} \sin^{2}(2\varphi) \cos^{2} \varphi$, $I_{z}^{2 \omega} = |\chi_{xxy}|^{2} \sin^{2}(2\varphi)$, and $I_{\parallel}^{2 \omega} = 0$. Note, that also here the symmetry relation $\chi_{yxx} = \chi_{yzz} + 2 \chi_{xxy}$ valid for $6mm$ hexagonal crystals is broken because of the symmetry reduction in presence of a magnetic field $B_x$ directed perpendicular to the $z$-axis. This field lifts the degeneracy of the $2px$ and $2py$ states.

All mechanisms considered above for field-induced SHG at the $s$ and $p$ exciton resonances are summarized in the Table I. The susceptibilities are presented for the geometry $k \parallel z$, $B \parallel x$, and $E \parallel y$. Resulting rotational anisotropy patterns corresponding to the different mechanisms are illustrated in Fig. 16.

We have to note, without going into details, that the considered mechanisms do not work in the Faraday geometry $B \parallel k \parallel z$. A magnetic field applied along the hexagonal $z$-axis does not mix the $\Gamma_1$ and $\Gamma_5$ states, therefore the mechanisms involving Zeeman spin mixing do not induce SHG signals. The orbital Zeeman term $L_z B_z$ also does not lead to admixture of the $2p_z$ states that is allowed for quadrupole emission when $k \parallel z$. The effective electric field $E_{\text{eff}}$ vanishes for the geometry $B \parallel k$, so there is also no magneto-Stark effect.

VI. DISCUSSION

The observed magnetic- and electric-field-induced SHG are specific to excitons, no induced signals are observed in the off-resonant energy range. In the following we discuss the various interactions between light fields and exciton states, leading to the different types of symmetry breaking presented in Sec. IV in order to explain our experimental data of Sec. V. As a general rule, we note that mixing of states with different symmetries is the key to induce resonant nonlinear susceptibilities. Rotational anisotropy measurements of the SHG signals give comprehensive information on the symmetry of the involved nonlinear susceptibilities and, therefore, of the underlying origins. Thus, they help to distinguish different nonlinear optical mechanisms, which is especially important when more than one mechanism become involved. Therefore, the measured rotational anisotropy patterns of the SHG intensity should reflect the anisotropies predicted by our theoretical considerations. For the sake of convenience, all discussed states will be referred to as excitons, although states that contain admixtures of $s$ envelope states can couple so strongly to the light field that exciton-polaritons may be formed.

The energy shifts of SHG lines in magnetic field and the field dependence of their intensities should be in accord with the theory as well. The computed energies depend strongly on the input parameters, which are the zero-field exciton energies and the electron and hole effective masses. Here we use the zero-field exciton energies from Ref. 42

$$E_{2p_x} = 3.4227 \text{ eV}, \quad E_{2s} = 3.4232 \text{ eV}, \quad E_{2p_z} = 3.4240 \text{ eV}, \quad \text{and } E_{2p_{z\perp}} = 3.4254 \text{ eV} \quad \text{for the A series as well as } E_{2s} = 3.4276 \text{ eV}, \quad E_{2sL} = 3.4304 \text{ eV}, \quad E_{2p_z} = 3.4292 \text{ eV}, \quad \text{and } E_{2p_{z\perp}} = 3.4303 \text{ eV} \quad \text{for the B series of excitons.}$$

We use the electron effective mass $m_e = 0.27 m_0$ and the following hole effective masses obtained from first principles calculations $55,56$ $m_{h} = 2.74 m_0$, $m_{\perp} = 0.54 m_0$ for the A excitons and $m_{\parallel} = 3.03 m_0$, $m_{\perp} = 0.55 m_0$ for the B excitons. The static dielectric constants $\epsilon_{\parallel} = 8.49$ and $\epsilon_{\perp} = 7.40$ are taken from Ref. 21.

Spin Zeeman splitting is not included in the calculations for the $2s/2p_z/2p_y$ states. The discussed interactions act on states with the same spin wave functions and thus the spin Zeeman splitting leads to an energy shift, that is the same for all involved states. Therefore, even though the number of lines in Fig. 8 will increase, it should not lead to additional contributions.

A. SHG mechanism for 1s exciton

The SHG signals at the 1s exciton resonance can be fully explained by the spin Zeeman effect, mixing one-photon allowed orthoexcitons and two-photon allowed paraexcitons leading to the relations $\chi_{yxx} = \chi_{yxz} \neq 0$ and $\chi_{xxy} = 0$, see Table I and Sec. V.C.1. The nonzero component $\chi_{yxx}$ given by Eq. (14) predicts the rotational anisotropies shown in Figs. 16(a)-(d) as well as a
TABLE I. Different mechanisms providing SHG in external electric and magnetic fields at the 1s, 2s, 2p exciton resonances in ZnO. Experimental geometry: \( \mathbf{k} \parallel z, \mathbf{E} = (0, E_y, 0) \), and \( \mathbf{B} = (B_z, 0, 0) \). Due to symmetry \( \chi_{xxy} = \chi_{xyx} \).

| Mechanisms                      | \( 1s, 2s \) | \( 2s/2p_y \) | \( 2p_x/2p_y \) | \( 2p_y \) | \( 2p_x \) |
|---------------------------------|---------------|---------------|----------------|-----------|-----------|
| Stark effect                    | \( \chi_{yyy} = 2\chi_{xxy} \neq 0 \), \( \chi_{yxx} = 0 \) |               |               |           |           |
| \( D_{i}^{22}D_{j}^{22}D_{l}^{22} \) \( E_y \neq 0, B_z = 0 \) |               |               |               |           |           |
| Magneto-Stark effect            | \( \chi_{yyy} = 2\chi_{xxy} \neq 0 \), \( \chi_{yxx} = 0 \) |               |               |           |           |
| \( D_{i}^{22}D_{j}^{22}D_{l}^{22} \) \( E_y = 0, B_z \neq 0 \) |               |               |               |           |           |
| Spin Zeeman effect              | \( \chi_{yyy} = \chi_{yxx} \neq 0 \), \( \chi_{xxy} = 0 \) |               |               |           |           |
| \( D_{i}^{22}Q_{i}^{m}D_{j}^{22} \) \( E_y = 0, B_z \neq 0 \) |               |               |               |           |           |
| Spin Zeeman effect              | \( \chi_{yyy} = \chi_{yxx} = 0 \) | \( \chi_{xxy} = 0 \) | \( \chi_{xyy} = \chi_{yxx} = 0 \) |           |           |
| \( Q_{i}^{22}D_{j}^{22}D_{l}^{22} \) \( E_y = 0, B_z \neq 0 \) |               |               |               |           |           |

The quadratic dependence of the SHG intensity on the magnetic field \( I_{zz} \propto B^2 \). The measured intensities \( I_{zz}^{22} \) and \( I_{zz}^{22} \) show indeed the predicted \( \cos^2 \phi \) and \( \sin^2 \phi \) shape and also have the same amplitude, see Fig. 7(c). Further, no signal was detected for \( I_{zz}^{22} \), \( I_{zz}^{22} \), and \( I_{zz}^{22} \) was found to be isotropic (not shown). Figure 7(a) proves the square dependence of \( I_{zz}^{22} \) on the magnetic field strength. For the 1s(\( A \)) exciton, which emerges from a different valence band, two SHG mechanisms may be active: (i) mixing of the \( \Gamma_5 \) and \( \Gamma_6 \) states due to the spin Zeeman effect, and (ii) mixing of the A and B valence bands due to exchange interaction.

**B. SHG mechanisms for 2s/2p excitons**

A similar process based on the magnetic-field-induced spin Zeeman effect, mixing the \( \Gamma_5 \) and \( \Gamma_1 \) states of the 1s(\( A \)) exciton, is valid also for the 2s(\( A \)) excitons. However, the comparison of Fig. 3(c) and Figs. 10(a,b) shows that the observed anisotropies of the \( n = 2 \) states are different from those of the 1s states: For the \( n = 2 \) (\( A \)) excitons the shape of \( I_{zz}^{22} \) cannot be described by the form \( \sin^2 \phi \), and \( I_{zz}^{22} \) and \( I_{zz}^{22} \) do not have the same amplitude. These anisotropies need to be explained by other mechanisms than the spin Zeeman effect on the \( s \) envelope. In Ref. 23 we have shown, that the magneto-Stark effect is the dominant mechanism in the 2s/2p(\( A \)) exciton region. It can explain the shapes shown in Figs. 10(a), 10(c), and 10(d), which closely resemble the predicted shapes in Figs. 16(e), 16(g), and 16(h), respectively. But a closer look at the non vanishing \( I_{zz}^{22} \) intensity reveals, that the spin Zeeman effect on both the s and p envelopes add a small contribution, note the multiplication factor 20 in Fig. 10(b). The complex shape of \( I_{zz}^{22} \) in Fig. 10(b) can only be explained by a combination of the spin Zeeman effects on the \( n = 2 \) states. Their predicted shapes are shown in Figs. 10(b) and 10(i), respectively. To compare their impact, Fig. 10(a and Fig. 11 give their ratio \( a/b \). a and b describe the relative strength of the spin Zeeman effect on the s and p envelope, respectively. Both contributions to \( I_{zz}^{22} \) can be estimated to be of about 5% of the peak intensity of \( I_{zz}^{22} \), while it follows from the fit in Fig. 10(b), that the spin Zeeman contribution from the 2p(\( A \)) part is twice as strong as from the 2s(\( A \)) part. As a consequence, the SHG induced by the magneto-Stark effect involving only ED excitation as well as ED emission processes is about 40 times more efficient than the SHG due to the spin Zeeman mixing utilizing a MD transition. The orbital Zeeman effect cannot be distinguished from the magneto-Stark effect via anisotropies (see non zero components of both contributions in Table I) and might be of importance too, due to the 2p(\( A \)) mixing, especially for the regions, where the 2p(\( A \)) part is large. However, the probability of MD emission from the 2p(\( A \)) part is very low in comparison with the probability of ED emission from the 2s state. Thus, we assume that the orbital Zeeman effect does not play a leading role and the magneto-Stark effect brings the dominant contribution to the SHG signal at the 2s/2p exciton resonances.

Further, the weak nonzero signals in the crossed geometry that do not follow from the magneto-Stark effect were also observed in the range of the \( n = 2 \) B excitons. The anisotropy shapes for the \( B \) series presented in Figs. 11(a), 11(b), 11(c), and 11(f) show many similarities to those of the \( A \) series: the strongest signals are observed for \( I_{zz}^{22} \) with a twofold \( \sin^2 \phi \) symmetry pattern, whereas \( I_{zz}^{22} \) is a mixture of a fourfold \( \sin^2 \phi \cos^2 \phi \) and a twofold \( \sin^2 \phi \) pattern, originating from the spin Zeeman effects. In addition, the contribution \( I_{zz}^{22} \propto \sin^2 \phi \)
in the range of the $n = 2$ $B$ exciton energies might also arise from the spin Zeeman effect on the $3s(A)$ or $1s(C)$ excitons, located in the same spectral range. However, the $3s(A)$ contribution is rather unlikely, because of the high main quantum number considerably reduces its oscillator strength in comparison to $1s$ and $2s$ states. By contrast, the $1s(C)$ is also seen as strong, broad feature in the crystallographic SHG spectra, see Fig. 2. Actually an additional contribution from the $1s(C)$ exciton would explain, why we observed a strong influence of the ‘$s$’ type spin Zeeman effect on the shape of the anisotropies for $2h\omega = 3.432$ eV; see Figs. 1(e) and (f). Only in this region the ratio $a/b$ is larger than 1. Further, the magneto-Stark effect is not as important as for the other...
energies; compare the ratios $I_{2\omega}^{\parallel}/I_{2\omega}^{\perp}$ at the three energies shown in Fig. 11.

The strongest SHG signals are observed for $I_{2\omega}^{\parallel}$ and their spectral maxima follow the energies of the states with dominant $2p_y(A, B)$ wave functions. In higher fields ($> 6$ T) the peaks follow lines with dominant $2s$ wave functions, because the admixture of the $2p_z$ to $2p_y$ states reduces the efficiency of the magneto-Stark induced SHG; see the black circles in Fig. 9. The analysis of the anisotropies in the regions where the $2p_y/2p_z$ wave functions dominate gives the same results as the analysis of states with large $2s$ contributions, but with less influence from the $s$-type spin Zeeman effect. Consequently, the SHG at the $2s/2p_y/2p_z$ states is governed mainly by the magneto-Stark effect.

The contributions from the spin Zeeman effect on the $2p_z$ states are best seen in Fig. 9 for $I_{2\omega}^{\parallel}$ in the geometry $\varphi(E^\omega) = 45^\circ$ and $E^{2\omega} \parallel B$. The spectral maxima follow the energies of the calculated energies of the $2p_z(A, B)$ exciton states; compare $2p_z$ lines and red circles in Fig. 9. In addition, the ratio of the spectrally integrated intensities $I_{2\omega}^{\perp}/I_{2\omega}^{\parallel}$ should be $1/4$ or less without the contribution of the spin Zeeman effect for the $2p_z$ states. We observed, however, a deviating ratio of about $1/3$ [compare area under curves in Fig. 9(b)], underlining the importance of the spin Zeeman mechanism for the $2p_z$ orbitals oriented parallel to the magnetic field. Nevertheless, the contributions of this mechanism to the $I_{2\omega}^{\parallel}$ signals are not significant and most of the integrated SHG intensity in the $I_{2\omega}^{\parallel}$ spectra comes from the $2s/2p_y/2p_z$ mixed states due to the magneto-Stark effect.

The developed model describes well the measured angular dependencies of the SHG intensities and it is in reasonable accordance with the energy shifts of the exciton states shown in Fig. 9 ensuring the validity of the presented SHG mechanisms.

Another intriguing feature of the discovered mechanisms is the complex behavior of the spectrally integrated SHG intensity shown in Fig. 7(b). The SHG signals from the magneto-Stark and orbital Zeeman effects are expected to saturate when the related energies become larger than the zero field splitting of the involved exciton states. The typical values of the $|2s_T - 2p_y|$ exciton splitting is about 3 meV for the $A$ and $B$ excitons in ZnO. While the longitudinal-transverse splitting of the $2s(A)$ exciton is about 0.5 meV, the respective splitting for the $B$ exciton is about 3 meV. Thus, the saturation condition is reached for the orbital Zeeman effect $(g_{arb}Bz_B)$ around $B \approx 8$ T, but it is not fulfilled for the magneto-Stark effect $(3eE_{arb}(B)\partial \varphi)$ even at the strongest field of $B \leq 10$ T. The spin Zeeman effect for the $2p_z$ state is independent of magnetic field, whereas the susceptibility decreases with the fraction of $C_{2p_z}$, as for the $2p_y$ state, compare Eq. 17. Due to the linewidths of the exciton resonances, we were not able to resolve in Fig. 8 individual lines, but rather the interplay of contributions from different energies leading to the observed complex behavior of the spectrally integrated intensity. For the geometry shown in Fig. 7(b) we take into account the magneto-Stark and orbital Zeeman effects to model the SHG intensity dependence.

The temperature dependence of the integrated SHG intensity can be qualitatively understood by a simple consideration. Eq. 4 shows that the susceptibility for resonant SHG depends inversely linear on the exciton damping $\Gamma_{exc}$, which is contributed by inhomogeneous and homogeneous broadening of the exciton. The inhomogeneous broadening in the studied sample does not exceed 1 meV, one can see that in Fig. 6(a), where it is already limited by the laser spectral width. Therefore, at temperatures exceeding 10 – 20 K the exciton linewidth is controlled by the homogeneous broadening due to scattering on acoustic phonons. This broadening increases linearly with the temperature. The SHG peak intensity, proportional to the susceptibility, depends inversely quadratically on the linewidth $I_{2\omega} \propto \Gamma_{exc}^{-2}$. The dependencies for the exciton resonances in Fig. 14 are spectrally integrated, for which the intensities in principle have to be multiplied with the linewidth leading to the integrated SHG being proportional to $\Gamma_{exc}^{-1}$ and respectively to $T^{-1}$. In contrast, the crystallographic SHG signal measured in the off-resonant region remains constant with increasing temperature, compare blue and red curves in the lower energy region in Fig. 13.

D. Origin of X-line

To our knowledge the observed strong SHG line at 3.407 eV has not been reported in linear absorption spectra studies. However, the observed temperature and angular dependencies of the SHG at this line correspond to those of the free 1s(C) exciton; compare Figs. 4(b) and 4(d). Thus, a correlation between these resonances is likely. In addition, we want to point out the recent observation of an unknown line at $\sim 3.405$ eV with polarization pattern and uniaxial pressure coefficients matching those of the $C_T(T_1)$ state,

suggesting to link the X-line to the C valence band. We did not find resonances at the corresponding energies for the $A$ and $B$ excitons. Clarification of the X-line origin needs further investigations. We also note, that phase synchronization for the fundamental and second harmonic waves are of great importance for SHG. Therefore, the strong SHG line at
3.407 eV might be due to phase matching as consequence of polaritonic effects in the dielectric function in the exciton energy range of ZnO.

E. Crossed electric and magnetic fields

To verify the magneto-Stark effect as dominant source of the observed SHG signals, it is instructive to discuss the joint action of external magnetic and electric fields. Theory predicts that an electric field produces the same type of symmetry breaking as the effective electric field induced by a magnetic field. This is proven by the fact, that the anisotropy of magnetic-field-induced signals is not changed by additionally applying an electric field. Nevertheless, the electric field acts very differently in comparison to the magnetic field. The effective electric field acts on exciton levels only, whereas the electric field creates a potential throughout the crystal.

Figure 15(b) shows, that an electric field of 550 V/cm has only a weak effect on the SHG intensity. The interference of its action with the effective electric field induced by a magnetic field of 1 T in Figure 15(a) shows, that the electric field gives indeed surprisingly small contributions. The magnitude of the effective electric field is $E_{\text{eff}} = \frac{\hbar}{M_{\text{exc}}} k_{\text{exc}} B_x$. The theoretical value for the exciton translational mass in ZnO is about $3m_0$ and $k_{\text{exc}} = n\varepsilon_{\text{exc}}/hc \approx 0.03$ nm$^{-1}$ for $\varepsilon_{\text{exc}} = 3.425$ eV with a refractive index $n \approx 1.97$. Thus, $E_{\text{eff}}$ can be estimated as $\approx 12$ V/cm for $B = 1$ T. Consequently, the ratio between the effective electric field and the electric field strength giving the same effect is $\gamma = \frac{12 \text{V/cm} / E}{E_{\text{eff}}} \approx 1.13 \times 10^{-2}$ T/V (where $\varepsilon_{\perp}$ is the relative dielectric permittivity) and would have to be used for the fit function $I^{\pm} \propto (\pm B - \gamma E)^2$. Instead the best fit to the data shown in the inset of Fig. 15(a) was achieved for a value that is 50 times smaller. Such a discrepancy evidences that much weaker electric field is in fact acting on the excitons in our experiments. Indeed, as it is shown in Fig. 15(c), the sample resistivity was reduced drastically when the $2\omega$ of the laser light approaches $2p$ states and after illumination the resistivity is only slowly restored. We suggest that the screening of the external field by carriers trapped in deep centers is responsible for the observed discrepancy.

VII. CONCLUSIONS

In summary, new exciton phenomena in bulk hexagonal ZnO have been thoroughly studied by optical second harmonic generation in the spectral range of the $1s(A,B)$, $2s(A,B)$, $2p(A,B)$, and $1s(C)$ excitons, both experimentally and theoretically. While symmetry considerations forbid any crystallographic SHG for $k \parallel z$, strong magnetic-field-induced contributions are found for this geometry. Novel microscopic mechanisms for these nonlinearities are identified and confirmed by detailed experimental studies, addressing the magnetic field, electric field, temperature and polarization dependencies of the SHG signals.

We present an in-depth theoretical analysis on the basis of phenomenological and microscopic approaches, which suggests several mechanisms induced by external magnetic field. The magnetic field produces a multifaceted action, depending on the exciton type. The nonlinear mechanisms are related to the spin and orbital Zeeman effects, and to the magneto-Stark effect. For $1s(A,B)$ excitons the main mechanism of magnetic-field-induced SHG is related to the spin Zeeman effect, which mixes the different spin wave functions. On the other hand, the mixing of envelope wave functions of opposite parity by the magneto-Stark effect due to an effective electric field is the key mechanism for magnetic-field-induced SHG at the closely spaced $2s/2p(A,B)$ excitons.

We show the key importance of magnetic- and electric-field-induced symmetry reductions for inducing nonlinearities in bulk hexagonal ZnO, a phenomenon which should occur in the same way also for other material systems. Tailoring these symmetry reductions of the exciton level structure opens new degrees of freedom in the nonlinear spectroscopy of excitons.

ACKNOWLEDGMENTS

The authors are thankful to D. Fröhlich for highly stimulating discussions and help with experiments, E. L. Ivchenko for discussions, and to B. Kaminski for his contribution to initial stage of this study. This work was supported by the Deutsche Forschungsgemeinschaft and the Russian Foundation for Basic Research. V. V. P. research stay in Dortmund was supported by the Alexander-von-Humboldt Foundation.

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APPENDIX: THEORETICAL CONSIDERATION OF EXCITON STATE MIXING IN ELECTRIC AND MAGNETIC FIELDS

Here we describe the mixed exciton states in hexagonal ZnO subject to external electric or magnetic fields. Only the geometry used in the experimental part of this paper is analyzed: \( \mathbf{k} \parallel \mathbf{z}, \mathbf{E} = (0, E_y, 0) \), and \( \mathbf{B} = (B_x, 0, 0) \).

1. Exciton states in electric field perpendicular to hexagonal \( z \)-axis.

The external electric field \( E_y \) mixes the 2\( s \) and 2\( p_y \) exciton states of opposite parity for the \( A \) and \( B \) exciton series, but does not affect their spin states. We neglect for simplicity the interaction between the \( A \) and \( B \) series and consider them independently within the polariton concept. Then for each series the exciton eigenenergies can be found from diagonalization of the Hamiltonian

\[
\hat{H}_{2s/2p_y} = \left( \begin{array}{cc} E_{2s} & 3 e E_y a_B \\ 3 e E_y a_B & E_{2p_y} \end{array} \right),
\]

where \( a_B \) is the exciton Bohr radius, \( E_{2s} = E_{2y} \) is the zero-field energy of the 2\( s \) transversal exciton, and \( E_{2p_y} \) is that of the 2\( p_y \) exciton state. The eigenenergies are

\[
E^{\pm}_{2s/2p_y} = \frac{1}{2} \left( E_{2s} + E_{2p_y} \pm \sqrt{(E_{2p_y} - E_{2s})^2 + 36(eE_y a_B)^2} \right)
\]

and the resulting wave functions can be written as

\[
\Psi_{2s/2p_y} = C_{2s}(E_y)\Psi_{2s} + C_{2p_y}(E_y)\Psi_{2p_y}
\]

and

\[
C_{2s}(E_y) = \frac{E_{2p_y} - E^{\pm}_{2s/2p_y}}{\sqrt{(3eE_y a_B)^2 + (E_{2p_y} - E^{\pm}_{2s/2p_y})^2}}
\]

\[
C_{2p_y}(E_y) = -\frac{3 e E_y a_B}{\sqrt{(3eE_y a_B)^2 + (E_{2p_y} - E^{\pm}_{2s/2p_y})^2}}
\]

In the considered geometry these exciton states are transversal excitons. Due to interaction with the light field two transverse polariton branches for each of the 2\( s \)/2\( p_y \) mixed states are formed. The energies of the lower polariton branches (LPB) are given by Eq. (20). To find the energies of the upper polariton branches one has to consider the interaction of the mixed excitons with photons and their corresponding contribution to the dielectric function. However, when the longitudinal-transverse splitting, \( \Delta_{LT}^2 \), is much smaller than all characteristic energies, the results can be approximated by considering the direct interaction between the 2\( p_y \) exciton and the upper 2\( s \) polariton branch. For this, one has to use the \( E_{2s} = E_{2sL} \) in the Hamiltonian [19]. The resulting eigenenergies of the upper polariton branches (UPB) are approximately given by

\[
E^{\pm}_{2sL/2p_y} \approx \frac{1}{2} \left( E_{2sL} + E_{2p_y} \pm \sqrt{(E_{2p_y} - E_{2sL})^2 + 36(eE_y a_B)^2} \right)
\]

where \( E_{2sL} = E_{2s} + \Delta_{LT}^2 \) is the energy of the 2\( s \)-longitudinal exciton and the upper polariton in zero electric field. The resulting wave functions can be found using Eqs. (20)-(23) after replacing the energy \( E_{2s} \) with \( E_{2sL} \).

2. 1\( s \) excitons in external magnetic field perpendicular to hexagonal \( z \)-axis.

The spin states of the \( A \) and \( C \) 1\( s \) excitons are formed from the conduction band of \( \Gamma_7 \) symmetry and the valence band of \( \Gamma_7 \) symmetry and thus can be of \( \Gamma_5 \), \( \Gamma_1 \) or \( \Gamma_2 \) symmetry, split from each other by the electron-hole exchange interaction. The external magnetic field \( B_z \) mixes the \( \Gamma_5y \) and \( \Gamma_1 \) spin states. The resulting SHG active states can be found from the Hamiltonian

\[
\hat{H}_{\Gamma_5y/\Gamma_1} = \left( \begin{array}{cc} E_{\Gamma_5} & \mu_B g_{\text{exc}} B_x/2 \\ \mu_B g_{\text{exc}} B_x/2 & E_{\Gamma_1} \end{array} \right)
\]

where \( E_{\Gamma_5} \) and \( E_{\Gamma_1} \) are the zero-field energies of the corresponding states, \( g_{\text{exc}} \) is the effective 1\( s \)-\( g \)-factor for B.L.Z. In ZnO, for the \( A \) exciton \( g_{\text{exc}} \approx 1.95 \) and \( g_{\text{exc}} \approx 0.09 \). The resulting energies of the 1\( s \)(\( A \))-states in magnetic field \( B_x \) are given by

\[
E^{\pm}_{\Gamma_5y/\Gamma_1} = \frac{1}{2} \left( E_{\Gamma_1} + E_{\Gamma_5} \pm \sqrt{\Delta_{1s}^2 + (\mu_B g_{\text{exc}} B_x)^2} \right)
\]

where \( \Delta_{1s} = |E_{\Gamma_5} - E_{\Gamma_1}| \) is the exchange splitting. The LPB is described exactly by Eq. (26) with energy \( E_{\Gamma_5} = E_{\Gamma_1} \), the UPB is described approximately by Eq. (26) with energy \( E_{\Gamma_5} = E_{\Gamma_5L} \). The resulting wave functions are given by

\[
\Psi_{\Gamma_5y/\Gamma_1} = C_{\Gamma_5}(B_x)\Psi_{\Gamma_5} + C_{\Gamma_1}(B_x)\Psi_{\Gamma_1}
\]

with

\[
C_{\Gamma_5}(B_x) = \frac{2(E_{\Gamma_5} - E_{\Gamma_5y/\Gamma_1})}{\sqrt{(\mu_B g_{\text{exc}} B_x)^2 + 4(E_{\Gamma_5} - E_{\Gamma_5y/\Gamma_1})^2}}
\]

\[
C_{\Gamma_1}(B_x) = -\frac{\mu_B g_{\text{exc}} B_x}{\sqrt{(\mu_B g_{\text{exc}} B_x)^2 + 4(E_{\Gamma_5} - E_{\Gamma_5y/\Gamma_1})^2}}
\]

3. 2\( s \) and 2\( p \) exciton states in magnetic field perpendicular to hexagonal \( z \)-axis.

Similar to the effect of the external electric field \( E_y \) considered above, the effective electric field \( E_{\text{eff}} = \)
that originates from the magneto-Stark effect [see Eq. (13)], mixes the 2s and 2p\textsubscript{y} excitons of opposite parity. At the same time, the Zeeman orbital effect mixes the 2p\textsubscript{x} and 2p\textsubscript{y} states of the same parity. The resulting energies $\mathcal{E}_{2s/2p\pm/2p_y}^i$ ($i = 1, 2, 3$ label eigenvalues) of the mixed 2s/2p\textsubscript{x}/2p\textsubscript{y} polariton branches can be found as the eigenenergies of the Hamiltonian

$$
\hat{H}_{2s/2p\pm/2p_y}^\pm = \begin{pmatrix}
\mathcal{E}_{2s}^\pm (B_x) & 3eE_{\text{eff}}a_B & 0 \\
0 & \mathcal{E}_{2p\pm}^\pm (B_x) & ig_{\text{orb}}\mu_B B_x \\
3eE_{\text{eff}}a_B & -ig_{\text{orb}}\mu_B B_x & \mathcal{E}_{2p_y}^\pm (B_x)
\end{pmatrix}
$$

Here

$$
\mathcal{E}_{2s}^\pm (B_x) = E_{2s} + 14C_d B_x^2 \pm \mu_B g_s^\pm /2,
$$

$$
\mathcal{E}_{2p\pm}^\pm (B_x) = E_{2p\pm} + 12C_d B_x^2 \pm \mu_B g_p^\pm /2, \quad \text{and}
$$

$$
\mathcal{E}_{2p_y}^\pm (B_x) = E_{2p_y} + 12C_d B_x^2 \pm \mu_B g_{p_y}^\pm /2,
$$

with $\mathcal{E}_{2s} = \mathcal{E}_{2s\pm}$ for the LPB and $\mathcal{E}_{2s \pm} = \mathcal{E}_{2s\pm}$ for the UPB. The resulting wave functions for the 2s/2p\textsubscript{x}/2p\textsubscript{y} mixed states contain all three components

$$
\Psi_{2s/2p\pm/2p_y}^i = C_{2s}^i (B_x) \Psi_{2s} + C_{2p\pm}^i (B_x) \Psi_{2p\pm} + C_{2p_y}^i (B_x) \Psi_{2p_y},
$$

with the coefficients

$$
C_{2s}^i = \frac{3eE_{\text{eff}}a_B (\mathcal{E}_i^\pm - \mathcal{E}_{2s}^\pm)}{\sqrt{(\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (3eE_{\text{eff}}a_B)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (g_{\text{orb}}\mu_B B_x)^2 (\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2}},
$$

$$
C_{2p\pm}^i = \frac{ig_{\text{orb}}\mu_B B_x (\mathcal{E}_i - \mathcal{E}_{2s}^\pm)}{\sqrt{(\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (3eE_{\text{eff}}a_B)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (g_{\text{orb}}\mu_B B_x)^2 (\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2}},
$$

$$
C_{2p_y}^i = \frac{(\mathcal{E}_i - \mathcal{E}_{2s}^\pm)(\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)}{\sqrt{(\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (3eE_{\text{eff}}a_B)^2 (\mathcal{E}_i - \mathcal{E}_{2p\pm}^\pm)^2 + (g_{\text{orb}}\mu_B B_x)^2 (\mathcal{E}_i - \mathcal{E}_{2s}^\pm)^2}}.
$$

It is worth to note, that the Hamiltonian (30) allows one to take into account the effects of both the external magnetic field $B_x$ and the external electric field $E_y$. For that purpose, $E_{\text{eff}}$ should be replaced with $E_{\text{eff}} \pm E_y$, where the choice of the sign depends on the direction of the applied electric field.

The magnetic field $B_x$ affects the 2p\textsubscript{x} exciton state only via the spin Zeeman effect and the diamagnetic shift, but does not mix it with the other 2p or 2s states. Its energy is given by

$$
\mathcal{E}_{2p_x}^\pm (B_x) = E_{2p_x} + 6C_d B_x^2 \pm \mu_B g_{p_x}^\pm /2.
$$

It is important to note, however, that the degeneracy of the 2p\textsubscript{x} and 2p\textsubscript{y} states is lifted by the magnetic field and the hexagonal symmetry is broken, i.e., $\chi_{ygg} = \chi_{yxx} + 2\chi_{xyy}$ is violated for these states.