Spin-forbidden $\Delta m_s = 2$ transitions in the optically detected magnetic-resonance spectra of excitons bound at complex neutral defects in GaP

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A rate-equation analysis of optically detected magnetic-resonance (ODMR) data for the singlet-triplet configuration of excitons bound at complex neutral (isoelectronic) defects in GaP is presented. A puzzling feature of these data, i.e., the observation of strong formally spin-forbidden $\Delta m_s = 2$ transitions, is discussed. It is shown that a strong $\Delta m_s = 2$ transition is a fingerprint of thermalized-triplet sublevels, still with relatively long spin-lattice relaxation times. The observed strong angular and temperature dependences of the intensities of the $\Delta m_s = 2$ transition are explained on the basis of the transition-rate equations for the bound exciton. This paper represents one of the first attempts to describe experimental ODMR results quantitatively for a semiconductor.

I. INTRODUCTION

One of the most puzzling features of optically detected magnetic-resonance (ODMR) experiments for the triplet configuration of excitons (BE's) bound at complex neutral (isoelectronic) defects in semiconductors is a common observation of relatively strong $\Delta m_s = 2$ spin-forbidden transitions.[1–5] While these transitions are very strong in some cases, they have not been observed (i.e., they are very weak) for some other BE systems, even though the electronic structure and defect symmetry are similar to the cases of BE's with strong $\Delta m_s = 2$ lines (see, e.g., Refs. 6–8).

In this paper we present an explanation of these features of the ODMR spectra for triplet BE's, based on a comprehensive model of the resonant transition rates for the triplet states. The kinetic rate equations for the BE recombination are introduced and analyzed for the case of thermalized and unthermalized excited triplet state of a given BE. The experimental results of relevant ODMR studies for hole-attractive BE complexes in GaP are then analyzed in the framework of the model presented. A previously noticed simple relation between the strength of the $\Delta m_s = 2$ transition and the low symmetry as well as the size of the D-tensor parameters is easily explained by the proposed theoretical description of the ODMR data. Furthermore, a relation between a strong $\Delta m_s = 2$ signal and a strong temperature dependence of the resonance signals is indicated.

This paper is organized in the following way. In Sec. II a short description is given of the GaP crystals studied and of the experimental techniques used. The discussion (Sec. III) starts with a short introduction regarding the singlet-triplet (S-T) electronic structure of the BE, and the spin Hamiltonian appropriate for the description of the resonance transitions within the triplet state is introduced. We explain here that the magnetic-field-induced mixing of the spin states does not relax the spin-selection rules enough to allow for the formally spin-forbidden transitions ($\Delta m_s = 2$) to be of a strength comparable to the case of the spin-allowed ($\Delta m_s = 1$) ones. The steady-state rate equations for the triplet BE recombination are then introduced (Sec. III B) and solved for the two "extreme" situations—a thermalized- and an unthermalized-spin-triplet BE state. In Sec. III C the experimental results from recent ODMR studies of BE's bound at complex isoelectronic defects in GaP are analyzed and explained within the proposed model. Finally, in Sec. IV some general conclusions regarding ODMR spectra for BE's associated with complex neutral defects are summarized.

II. EXPERIMENT

A. Equipment and samples

The ODMR experiments in this work have been performed on a modified Bruker 200D-SRC 9-GHz spectrometer, equipped with an Oxford ESR 10 He continuous flow cryostat and a cylindrical cavity with optical access from all directions. Microwave power up to 600 mW could be employed and samples could be cooled down to 2 K.

For the optical excitation Ar^+ or Kr^+ lasers have been used. Optical detection of photoluminescence (PL) has been done with S-20 and S-1 type photomultipliers in the visible spectral range, and a North-Coast EO 817 Ge detector for infrared radiation, in phase with the chopped microwave excitation. Experiments could be performed in both Faraday and Voigt configurations.

A variety of GaP crystals has been used in the studies presented. The samples have been either liquid-encapsulated-Czochralski-grown (LEC) bulk samples or epitaxial wafers. Crystals used for the investigations of (Cu-Li)-related neutral defects have been doped in two steps, as described separately.[3,7,9] Copper-only doped crystals have been used in the studies of the 1.911-eV BE.[4] Bulk LEC crystals doped with Cu and Li have been used to study the so-called $(Cu\text{-}Li)_V$ BE spectrum,[3] and have shown a range of P_{Ga}-antisite-related emissions in the infrared. For the studies of (Cu-C)-related defects carbon-rich starting material has been used. The Cu-C BE spectrum with maximum at about 1.4 eV has been observed for carbon rich crystals diffused with copper for diffusion temperatures larger than 850 °C.

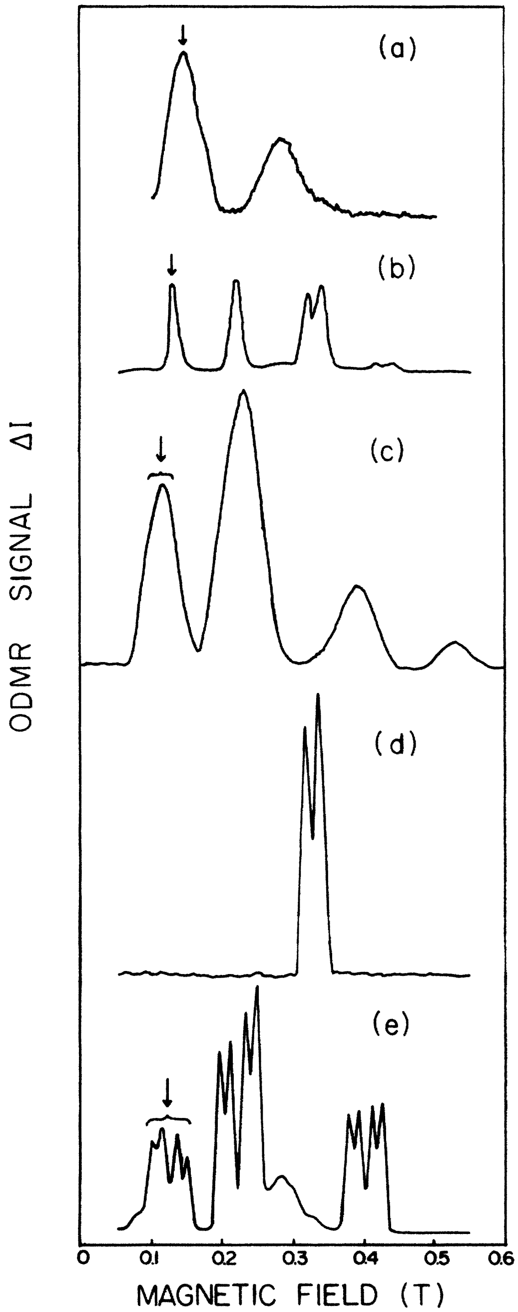

FIG. 1. The ODMR spectra of a range of bound excitons associated with neutral (isoelectronic) centers observed in copper-, lithium-, and carbon-doped GaP, taken with 5145-Å Ar^+ laser excitation and at 4 K. The spectra shown are due to (a) the 1.911-eV BE, (b) the $(Cu\text{-}Li)_V$ defect with no-phonon line at 2.172 eV, (c) a Cu-C-related defect with a 1.4-eV infrared PL band, (d) the 2.25-eV BE, and (e) an antisite-related P_{Ga}-Cu complex. "$\Delta m_s = 2$" transitions are marked with an arrow.

B. Summary of experimental results

The detailed analysis of the PL and ODMR spectra observed in these crystals can be found in the original papers.[3–5,8,10,11] In Fig. 1 we show the relevant ODMR spectra for five different spin-triplet BE systems studied by us recently. In the three first cases a strong "spin-forbidden" $\Delta m_s = 2$ transition has been observed (1.911 eV [Fig. 1(a)], $(Cu\text{-}Li)_V$ [Fig. 1(b)], and Cu-C [Fig. 1(c)], in contrast to the situation found for the 2.25-eV BE [Fig. 1(d)] (no $\Delta m_s = 2$ transition) and for the antisite related P_{Ga}-Cu complexes [Fig. 1(e)]. In the latter case a fairly weak $\Delta m_s = 2$ transition could be seen.

The relative intensity of the $\Delta m_s = 2$ resonance compared to the $\Delta m_s = 1$ one depends on the sample orientation, and the $\Delta m_s = 2$ transition has been found to be weakest for the magnetic field oriented along the principal axes of the g and D tensors, as shown in Fig. 2.

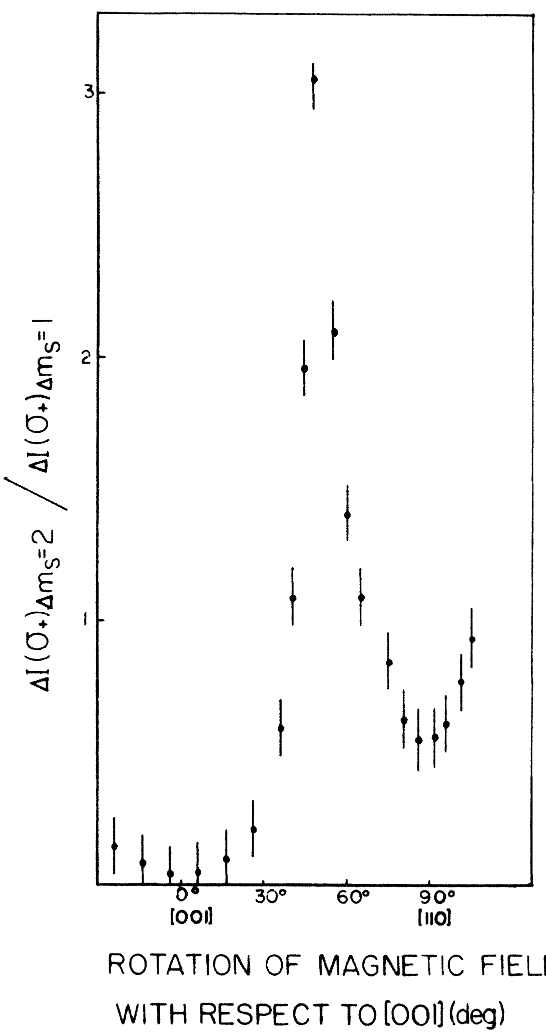

FIG. 2. The angular dependence of the relative strength of the low-field $\Delta m_s = 2$ resonance of the 1.911-eV BE. The relative magnitude of the $\Delta m_s = 2$ and $\Delta m_s = 1$ transition is distorted by the overlapping resonance lines, leading to an overestimation of the strength of the $\Delta m_s = 2$ transition.

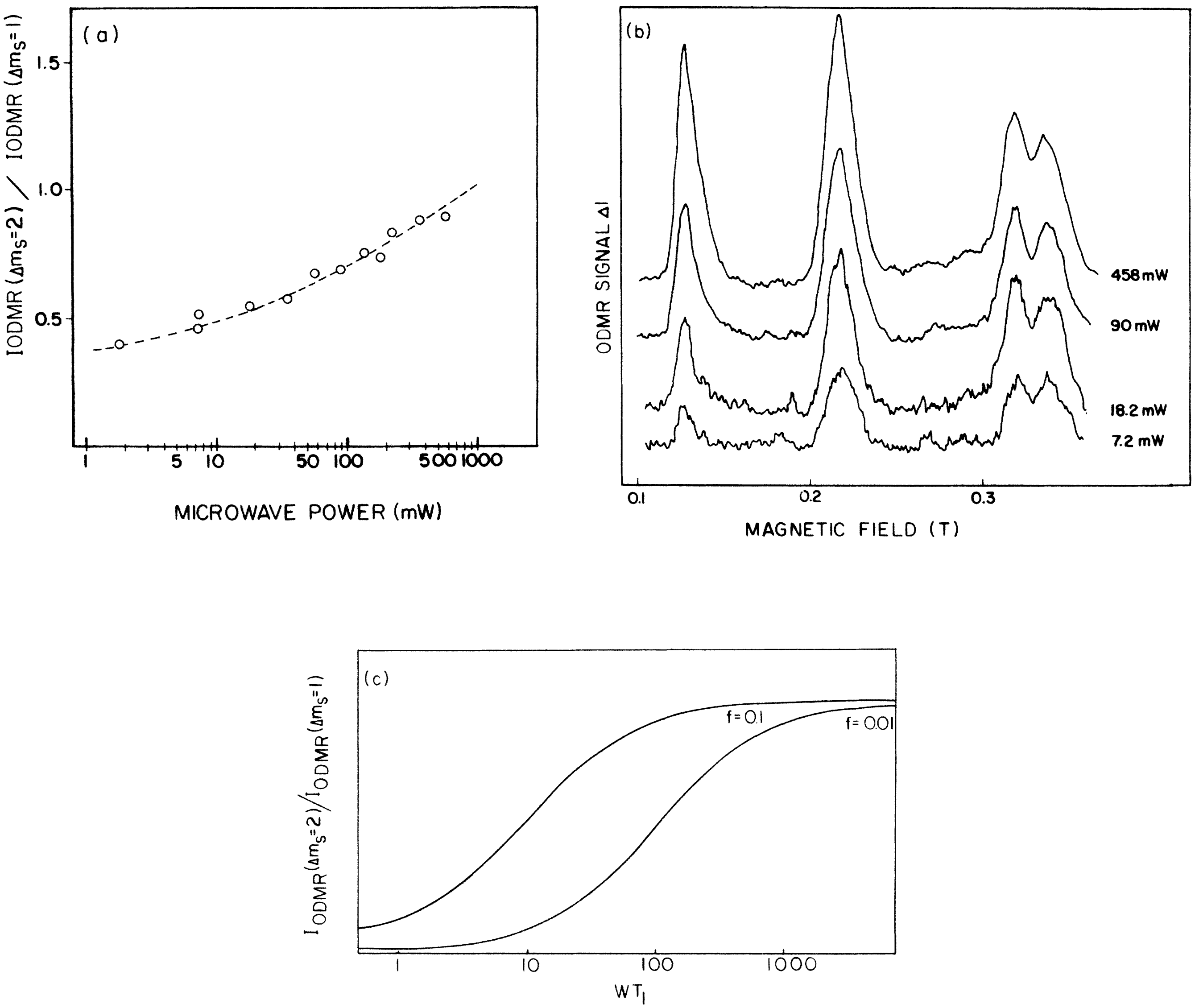

FIG. 3. (a) The microwave power dependence of the relative magnitudes of the $\Delta m_s=2$ and $\Delta m_s=1$ transitions in the ODMR spectrum of the (Cu-Li)$_V$ BE system at 4 K. In (b) the (Cu-Li)$_V$ resonance spectrum for four different microwave power levels is shown. The double-line structure at 0.33 T is due to the 2.25-eV BE system, showing a weaker microwave power dependence. (c) represents the dependence of the ratio of the $\Delta m_s=2$ and $\Delta m_s=1$ resonance signals on the transition rate (W) times spin-lattice relaxation times (T_1), calculated for two different admixtures of $|0\rangle$ to $|\pm 1\rangle$ spin functions ($f=0.01$ and $f=0.1$).

In Fig. 3(a) and 3(b) we show the microwave power dependence of the resonance signals for two distinctly different BE systems, i.e., the (Cu-Li)$_V$ BE with strong $\Delta m_s=2$ transitions, versus the 2.25-eV BE, for which only $\Delta m_s=1$ resonances have been observed in ODMR.

One of the most striking features of the strong $\Delta m_s=2$ transition systems is their rapid quenching observed when increasing the temperature. This is demonstrated in Fig. 4 for the (Cu-Li)$_V$ and 2.25-eV BE's. A strong temperature dependence of the BE ODMR spectra has been utilized by us in our previous studies to separate resonances of different origin, in cases where overlapping signals obscured the angular dependence measurements.[8,10,11] Three different antisite-related neutral defects, P_{Ga}-Cu (Ref. 9) and the so-called P_{Ga}-A, P_{Ga}-B (Ref. 11), could easily be separated by changing the temperature. The [110]-axis-oriented P_{Ga}-Cu defect dominates at 4 K, and has the strongest $\Delta m_s=2$ transition. Its ODMR spectrum has not been observed for elevated temperature, however, in which case the P_{Ga}-A and P_{Ga}-B complexes are still observed, both characterized by weak $\Delta m_s=2$ signals.

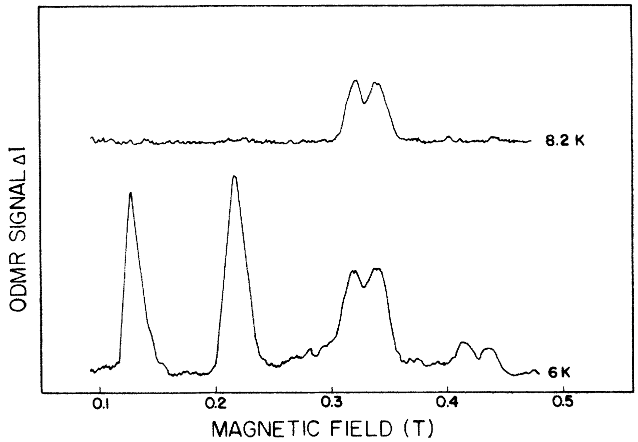

FIG. 4. The ODMR spectrum of a GaP:Cu-Li sample under 5145-Å excitation at two different temperatures, 6 and 8.2 K. The strongly structured ODMR spectrum observed at 6 K and lower temperatures disappears with rise in temperature. A double-line structure at 0.33 T is due to the 2.25-eV BE system ODMR, showing weaker temperature dependence. This spectrum is observed up to 25 K.

III. DISCUSSION

A. The singlet-triplet bound exciton configuration

The electronic structure of the bound excitons has recently been discussed in detail.[12,13] The S-T configuration of the BE excited state for complex neutral defects (a situation relevant for the BE's systems discussed in this work) results from quenching of the hole angular momentum by the low-symmetry local crystal field (strain field), leading to spinlike hole behavior. [The triplet ($S=1$) state occurs for parallel orientation of electron spin ($S_e=\frac{1}{2}$) and hole spin ($S_h=\frac{1}{2}$), while in the singlet states ($S=0$) these spins are antiparallel.] The main physical condition for quenching of the hole orbital angular momentum is the presence of a strong hole-attractive local potential, which ensures a strong overlap of the bound hole wave function with the defect potential, which should be of a low symmetry to leave an orbitally nondegenerate hole state at the lowest energy.[13] Such a situation typically arises for hole-attractive neutral complex defects in GaP (Refs. 3–9 and 14–24) and, as has recently been observed, also for "deep" BE systems for which both the electron and hole are tightly bound at the complex defect.[10,11] The energy splitting of the two S-T states is caused by the isotropic part of the electron-hole (e-h) exchange interaction, leaving the triplet state at the lowest energy. The anisotropic part of the e-h exchange interaction, the dipole-dipole e-h magnetic interaction, and the spin-orbit related so-called fine-structure splitting lead to splitting of the triplet. This splitting is, however, usually quite small when compared to the S-T separation.

The "standard" approach to describe the magnetic-resonance data obtained in the ODMR experiments for triplet BE systems is based on the concept of the $S=1$ spin Hamiltonian, originally introduced for the analysis of electron-spin resonance (ESR) data taken for the ground state of defect systems. This spin Hamiltonian is of the form[25]

$$\hat{\mathcal{H}}_s=\mu_B\hat{\mathbf{S}}\cdot\overleftrightarrow{g}\cdot\mathbf{B}+\hat{\mathbf{S}}\cdot\overleftrightarrow{D}\cdot\hat{\mathbf{S}}\ . \tag{1}$$

Before proceeding to further analysis of the triplet ODMR data it should be stressed here that even though formally the spin Hamiltonian given by Eq. (1) is analogous to the one used in the ESR studies, the g and D tensors appearing in Eq. (1) are of different nature for a BE system. $\overleftrightarrow{g}$ is given by the average of the electron (e) and hole (h) g tensors: $\overleftrightarrow{g}=\frac{1}{2}(\overleftrightarrow{g}_e+\overleftrightarrow{g}_h)$, whereas $\hat{\mathbf{S}}=\hat{\mathbf{S}}_e+\hat{\mathbf{S}}_h$. As already explained, the fine-structure term described by the D tensor may be dominated by the spin-spin magnetic interactions (spin-spin magnetic dipole-dipole interaction or anisotropic exchange interaction), a case rarely encounted in ESR studies.

If the S-T separation is small the Zeeman term of the form $\frac{1}{2}\mu_B(\hat{\mathbf{S}}_e-\hat{\mathbf{S}}_h)\cdot\Delta\overleftrightarrow{g}\cdot\mathbf{B}$ (where $\Delta\overleftrightarrow{g}=\overleftrightarrow{g}_e-\overleftrightarrow{g}_h$) may strongly admix singlet and triplet wave functions, and hence can change the resonance transition rates, radiative recombination rates, etc. This fact, not commonly realized, has been pointed out and discussed in detail in our recent publications.[4,26] The exchange splitting of the S-T configuration is, however, relatively large when compared to the Zeeman mixing term for most of the BE spectra we have studied in GaP. It is as large as 91 meV for the 1.911-eV BE,[4] but in the range of 1–2 meV for (Cu-Li)-related BE's (Refs. 3, 7, 8, and 26). Even in the latter case we found that the admixture of the higher singlet state still does not affect the triplet spin resonance measurably.[26] Therefore, in the further discussion we restrict ourself to the triplet state.

For the T_d-defect symmetry a spin triplet remains degenerate and is split by the magnetic field. In that case the spin-selection rules for the magnetic-dipole transitions are strict, and $\Delta m_s=2$ transitions are spin forbidden and are not observed. For lower defect symmetry this is no longer true, and off-diagonal Zeeman terms mix the spin functions of the $|0\rangle$ and $|\pm1\rangle$ sublevels of the triplet. The above explains the observation of formally spin-forbidden transitions in the ESR experiments. For example, for the case of Cr^{2+} ions in II-VI semiconductor compounds "strongly" spin-forbidden $\Delta m_s=4$ transitions have commonly been observed.[27–29] The relative intensity of the $\Delta m_s=2$ and $\Delta m_s=1$ transitions scales down with the rate of the spin-function admixture of the $m_s=0$ ($|0\rangle$) sublevel to the $m_s=1,-1$ ($|1\rangle, |-1\rangle$) ones, and may for large-zero-field splitting of the triplet sublevels be estimated by a perturbation approach, as being proportional, e.g., to $g_x\mu_B B/D$.

Taking typical parameters determined in recent ODMR studies for BE's in GaP such an admixture can be shown to be in the range of 10%. Therefore, even though the selection rules are relaxed, the $\Delta m_s=2$ transitions should be weak when compared to the $\Delta m_s=1$ ones, as commonly observed in ESR studies. The strong $\Delta m_s=2$ transitions observed for triplet BE's hence cannot be explained by a relaxation of the selection rules. As will be shown in the following section, the strength is a consequence of the resonance transitions within the excited states of the BE system. In this case the population of the spin sublevels must depend both on the feeding rates from higher excited states, and also on recombination rates, which both are spin dependent.

B. Rate-equation analysis of the spin triplet BE recombination

In this section we introduce the rate equations describing the kinetics of the triplet BE excited state regarding population, recombination, and magnetic-resonance-induced transitions. We follow here the approach introduced by Solomon[30] and Morigaki[31,32] for the discussions of the spin-dependent recombination. The symbols used in the rate equations are as follows: $n_{|0\rangle}, n_{|\pm1\rangle}$ refer to the population of $|0\rangle$, $|\pm1\rangle$ sublevels of the triplet,[33] $G_{|0\rangle}, G_{|\pm1\rangle}$ are the generation (feeding) rates of the triplet sublevels, $R_{|0\rangle}, R_{|\pm1\rangle}$ are the spin-dependent recombination rates (including transfer to another center) for the $|0\rangle$, $|\pm1\rangle$ sublevels of the triplet, T_1 is the spin-lattice relaxation time within the triplet subsystem, W_1-W_3 refer to the magnetic-resonance transition rates between the triplet sublevels $|0\rangle$ and $|\pm1\rangle$ ($W_{1,2}$) and $|1\rangle$ and $|-1\rangle$ (W_3); $E_{|1\rangle}$ and $E_{|-1\rangle}$ are the energy splittings between the sublevels $|1\rangle$ and $|0\rangle$ and $|-1\rangle$ and $|0\rangle$, respectively ($E_{|0\rangle}=0$). Finally, σ_+, σ_- denote the σ_+ and σ_- circularly polarized components of the BE emission in the Faraday configuration. The appropriate rate equations are then as follows:

$$\frac{dn_{|1\rangle}}{dt}=G_{|1\rangle}-R_{|1\rangle}n_{|1\rangle}+W_1(n_{|0\rangle}-n_{|1\rangle})+W_3(n_{|-1\rangle}-n_{|1\rangle})-\frac{1}{T_1}n_{|1\rangle}+\frac{1}{T_1}\frac{(n_{|1\rangle}+n_{|0\rangle}+n_{|-1\rangle})\exp(-E_{|1\rangle}/kT)}{[1+\exp(-E_{|1\rangle}/kT)+\exp(-E_{|-1\rangle}/kT)]} \tag{2}$$

$$\frac{dn_{|0\rangle}}{dt}=G_{|0\rangle}-R_{|0\rangle}n_{|0\rangle}+W_2(n_{|-1\rangle}-n_{|0\rangle})+W_1(n_{|1\rangle}-n_{|0\rangle})-\frac{1}{T_1}n_{|0\rangle}+\frac{1}{T_1}\frac{n_{|1\rangle}+n_{|0\rangle}+n_{|-1\rangle}}{[1+\exp(-E_{|1\rangle}/kT)+\exp(-E_{|-1\rangle}/kT)]} \tag{3}$$

$$\frac{dn_{|-1\rangle}}{dt}=G_{|-1\rangle}-R_{|-1\rangle}n_{|-1\rangle}+W_3(n_{|1\rangle}-n_{|-1\rangle})+W_2(n_{|0\rangle}-n_{|-1\rangle})-\frac{1}{T_1}n_{|1\rangle}+\frac{1}{T_1}\frac{(n_{|1\rangle}+n_{|0\rangle}+n_{|-1\rangle})\exp(-E_{|-1\rangle}/kT)}{[1+\exp(-E_{|1\rangle}/kT)+\exp(-E_{|-1\rangle}/kT)]}\ . \tag{4}$$

In Eqs. (2)–(4) the first two terms describe generation and recombination rates, respectively, for a given sublevel. The following two terms are related to the change in population of the sublevel at magnetic resonance, taking into account transitions both from and to the level. The last two terms in each of the equations account for the thermalization within the triplet sublevels, caused by the spin-lattice relaxation.

Equations (2)–(4) are now solved for the steady-state condition ($dn_{|i\rangle}/dt=0$) ($i=0,\pm1$) for two extreme experimental situations—thermalized and unthermalized system. (A thermalized system is understood here as a spin triplet where the relative population of the triplet sublevels are described by Boltzmann statistics. For an unthermalized system, on the other hand, the relative population of the sublevels depends only on the generation and recombination rates for each sublevel.) We feel that this approach enables us to get some general information about magnetic resonance and recombination rates without the necessity of performing elaborate calculations. Moreover, this is not a severe restriction, since most of the systems studied are commonly classified either as thermalized or unthermalized, and the number of intermediate situations seems to be quite limited.

For the unthermalized case the relative population of the $|0\rangle$ and $|\pm1\rangle$ sublevels is totally ruled by the generation and recombination rates, and terms with T_1 can simply be omitted. In contrast, for the thermalized case this population is ruled by a spin-lattice relaxation which is much faster than the relevant generation and recombination transitions. In the latter case, e.g., Eq. (2) takes the form

$$\frac{dn_{|1\rangle}}{dt}=W_1(n_{|0\rangle}-n_{|1\rangle})+W_3(n_{|-1\rangle}-n_{|1\rangle})-\frac{1}{T_1}n_{|1\rangle}+\frac{1}{T_1}\frac{G\exp(-E_{|1\rangle}/kT)}{[1+\exp(-E_{|1\rangle}/kT)+\exp(-E_{|-1\rangle}/kT)]}\ , \tag{5}$$

where G is an average generation rate for the triplet substates of the BE. Analogous equations can be introduced for the $|0\rangle$ and $|-1\rangle$ sublevels.

A further analysis of the rate equations is quite straightforward. We calculate first the magnetic-resonance-induced changes of the population of the $|0\rangle$ and $|\pm1\rangle$ sublevels for the $\Delta m_s=1$ and $\Delta m_s=2$ processes, whereas the strength of the ODMR signals for experiments performed in the Faraday configuration is calculated, from e.g.,

$$\frac{\Delta\sigma_+}{\sigma_+}=\frac{\sigma_+(\text{resonance})-\sigma_+}{\sigma_+} ,$$

where σ_+ is the intensity of the circularly polarized emission for microwaves off, being proportional to $n_{|1\rangle}$ ($\sigma_+ \propto n_{|1\rangle}$), and similarly for the σ_- emission. The resulting formulas are summarized in Table I for the unthermalized, and in Table II for the thermalized case of the triplet BE. The expressions for the total change of the emission intensity at resonance ($\Delta I/I$) have been obtained under the assumption that the σ components in the PL dominate over the π ones. Otherwise no approximations have been necessary to derive the formulas in Tables I and II.

The assumption of dominant σ components is obvious for the case of ODMR experiments in the Faraday configuration, where only σ components are detected in PL. In the case of the Voigt configuration and the C_{3V}-defect symmetry the π component may be observed only as a result of mixing of the triplet spin functions by the Zeeman term, and hence is very weak. For lower defect symmetry, the triplet spin functions are mixed even at zero magnetic field, and one might expect a noticeable contribution from the π component in PL. However, experimental data, e.g., from level-crossing measurements, indicate that the radiative recombination from the $|0\rangle$ sublevel of the triplets is slow, and that the σ components dominate in PL.

C. Analysis of the experimental results

In this section we apply the formulas obtained from the rate-equation analysis to obtain a relevant description of the experimental results. Before proceeding further we utilize first some characteristic properties of the S-T BE system. Such a BE is excited first in its singlet state, split from the lower energy triplet state by the exchange interaction. For direct excitation in the BE absorption spectrum, the electric-dipole-allowed ground-state-singlet–BE-singlet transition is strong, whereas the ground-state-singlet–BE-triplet transition is forbidden, and is only partially allowed at low defect symmetry, due to mixing of wave functions. In the case of band-to-band excitation, the capture to the higher singlet BE state occurs first, followed by a (usually fast) thermalization down to the triplet state. At low temperatures this thermalization dominates over the singlet-singlet radiative recombination, and the triplet substate is fed fast and may dominate in PL, as observed in many experiments.[3,7,9] The high success of the ODMR technique when applied to the S-T BE systems comes from the spin-memory effects. For most of the BE systems the S-T thermalization proceeds within the spin-memory time, which means that $G_{|0\rangle} \gg G_{|1\rangle}$ and $G_{|-1\rangle}$. This fact together with slow recombination from the $|0\rangle$ sublevel, as described above, explains the large ODMR signals typically observed for S-T BE configuration in GaP. Changes of the total light intensity at resonance as large as 5% have been reported.[3,4,26] This fact is utilized in the further discussion, where we analyze the relative strength of the $\Delta m_s=2$ and $\Delta m_s=1$ transitions for experiments performed in the Faraday configuration. We describe the ODMR data only for the σ_+ component of the emission, since analogous results are immediately derived for σ_- simply by replacing the relevant generation and recombination rates (see Tables I and II).

The following approximations are introduced in the further discussion of the *unthermalized*-triplet system. We assume that the feeding rates for the $|\pm1\rangle$ sublevels depend on the admixture of the $|0\rangle$ spin function to the $|\pm1\rangle$ ones, induced by the Zeeman terms in the spin Hamiltonian ($G_{|0\rangle}\equiv G$ and $G_{|\pm1\rangle}\simeq Gf$). The above is a consequence of the already-mentioned spin-memory effects in the S-T thermalization. The admixture of the $|0\rangle$ state into the $|1\rangle$ and $|-1\rangle$ spin functions is not exactly equal, but introduction of two parameters such as $f_{|0\rangle}(-1)$ and $f_{|0\rangle}(+1)$ would only complicate the final expression derived to estimate the relative intensity of $\Delta m_s=2$ and $\Delta m_{s=1}$ signals. [For the thermalized-triplet substates, this approximation is not needed, since then the sublevel populations are controlled by spin-lattice relaxation processes within the triplet, and an average feeding rate can be introduced, as in Eq. (5).] Since we analyze only the σ_+ component of the emission, the recombination rates from different sublevels of the triplet state depend on the admixture of the $|1\rangle$ spin function to $|0\rangle$ (approximation by the f parameter) and to $|-1\rangle$ (described by the g parameter). The relevant expressions for the ODMR signals for an *unthermalized* BE system are now as follows:

$$\frac{\Delta\sigma_+}{\sigma_+}(\Delta m_s=2)\simeq W_3\frac{1-g}{(1+g)W_3+Rg} , \tag{6}$$

$$\frac{\Delta\sigma_+}{\sigma_+}(\Delta m_s=1)\simeq \frac{W_1}{f}\frac{1-f}{(1+f)W_1+Rf} . \tag{7}$$

W_1 and W_3 in Eqs. (6) and (7) are the magnetic-resonance transition rates between the sublevels ($|0\rangle$ and $|1\rangle$) and ($|-1\rangle$ and $1\rangle$), respectively. The second transition is formally a spin-forbidden process, allowed by the admixture of the $|0\rangle$ spin function to both the $|1\rangle$ and $|-1\rangle$ substates (both described by the f parameter, $f \ll 1$), which means that $W_1\equiv W$ and $W_3\approx 2fW$. Including all the above approximations the relative strength of the $\Delta m_s=2$ versus $\Delta m_s=1$ transitions can be described as follows:

$$\Delta m_s=2/\Delta m_s=1\simeq 2f^2\frac{(1-g)(W+Rf)}{2fW(1+g)+Rg} \tag{8}$$

which for large microwave power (large W) takes the form

TABLE I. ODMR signal intensities for $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions for an unthermalized triplet BE system.

Transition	$\dfrac{\Delta\sigma_+}{\sigma_+}$	$\dfrac{\Delta\sigma_-}{\sigma_-}$	$\dfrac{\Delta I}{I}$
$\Delta m_s = 2$ $(\lvert -1\rangle \rightarrow \lvert 1\rangle)$	$\dfrac{W_3}{G_{\lvert 1\rangle}} \dfrac{R_{\lvert 1\rangle} G_{\lvert -1\rangle} - R_{\lvert -1\rangle} G_{\lvert 1\rangle}}{(R_{\lvert -1\rangle} + R_{\lvert 1\rangle}) W_3 + R_{\lvert -1\rangle} R_{\lvert 1\rangle}}$	$\dfrac{W_3}{G_{\lvert -1\rangle}} \dfrac{R_{\lvert -1\rangle} G_{\lvert 1\rangle} - R_{\lvert 1\rangle} G_{\lvert -1\rangle}}{(R_{\lvert -1\rangle} + R_{\lvert 1\rangle}) W_3 + R_{\lvert -1\rangle} R_{\lvert 1\rangle}}$	$W_3 \dfrac{G_{\lvert 1\rangle} R_{\lvert -1\rangle} - G_{\lvert -1\rangle} R_{\lvert 1\rangle}}{G_{\lvert 1\rangle} R_{\lvert -1\rangle} + G_{\lvert -1\rangle} R_{\lvert 1\rangle}} \times \dfrac{(R_{\lvert 1\rangle} - R_{\lvert -1\rangle})}{(R_{\lvert -1\rangle} + R_{\lvert 1\rangle}) W_3 + R_{\lvert -1\rangle} R_{\lvert 1\rangle}}$
$\Delta m_s = 1$ $(\lvert 0\rangle \rightarrow \lvert 1\rangle)$	$\dfrac{W_1}{G_{\lvert 1\rangle}} \dfrac{G_{\lvert 0\rangle} R_{\lvert 1\rangle} - G_{\lvert 1\rangle} R_{\lvert 0\rangle}}{R_{\lvert 0\rangle} R_{\lvert 1\rangle} + W_1 (R_{\lvert 0\rangle} + R_{\lvert 1\rangle})}$	0	$\dfrac{R_{\lvert 1\rangle} R_{\lvert -1\rangle} \omega_1}{G_{\lvert 1\rangle} R_{\lvert -1\rangle} + G_{\lvert -1\rangle} R_{\lvert 1\rangle}} \times \dfrac{G_{\lvert 0\rangle} - \dfrac{R_{\lvert 0\rangle}}{R_{\lvert 1\rangle}} G_{\lvert 1\rangle}}{R_{\lvert 0\rangle} R_{\lvert 1\rangle} + \omega_1 (R_{\lvert 0\rangle} + R_{\lvert 1\rangle})}$
$\Delta m_s = 1$ $(\lvert 0\rangle \rightarrow \lvert -1\rangle)$	0	$\dfrac{W_2}{G_{\lvert -1\rangle}} \dfrac{G_{\lvert 0\rangle} R_{\lvert -1\rangle} - G_{\lvert -1\rangle} R_{\lvert 0\rangle}}{R_{\lvert 0\rangle} R_{\lvert -1\rangle} + W_2 (R_{\lvert 0\rangle} + R_{\lvert -1\rangle})}$	$\dfrac{R_{\lvert 1\rangle} R_{\lvert -1\rangle} \omega_2}{G_{\lvert 1\rangle} R_{\lvert -1\rangle} + G_{\lvert -1\rangle} R_{\lvert 1\rangle}} \times \dfrac{G_{\lvert 0\rangle} - \dfrac{R_{\lvert 0\rangle}}{R_{\lvert -1\rangle}} G_{\lvert -1\rangle}}{R_{\lvert 0\rangle} R_{\lvert -1\rangle} + \omega_2 (R_{\lvert 0\rangle} + R_{\lvert -1\rangle})}$

TABLE II. ODMR signals intensities for $\Delta m_s=1$ and $\Delta m_s=2$ transitions for a thermalized triplet BE system.

Transition	$\frac{\Delta\sigma_+}{\sigma_+}$	$\frac{\Delta\sigma_-}{\sigma_-}$	$\frac{\Delta I}{I}$
$\Delta m_s=2$ $(\lvert -1\rangle \to \lvert 1\rangle)$	$\frac{W_3T_1\left[\exp\frac{E_{\lvert 1\rangle}}{kT}-1\right]}{1+W_3T_1}$	$\frac{(W_3T_1)^2\left[\exp\frac{E_{\lvert -1\rangle}}{kT}-1\right]}{(1+W_3T_1)^2}$	$\frac{W_3T_1}{1+W_3T_1} \times \frac{1-\left[\exp\left(\frac{E_{\lvert 1\rangle}}{kT}\right)+\exp\left(\frac{E_{\lvert -1\rangle}}{kT}\right)\right]+\frac{W_3T_1+\exp\left(-\frac{E_{\lvert 1\rangle}}{kT}\right)}{1+W_3T_1}}{\exp\left(-\frac{E_{\lvert 1\rangle}}{kT}\right)+\exp\left(-\frac{E_{\lvert -1\rangle}}{kT}\right)}$
$\Delta m_s=1$ $(\lvert 0\rangle \to \lvert 1\rangle)$	$\frac{W_1T_1\left[\exp\frac{E_{\lvert 1\rangle}}{kT}-1\right]}{1+2W_1T_1}$	0	$\frac{W_1T_1}{1+2W_1T_1}\frac{1-\exp\left(-\frac{E_{\lvert 1\rangle}}{kT}\right)}{\exp\left(-\frac{E_{\lvert 1\rangle}}{kT}\right)+\exp\left(-\frac{E_{\lvert -1\rangle}}{kT}\right)}$
$\Delta m_s=1$ $(\lvert 0\rangle \to \lvert -1\rangle)$	0	$\frac{W_2T_1\left[\exp\frac{E_{\lvert -1\rangle}}{kT}-1\right]}{1+2W_2T_1}$	$\frac{W_2T_1}{1+2W_2T_1}\frac{1-\exp\left(-\frac{E_{\lvert -1\rangle}}{kT}\right)}{\exp\left(-\frac{E_{\lvert 1\rangle}}{kT}\right)+\exp\left(-\frac{E_{\lvert -1\rangle}}{kT}\right)}$

$$\Delta m_s=2/\Delta m_s=1\approx f\frac{1-g}{1+g}\ , \tag{9}$$

and in the limit of the low microwave power ($W \ll Rf$) becomes

$$\Delta m_s=2/\Delta m_s=1\approx \frac{2f^3}{g}(1-g)\ . \tag{10}$$

It is evident from the form of Eqs. (8)–(10) that for an unthermalized-triplet BE system one should observe very strong $\Delta m_s=1$ transitions, whereas the $\Delta m_s=2$ transition is very weak ($f \ll 1$), if observed. This has a simple intuitive explanation. The large intensity of the $\Delta m_s=1$ transition is due to a large population difference between the $|0\rangle$ and $|\pm1\rangle$ sublevels. This population difference, in turn, is caused by a large $|0\rangle$ sublevel feeding rate and a slow radiative recombination rate from this sublevel.

A similar analysis for the *thermalized*-triplet bound-exciton state results in

$$\Delta m_s=2/\Delta m_s=1\simeq 2f\frac{1+2WT_1}{1+2fWT_1}\ . \tag{11}$$

This means that in the limit of large microwave power ($2fWT_1 \gg 1$) the $\Delta m_s=2$ ODMR signals approach twice the intensity of the $\Delta m_s=1$ transitions, as in fact observed in the experimental data shown in Fig. 1. In Fig. 3(c) we show the microwave power dependence (W is proportional to the microwave power) of the $\Delta m_s=2/\Delta m_s=1$ ratio of the ODMR signal intensities, calculated for two different f parameters ($f=0.01$ and $f=0.1$). This figure should be compared with the data shown in Figs. 3(a) and 3(b), where the microwave power dependences are shown for the 2.25 eV and the $(\text{Cu-Li})_V$ BE systems. The large intensities of the $\Delta m_s=2$ transitions resulting for large WT_1 (large microwave power and long spin-lattice relaxation times) are a consequence of a faster saturation of the $\Delta m_s=1$ transition and much larger population differences between the sublevels $|1\rangle$ and $|-1\rangle$ compared to that between $|0\rangle$ and $|+1\rangle$. This is of course a situation quite different from the one usually encountered in ESR experiments taken at the ground state of a given defect system.

A rather long T_1 relaxation time, necessary for observation of a relatively strong $\Delta m_s=2$ transition for a thermalized-triplet BE system, explains a puzzling connection between the strength of the $\Delta m_s=2$ transition and a fast temperature-induced quenching of the ODMR signals (see, e.g., the data shown in Fig. 4). As already stated the strong ODMR signals observed for the S-T configuration of the BE's are related to two conditions.

1. Fast thermalization between singlet and triplet substates leads to an increased role of the electric-dipole-forbidden triplet–ground-state-singlet transitions.

2. Due to spin-memory effects the $m_s=0$ sublevel of the triplet, which is characterized by slow radiative recombination, is fed much faster than the $m_s=\pm1$ sublevels.

Our analysis shows [Eq. (11)] that the strong $\Delta m_s=2$ ODMR transitions indicate a thermalized-triplet state with relatively large spin-lattice relaxation times. A large spin-lattice relaxation time T_1 within the triplet substates means, on the other hand, slower S-T transitions. Even though the spin-lattice relaxation time for S-T thermalization may be of a different magnitude from T_1, it is then possible that excited-state-singlet–ground-state-singlet recombination processes can dominate over the S-T thermalization.

The relative importance of these processes depends on both the S-T separation, which, e.g., for the two BE systems compared in Fig. 4 is fairly small (2 meV), and on the spin-lattice relaxation times. The strong $\Delta m_s=2$ transition for the $(\text{Cu-Li})_V$ BE, and its absence for the 2.25-eV BE, is explained by thermalized $(\text{Cu-Li})_V$ and unthermalized (2.25-eV BE) configurations, respectively, of the triplet states of these two BE systems. This can be verified by measuring the so-called level-crossing spectrum for the 2.25 eV and $(\text{Cu-Li})_V$ BE's. In this experiment we measure the intensity difference of the circularly polarized components of the PL ($\sigma_- - \sigma_+$) as a function of the magnetic field strength. For a thermalized system the $\sigma_- - \sigma_+$ difference increases with an increase in the magnetic-field strength due to an increase of the triplet energy splitting, as demonstrated in Fig. 5(a) for the $(\text{Cu-Li})_V$ BE system. For an unthermalized system, for which the $|\pm\rangle$ spin sublevels are not thermally coupled, the $\sigma_- - \sigma_+$ difference does not depend on the magnetic field strength. The data shown in Fig. 5(b) confirm our assumption of an unthermalized-triplet state for the 2.25-eV BE system.

The observed strong angular dependence of the intensity of the $\Delta m_s=2$ transition in the ODMR data (see Fig. 2) has a quite simple explanation. For a thermalized BE system (only in this case are the $\Delta m_s=2$ transitions relatively strong) the strength of the ODMR signal is described by

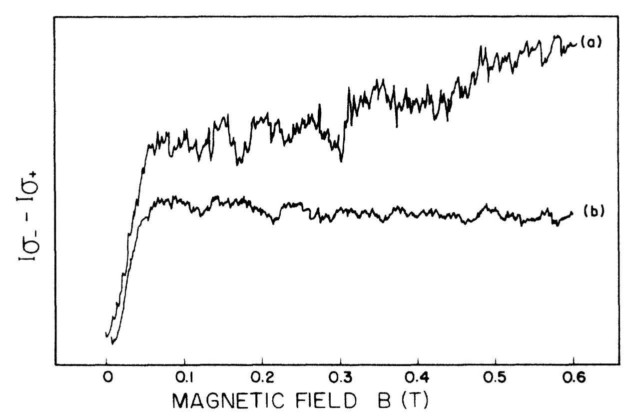

FIG. 5. The level-crossing spectrum for two BE systems: (a) the $(\text{Cu-Li})_V$ BE with no-phonon line at 2.172 eV and (b) the 2.25-eV BE. The experiment has been performed in the Faraday configuration and the difference between two circularly polarized components of the BE emissions has been measured. The rise of the $\sigma_- - \sigma_+$ difference with increase in magnetic field for the $(\text{Cu-Li})_V$ BE indicates a thermalized-spin-triplet excited state of this defect.

$$\frac{\Delta\sigma_+}{\sigma_+}(\Delta m_s=2)=\frac{2fWT_1[\exp(E_{|1\rangle}/kT)-1]}{1+2fWT_1} \tag{12}$$

which means that it is directly related to the admixture of the $|0\rangle$ wave function to the $|1\rangle$ wave function, described here by the f parameter. This is true, however, for low or intermediate microwave power. For large microwave power and long T_1 times ($2fWT_1 \gg 1$) we have

$$\frac{\Delta\sigma_+}{\sigma_+}(\Delta m_s=2)\approx[\exp(E_{|1\rangle}/kT)-1] \tag{13}$$

which means that practically it does not depend any longer on spin-selection rules, in striking contrast to the situation encountered in ESR studies. Then the relatively large ($\Delta m_s=2$) signals only relate to a large population difference between the $|1\rangle$ and $|-1\rangle$ sublevels. Otherwise (if the WT_1 term is small) the angular dependence of the $\Delta m_s=2$ ODMR signal intensity may be used for cross checking of the fit of the spin Hamiltonian to the experimental data. This transition should be of smallest intensity with the magnetic field along the main axes of the g tensor, where the admixture of the spin-$|0\rangle$ function is smallest (smallest f parameter). This conclusion is well demonstrated by the data shown in Fig. 2 for the 1.911-eV BE system, with [001] and [1$\bar{1}$0] major axes of the D- and g-tensor terms.[4]

IV. CONCLUSIONS

In this paper we explain the frequent observation of formally spin-forbidden $\Delta m_s=2$ transitions in the ODMR spectra of bound excitons with singlet-triplet configuration in GaP. It is shown that a strong $\Delta m_s=2$ transition is a fingerprint of thermalized sublevels of the triplet. Indirectly the strength of this transition is also a measure of the relative size of the magnetic-resonance transition rate W times the spin-lattice relaxation time T_1. For systems with strong $\Delta m_s=2$ transitions T_1 is relatively long. A strong decrease of the ODMR signal is expected at elevated temperatures, due to an efficient excited-state-singlet–ground-state-singlet radiative recombination. This singlet recombination is an electric-dipole-allowed process of much larger probability than the triplet–ground-state-singlet transition, and may dominate over the S-T thermalization.

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[33]For excitons bound at complex defects of low symmetry, the Zeeman and "fine-structure" terms mix the spin sublevels, and $|m_s\rangle$ are no longer proper wave functions. However, for simple reference, we keep the $|0\rangle$ and $|\pm1\rangle$ notation throughout this paper, even if formally not proper for centers of low symmetry.