Time-resolved spectroscopy of the level-anticrossing effect in exciton emission

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The paper reports a time-resolved study of the Zeeman (spin) sublevel anticrossing effect in triplet bound-exciton emission in GaSe crystals. The shape of the anticrossing signal was found to vary substantially during the excited-state lifetime. One observes, in particular, a splitting of the Lorentzian-shaped peak of the signal into two peaks, with their separation increasing with time. A theoretical description of the effect is proposed, which permits explanation of the nature of the observed changes and determination of the lifetime of the interacting states.

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The level-anticrossing effect was discovered by Eck, Foldy, and Wieder[1] in a study of the resonance fluorescence of atomic lithium. This effect has thereafter been widely used in optical spectroscopy to probe the fine structure of energy levels in various atomic systems, from atoms to crystals.[2–7] Level anticrossing occurs when one, slowly varying, perturbation (e.g., the magnetic field) tends to make levels degenerate, while another, a constant one (which can be an external factor or a specific feature of the system itself), prevents the levels from the degeneracy (i.e., from crossing).[1] The appearance of an anticrossing signal is accounted for by a change of the properties of the initial electronic states owing to their mixing, which is the largest in the region of the closest approach of the energy levels. The obvious merit of the method consists in the possibility of obtaining information on the parameters of quasidegenerate electronic states and their interaction in the conditions where the corresponding structure in the spectrum cannot be spectrally resolved because of the relatively broad emission lines, which may be caused, for instance, by inhomogeneous broadening. This situation is characteristic, in particular, of the spin structure of excitonic states in anisotropic semiconductors.

In the conditions of cw excitation, the level-anticrossing effect manifests itself in the form of a maximum or minimum of Lorentzian shape in the magnetic-field dependence of the intensity of the total emission from the states under study. (In Ref. 1 this change in the emission intensity was called the level-anticrossing signal.) However, our investigation of the level-anticrossing effect in the afterglow spectra of triplet bound excitons in GaSe crystals revealed that the above simple signal shape is only a particular case relating to the emission of excitons within a short time interval after the excitation.

This work was aimed at studying the level-anticrossing effect at various instants within the lifetime of the excitonic states. It is shown that during the exciton lifetime t the shape of the level-anticrossing signal undergoes substantial changes, from practically a zero signal at $t \approx 0$ to a Lorentzian peak at intermediate times t, to finally a complex double-peak structure at large t. The purpose of this paper is to demonstrate the evolution of the level-anticrossing signal during the exciton-state lifetime and to discuss its nature.

The crystals were grown by the Bridgman method and were not doped intentionally. The samples for the study were prepared from ingots by cleaving along the planes of the crystalline layers perpendicular to the optical axis c of the crystal. The exciton luminescence was excited by radiation from a pulsed copper-vapor laser with a pulse duration $\tau_p = 20$ ns. The excitation density was about 200 W/cm^2. The exciting radiation with photon energy $h\nu_{exc} = 2.144$ eV $> E_g$ (E_g is the crystal band gap) was incident at a small angle to the normal to the sample surface, and the emitted light was detected in the direction of the normal parallel to the c axis. The spectra were recorded using a grating spectrometer equipped with a photon-counting system with a time resolution ~ 30 ns. To investigate the emission at different instances of the exciton lifetime the detection gate of the photon-counting system was delayed with respect to the excitation pulse. During the experiment, the samples were kept immersed in liquid helium at 2 K. The magnetic field was produced by a superconducting coil and oriented parallel to the c axis of the crystal.

Figure 1 presents a GaSe emission spectrum in the region of the fundamental absorption edge, which was obtained during the first 30 ns after the excitation pulse. The shortest-wavelength line at $h\nu = 2.108$ eV is due to radiative recombination of free direct excitons, and the lines α and β with the maxima at 2.096 and 2.089 eV are produced by the emission of triplet excitons bound to ionized centers (or to isoelectronic traps).[8] The β line has an intense acoustic wing, whose maximum is shifted to lower energy by ~ 1 meV with respect to that of the β line.

In a longitudinal magnetic field $B \geqslant 2$ T (Faraday geometry, $\vec{B} \| c \| \vec{k}_{photon}$), the bound-exciton lines split into doublets, whose components are strictly right (σ^+) or left (σ^-) circularly polarized. While in weaker fields no splitting of the α and β lines is observed because of their relatively large widths, the magnetic-field dependence of the exciton emission intensity exhibits a hump,[8] which is due to the bound-exciton Zeeman sublevel anticrossing in the magnetic field. Because the magneto-optical effects on the α and β lines have the same pattern, we shall restrict ourselves in what follows to an analysis of the β line behavior.

Figure 2 shows $I_{\sigma^-}(B,t)$ dependence of the β-line intensity in σ^- polarization ($0 \leqslant B < 1$ T, $\vec{B} \| c \| \vec{k}_{photon}$) obtained at various delay times t with respect to the excitation pulse. (The detection gate width was $\Delta t \approx 30$ ns.) As seen from

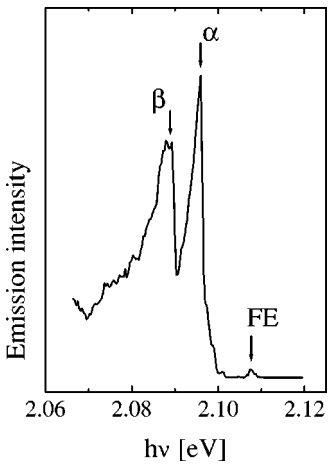

FIG. 1. Emission spectrum of GaSe crystal. $T=2$ K.

Fig. 2, at $t=0$ the $I_{\sigma^-}(B,0)$ plot exhibits only a barely discernible maximum at $B=0.36$ T$\equiv B_c'$. [For $\Delta t<30$ ns, the maximum in $I_{\sigma^-}(B,0)$ is practically indistinguishable.]

As the delay time is increased from 0 to 0.6 μs, the relative intensity of the maximum at 0.36 T increases dramatically (though the absolute β-line intensity measured at $B=0$ naturally decreases with increasing the delay), to produce a pronounced peak in the $B=B_c'$ region (see Fig. 2). Thus in this delay-time interval the $I_{\sigma^-}(B,t)$ relation obtained at a fixed t is similar to the $I_{\sigma^-}(B)$ dependence of the β-line σ^--emission intensity observed in the case of cw luminescence excitation.[8] As the delay time is progressively increased, the relative peak intensity continues to rise, but a shallow dip forms in the region of the peak maximum (Fig. 2). A further increase of t entails an increase of the dip width and depth (Fig. 2), so that at $t=2$ μs the $I(B,t)$ dependence

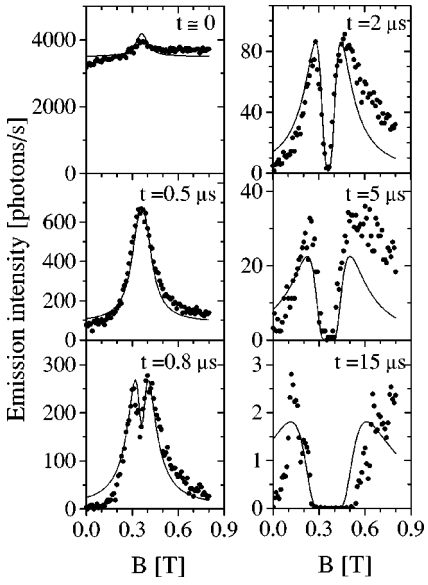

FIG. 2. Level-anticrossing signal in the β-exciton emission, $I_{\sigma^-}(B,t)$, measured at different times t during the excited-state lifetime. The time t is specified in the figure. The points are experimental data, and the solid lines are plots of the theoretical relation (6).

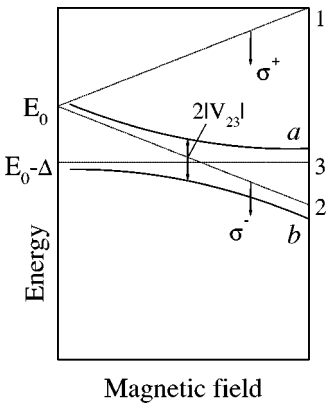

FIG. 3. Energy level diagram of the triplet exciton in GaSe in the presence of a magnetic field. $\vec{B}\|c$

exhibits already two well-resolved peaks, whose separation continues to grow with increasing t (Fig. 2). Thus, the experimental data presented demonstrate that the shape of the level-anticrossing signal measured at different instants within the bound-exciton lifetime varies essentially from a practically complete absence of the signal (at $t=0$) to a complex structure with two maxima (at large t).

To interpret the observed evolution of the level-anticrossing signal, consider the energy level structure of triplet bound excitons in GaSe. In GaSe crystals, the orbitally nondegenerate state Γ_4 of an exciton bound to an ionized center (or an isoelectronic trap), like the ground state of the free direct exciton,[9,10] is split by exchange interaction into two states, a singlet and a triplet one. For free excitons, the splitting between these states $\Delta_1=2$ meV.[9] The total electron and hole spin in a singlet exciton is zero, and transitions to this state are allowed for radiation polarized with $\vec{E}\|c$. In our experiment ($\vec{E}\perp c$), the singlet state does not manifest itself.

Triplet excitons have a total spin $S=1$ and spin projections on the c axis $S_z=0,\pm 1$. Optical transitions to the $S_z=\pm 1$ state are allowed in the $\vec{E}\perp c$ polarization, while the $S_z=0$ state is optically inactive. Because of the crystal anisotropy, the $S_z=0$ state is split from the $S_z=\pm 1$ states by an amount $\Delta \ll \Delta_1$ (Fig. 3). A longitudinal magnetic field $\vec{B}\|c$ splits the $S_z=\pm 1$ level into two sublevels with $S_z=+1$ and $S_z=-1$, which yield right-hand and left-hand circularly polarized emission, respectively (Fig. 3). The energies of the triplet exciton states in a longitudinal field are given by the expressions[10]

$$E_{1,2}=E_0\pm 0.5 g_{zz}\mu_0 B, \quad E_3=E_0-\Delta, \tag{1}$$

where g_{zz} is the longitudinal component of the exciton g factor, and μ_0 is the Bohr magneton. According to Eq. (1), in the field $B=2\Delta/g_{zz}\mu_0\equiv B_c$, the energies of states 2 and 3 become equal; i.e., the corresponding energy levels cross. We further assume the existence in the crystal of a static perturbation V (Ref. 11) which mixes the exciton states $|0\rangle$ and $|\pm 1\rangle$. In this case, the crossing of levels 2 and 3 will be replaced by their anticrossing (Fig. 3). Consider this effect in more detail. For $g_{zz}\mu_0 B\approx 2\Delta$, one will observe the mixing

primarily of states 2 and 3 (i.e., states $|-1\rangle$ and $|0\rangle$), because in these conditions the energy difference between these states will be substantially smaller than that between states 1 and 3. Taking into account the perturbation V, the wave functions $\Psi_{a,b}$ of the states originating from states 2 and 3 can be written as

$$\Psi_a = C_2\Psi_2 + C_3\Psi_3, \quad \Psi_b = C_3\Psi_2 - C_2\Psi_3. \tag{2}$$

Recalling that state 3 is optically inactive, one finds that the radiative transitions from states a and b are polarized in the same way as those from state 2. The coefficients $C_{2,3}$ are normalized to unity, $C_2^2 + C_3^2 = 1$, and have the form

$$C_{2,3}(B) = \frac{1}{\sqrt{2}}\left\{1 \pm \frac{\Delta' - 0.5 g_{zz}\mu_0 B}{[(\Delta' - 0.5 g_{zz}\mu_0 B)^2 + 4|V_{23}|^2]^{0.5}}\right\}^{0.5}, \tag{3}$$

where $V_{ik} = \langle \Psi_i | V | \Psi_k \rangle$ $(i,k = 2,3)$ and $\Delta' = \Delta + V_{22} - V_{33}$. The fraction of the optically active state 2 in the wave functions (2) determines the radiative lifetimes $\tau_{ar,br}$ of the states of triplet excitons with wave functions $\Psi_{a,b}$: $\tau_{ar}(B) = [C_2^2(B)\tau_r^{-1}]^{-1}$ and $\tau_{br}(B) = [C_3^2(B)\tau_r^{-1}]^{-1}$, where τ_r is the radiative lifetime of state 2. Assuming the nonradiative lifetime of bound triplet excitons τ_0 to be independent of their spin state, we obtain, for the total effective lifetimes of states a and b, $\tau_a(B) = [\tau_{ar}^{-1}(B) + \tau_0^{-1}]^{-1}$ and $\tau_b(B) = [\tau_{br}^{-1}(B) + \tau_0^{-1}]^{-1}$. When the crystal is excited by unpolarized light with $h\nu_{exc} > E_g$ and neglecting the exciton spin relaxation, the intensities of the emission from states a and b, $P_i(B,t)$ $(i = a,b)$, can be presented in the form

$$P_i(B,t) = P_0 \tau_{ir}^{-1}(B) \exp[-t/\tau_i(B)], \tag{4}$$

where the quantity P_0 is proportional to the exciton generation rate and is the same for all i. [Equation (4) was derived under the assumption that the excitation pulse duration $\tau_p < \tau_i$]. Because optical transitions from states a and b are not spectrally resolved, one observes experimentally the total emission

$$P_{\sigma^-}(B,t) = P_a(B,t) + P_b(B,t). \tag{5}$$

Strictly speaking, afterglow spectra are measured during a finite time interval Δt (in our case $\Delta t \approx 30$ ns), and therefore the experimentally measured signal should actually be written in the form

$$I_{\sigma^-}(B,t) = I_a(B,t) + I_b(B,t) = \frac{1}{\Delta t}\int_t^{t+\Delta t} P_{\sigma^-}(B,t)\,dt,$$

$$I_{a,b}(B,t) = \frac{1}{\Delta t}\int_t^{t+\Delta t} P_{a,b}(B,t)\,dt. \tag{6}$$

Figure 2 displays the relation calculated for different times t by solid lines. As seen from Fig. 2, relation (6) reflects quite well the features in the level-anticrossing signal observed at various instants during the exciton lifetime. The theoretical curves in Fig. 2 were obtained for the parameters $g_{zz} = 3.4$,[8] $\tau_r = 1.25 \times 10^{-7}$ s, $\tau_0 = 7 \times 10^{-6}$ s, $\Delta' = 0.0357$ meV, and $2|V_{23}| = 0.0045$ meV. The values of τ_r and τ_0 thus found permit one to determine the exciton effective lifetimes in initial states 2 and 3: $\tau_2 = 1.22 \times 10^{-7}$ s and $\tau_3 = \tau_0 = 7 \times 10^{-6}$ s.

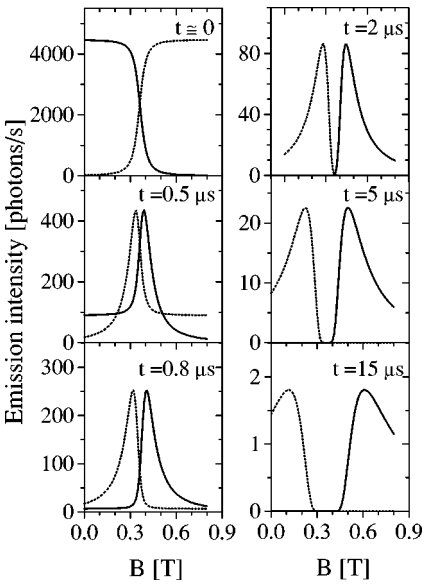

FIG. 4. Theoretical magnetic-field dependences of the intensity of radiative transitions from the excitonic states a and b, $I_a(B,t)$ (solid line) and $I_b(B,t)$ (dotted line), calculated for various instants t of their lifetime.

The reasons for the observed temporal evolution of the level-anticrossing signal can be conveniently considered by analyzing separately the behavior of the emission components $P_a(B,t)$ and $P_b(B,t)$ [or $I_a(B,t)$ and $I_a(B,t)$, if the finite width of the detection gate is taken into account]. As follows from Eq. (4), for $t = 0$, when the population of states a and b is determined only by the exciton generation rate in these states, the $P_a(B,0)$ and $P_b(B,0)$ relations simply reproduce the magnetic-field dependences of the exciton radiative-recombination probabilities in these states, $\tau_{ar}^{-1}(B)$ and $\tau_{br}^{-1}(B)$, respectively, with the total emission intensity $P_{\sigma^-}(B,0)$ being independent of B. However, for $t > 0$, the populations of states a and b are determined already not only by the exciton generation rate but by the rates of their decay in these states too, which are characterized by the exciton effective lifetimes $\tau_a(B)$ and $\tau_b(B)$. At fields $B \approx 2\Delta'/g_{zz}\mu_0 \equiv B_c'$, the lifetime of state a, $\tau_a(B)$, increases comparatively rapidly, whereas the radiative recombination rate $\tau_{ar}^{-1}(B)$ falls off (for state b one has the opposite situation). As a result of the competition between these opposite trends, at any time $t > 0$ the emission intensity of excitons from state a, $I_a(B,t)$, near $B \approx B_c'$ first reaches a maximum, to subsequently fall off as B continues to increase. The emission component $I_b(B,t)$ in the field follows a similar behavior, but the maximum is reached here at a different field than for $I_a(B,t)$ (Fig. 4). As a result, at not too large t the total emission intensity $I_{\sigma^-}(B,t)$ exhibits a maximum at $B = B_c'$ (Fig. 2). (It is the exciton emission in this time interval that determines primarily the profile of the level anticrossing signal of triplet excitons under cw excitation.) As the delay time

t increases, the maximum of the $I_a(B,t)$ function shifts toward higher magnetic fields, whereas that of $I_b(B,t)$ displaces in the opposite direction. Starting from certain values of $t \geqslant 4\tau_r$, this gives rise to the formation in the $I_{\sigma^-}(B,t)$ dependence of two maxima separated by a minimum (dip) at $B=B_c'$, whose relative depth increases with t (Figs. 2 and 4). [Actually, the existence of the minimum is connected with the fact that the total exciton effective lifetime in states a and b, $\tau_a(B)+\tau_b(B)$, reaches a minimum at $B=B_c'$, and therefore both states turn out to be depleted in this field region for long enough times t.] It should be stressed that one of the maxima in $I_{\sigma^-}(B,t)$ corresponds to the contribution of state a to the emission and the other to the emission from state b. Thus by investigating the level-anticrossing effect at different instants during the excited-state lifetimes one can isolate the contribution of each of the states to the emission, although the radiative transitions from these states (i.e., a and b) are not resolved spectrally.

To sum up, an investigation of the level-anticrossing effect in afterglow spectra reveals that the well-known shape of the anticrossing signal in the form of a simple maximum (minimum) is only a particular case corresponding to the emission of a system at a certain time after the excitation. The signal profile may vary substantially with time, and it is possible to isolate the contributions to this signal due to different interacting states which cannot be discriminated spectrally in emission. It should be added that investigation of the level-anticrossing effect in afterglow spectra offers also, in principle, a possibility of obtaining information on the lifetimes of any one of the interacting states. We note also that the phenomenon observed should have a fairly general character and be observable in various atomic systems.

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