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Time-resolved zero-field optically detected magnetic-resonance study of the $(Cu\text{-}Li)_V$ neutral defect complex in GaP

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A study of the lowest excited triplet state T_0 of the neutral hole-attractive defect complex $(Cu\text{-}Li)_V$ in GaP with the aid of both cw and time-resolved optically detected magnetic resonance in zero magnetic field is presented. From the cw experiments, the zero-field splitting of T_0 is determined, and it is concluded that the $(Cu\text{-}Li)_V$ defect is of C_{2v} or lower symmetry. From time-resolved microwave-induced delayed phosphorescence experiments, information on the dynamics of population and decay of the T_0 substates is obtained. A large difference in the total and radiative decay rates of the spin levels is found. The interpretation of these results in terms of spin-orbit coupling is not yet possible because a detailed model for the electronic structure of the $(Cu\text{-}Li)_V$ defect is lacking. It is observed that the creation of the photoexcited triplet state via capture of a conduction electron by the ionized defect does not show any spin selectivity, in contrast to the decay from the triplet sublevels.

I. INTRODUCTION

During the past few years there has been considerable interest in neutral or "isoelectronic" defect complexes in semiconductors. Unlike donors and acceptors, they do not contribute excess holes or electrons to the semiconducting material, but in many cases they introduce localized electronic states within the forbidden band gap. The excited states of these complex defects are usually described in terms of bound excitons.[1,2]

There are two groups of isoelectronic complex defects: hole-attractive and electron-attractive.[3] In the first type, the hole of the bound exciton is tightly bound to the defect and usually the orbital angular momentum is quenched as a result of the low symmetry of the local crystal field. Thus only its spin angular momentum is retained, and in combination with the spin of the electron, excited singlet and triplet states are formed within the band gap. The triplet states are at somewhat lower energy with respect to the singlet states as a result of the electron-hole exchange interaction.[4]

Since the recombination of the excitons bound to the neutral defect complexes is usually of a radiative nature, one can study the electronic structure of the bound exciton by means of photoluminescence spectroscopy. More detailed information is obtained with (optically detected) magnetic-resonance (ODMR) spectroscopy by making use of the paramagnetic character of the excited triplet state. In the recent past, several studies of such defects in magnetic field have been carried out.[2]

So far very few zero-field ODMR experiments on bound excitons have been reported,[5] in contrast to the situation in molecular crystals.[6,7] It is well-known that in zero field the degeneracy of the spin levels of the excited triplet state T_0 is lifted as a result of the low symmetry of the defect. These splittings can be determined very accurately in cw zero-field ODMR experiments. In addition, by using time-resolved ODMR techniques such as microwave-induced delayed phosphorescence (MIDP), one obtains information on the dynamic properties of the triplet sublevels such as their populating and decay rates. Such information is valuable for understanding the role of the spin-orbit coupling in the exciton bound to the complex defect.

In this paper we describe the results of a zero-field ODMR study of the $(Cu\text{-}Li)_V$ neutral defect complex in GaP. This hole-attractive defect has been studied previously by both optical spectroscopy[8] and X-band ODMR,[9] and the results prove that the photoluminescence stems from a metastable triplet state T_0. From the zero-field ODMR study presented here we not only obtain very precise values of the zero-field splitting parameters, but also detailed information about the dynamic properties of the triplet spin levels.

II. cw AND TIME-RESOLVED OPTICAL DETECTION OF MAGNETIC RESONANCE

In Fig. 1 the sublevels T_x, T_y, and T_z of the triplet state T_0 of the $(Cu\text{-}Li)_V$ complex are shown. N_i denotes the population of the ith sublevel, P_i the populating rate, and k_i and k_i^r the total decay rate and radiative decay rate, respectively. The splitting of the sublevels of T_0 is caused by spin-spin interaction with a possible contribution of second-order spin-orbit interaction.[10] The electric-dipole transition from the excited triplet state T_0 to the singlet ground state S_0 is spin forbidden. However, spin-orbit coupling gives the triplet state some singlet

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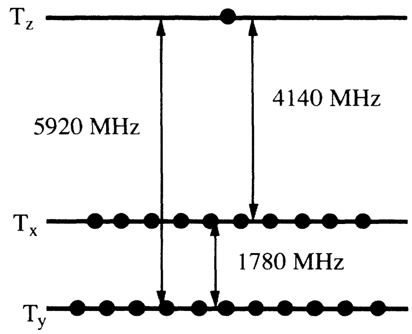

FIG. 1. Zero-field splitting of the lowest excited triplet state T_0 of the $(Cu\text{-}Li)_V$ defect complex. The labels of the spin levels are according to Ref. 9. The dots are a measure for the steady-state populations of the substates.

character derived from excited singlet states,[11] and as a consequence this selection rule is relaxed. Since the mixing of the triplet state with the excited singlet states through spin-orbit interaction is spin selective, the radiative decay rates k_i^r of the triplet sublevels usually differ strongly. It is this property that is used for the optical detection of magnetic-dipole transitions between the triplet sublevels.

In the cw ODMR experiments one monitors the phosphorescence from the lowest excited triplet state of the defect under continuous optical excitation while slowly varying the frequency of an applied microwave field. When the microwaves are resonant with one of the zero-field splittings, population is transferred from a radiative to a less radiative sublevel or vice versa, resulting in a decrease or increase of the phosphorescence intensity.

In the time-resolved MIDP experiments the optical and microwave irradiation are applied in a pulsed manner. If the triplet sublevels are isolated, i.e., if the spin-lattice-relaxation (SLR) rates among the sublevels are slow compared to the decay rates k_i, this method allows us to determine the decay rates k_i, the relative radiative decay rates k_i^r, and the relative populating rates P_i of the sublevels.[7] In the case of the triplet state T_0 of the $(Cu\text{-}Li)_V$ defect this condition appears to be fulfilled at 1.2 K, as is evident from the experimental results shown below. In the experiment we first apply optical excitation during a period long enough to establish a steady-state population:

$$N_i = \frac{P_i}{k_i} \quad (i = x, y, z) \tag{1}$$

over the three sublevels. If the laser is then suddenly shut off at $t=0$, the decay of the phosphorescence intensity, shown in Fig. 2(a), is described by

$$I_{ph}(t) = c[k_x^r N_x(0)\exp(-k_x t) + k_y^r N_y(0)\exp(-k_y t) + k_z^r N_z(0)\exp(-k_z t)] , \tag{2}$$

where c is a constant depending on experimental conditions.

At a time t_d after shutting off the optical excitation, a microwave pulse, resonant with, for instance, the zero-field splitting between levels T_z and T_y, is given. In Fig. 2(b), a typical result of this experiment is shown. The pulse length is chosen short compared to the lifetimes k_z^{-1} and k_y^{-1} such that the total population of the levels T_z and T_y is approximately constant during the microwave pulse. Then, the phosphorescence intensity $I_{ph,m}$ after the resonant microwave pulse is given by

$$I_{ph,m}(t) = c\{N_z(t_d) + f[N_y(t_d) - N_z(t_d)]\}k_z^r\exp[-k_z(t-t_d)] + c\{N_y(t_d) - f[N_y(t_d) - N_z(t_d)]\}k_y^r\exp[-k_y(t-t_d)] + cN_x(t_d)k_x^r\exp[-k_x(t-t_d)] . \tag{3}$$

The factor f is called the transfer factor and is a measure for the population transferred by the microwave pulse from level T_y to T_z or vice versa.

The signal obtained from the difference of the phosphorescence decay curves with and without a microwave pulse at $t=t_d$ is called the microwave-induced delayed phosphorescence (MIDP) signal and is described by the difference of Eqs. (2) and (3) for $t \geq t_d$:

$$I_{MIDP}(t) = cf[N_y(t_d) - N_z(t_d)]\{k_z^r\exp[-k_z(t-t_d)] - k_y^r\exp[-k_y(t-t_d)]\} . \tag{4}$$

From Eq. (4) it follows that the MIDP signal can be fitted to the difference of two exponentials, the time constants of which correspond to the decay rates k_z and k_y of the triplet sublevels connected by the microwave pulse. The ratio of the prefactors of the two exponentials gives the ratio of the radiative decay rates k_z^r and k_y^r.

The amplitude of the MIDP signal at $t=t_d$ is given by

$$I_{MIDP}(t_d) = cf(k_z^r - k_y^r)[N_y(0)\exp(-k_y t_d) - N_z(0)\exp(-k_z t_d)] . \tag{5}$$

Thus, repeating the experiment and measuring this amplitude as a function of t_d, one finds a decay curve described again by the difference of two exponentials with time constants equal to the decay rates k_z and k_y. From the ratio of the prefactors of the exponentials, the ratio of the steady-state populations $N_z(0)$ and $N_y(0)$ can be determined. If the relative values for $N_z(0)$ and $N_y(0)$ and the decay rates k_z and k_y are known, the relative

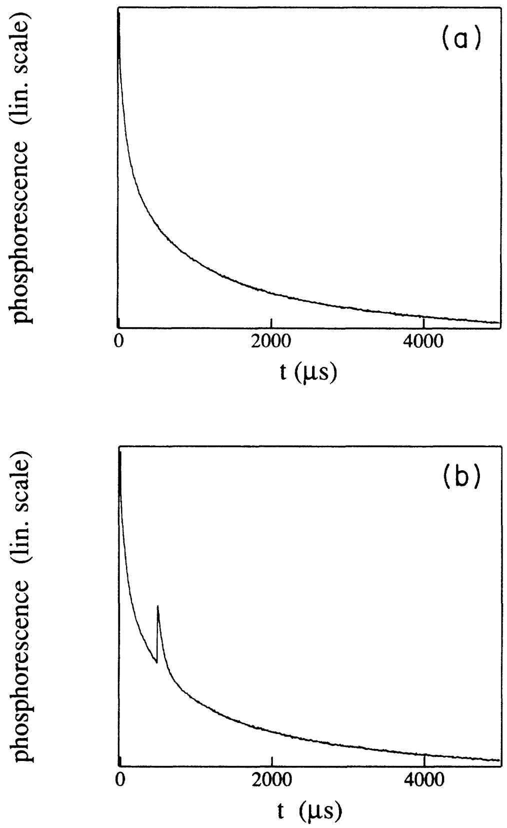

FIG. 2. The decay of the phosphorescence intensity after shutting off the laser at $t=0$ (a) without a microwave pulse and (b) with a 5920-MHz microwave pulse resonant with the yz transition at $t_d=500$ μs.

populating rates P_i can be calculated with the aid of Eq. (1). By performing similar experiments on the xz or xy transition, the dynamic properties of the T_x level can be obtained in a similar way.

III. EXPERIMENT

In both cw and time-resolved ODMR experiments, the GaP:(Cu-Li)$_V$ sample was immersed in liquid helium pumped down to a pressure corresponding to 1.2 K. The (Cu-Li)$_V$ defect was excited via the conduction band with a Spectra Physics 2016 Ar-ion laser (all lines, 30 mW). The luminescence from the GaP crystal was passed through a 570-nm optical high-pass filter and detected with an S4 photomultiplier (Hamamatsu 931A).

The microwave source consisted of a Hewlett Packard 8690B sweep oscillator in combination with the HP 8691B (1 to 2 GHz) or the HP 8693B (4 to 8 GHz) backward wave oscillator. The output could be amplified with a Varian traveling wave tube amplifier to a maximum power of 10 W. When working in the frequency range from 1 to 2 GHz, a 2000-MHz low-pass filter was placed after the TWT amplifier to suppress higher harmonics.

In the case of the cw ODMR experiments the sample was placed in a helix and continuously irradiated with the laser. The microwaves were amplitude modulated at a frequency of 1.2 kHz with the help of a HP p-i-n diode switch and the ODMR signal was obtained by synchronous detection of the phosphorescence intensity.

For the time-resolved experiments the helix was replaced by a tunable (1 to 2 GHz or 4 to 8 GHz) re-entrant cavity.[12,13] The advantage here is that a higher B_1 field with a well-defined polarization can be obtained. Light access is provided by two holes in the walls of the cavity allowing for optical excitation and detection at right angles. After excitation of the (Cu-Li)$_V$ defect during 30 ms the laser was shut off by means of a Quantum Technology acousto-optic modulator, and a time t_d later a 5-μs microwave pulse resonant with one of the zero-field transitions was applied. The decay of the phosphorescence intensity with and without a microwave pulse were both recorded with a LeCroy 9400 digital oscilloscope and averaged if necessary. Subsequently, the two traces were subtracted from each other to obtain the MIDP signal.

IV. RESULTS AND DISCUSSION

A. cw experiments

Three zero-field transitions, shown in Fig. 3, are observed. The transitions at 5920 and 4140 MHz both correspond to an increase of about 9% in phosphorescence intensity, whereas the transition at 1780 MHz corresponds to an increase of about 0.9%. The observed zero-field frequencies, which are depicted in Fig. 1, are in good agreement with the zero-field splitting derived from X-band ODMR data.[9]

Labeling the triplet subcomponents as in Ref. 9, the zero-field splitting parameters X, Y, and Z can be calculated from the resonance frequencies, giving

$$X=-787(\pm 10)\ \text{MHz}\ ,$$

$$Y=-2567(\pm 10)\ \text{MHz}\ ,$$

$$Z=3353(\pm 10)\ \text{MHz}\ .$$

Since the ordering of the triplet sublevels cannot be obtained directly from the ODMR experiment, the values X, Y, and Z given above can have the opposite sign. However, from the fact that the threefold degeneracy of T_0 is completely lifted, it can be concluded that the three spin axes x, y, and z are inequivalent. As a consequence, the (Cu-Li)$_V$ defect is of rhombic or lower symmetry, which is consistent with the C_{2v} assignment for the defect symmetry based on the X-band ODMR experiments.[9]

All three zero-field transitions have a full width at half maximum of 50($\pm$5) MHz and are probably inhomogeneously broadened. In contrast, the linewidth of the ODMR transitions at 9 GHz, in a magnetic field, is about 10 mT, which corresponds to 280 MHz for $g\approx 2$. This considerable difference in linewidth can be understood in terms of magnetic hyperfine interaction. Since in zero magnetic field the expectation value for the electronic spin is zero for all three triplet sublevels, no first-order hyperfine splitting of the substates occurs. However, with the external magnetic field turned on, the hyperfine interaction becomes a first-order effect. Then the spin is almost quantized along the direction of the magnetic field and the three Zeeman levels in good approximation are given by the eigenfunctions $m_s=+1$, 0, and -1 of S_z.

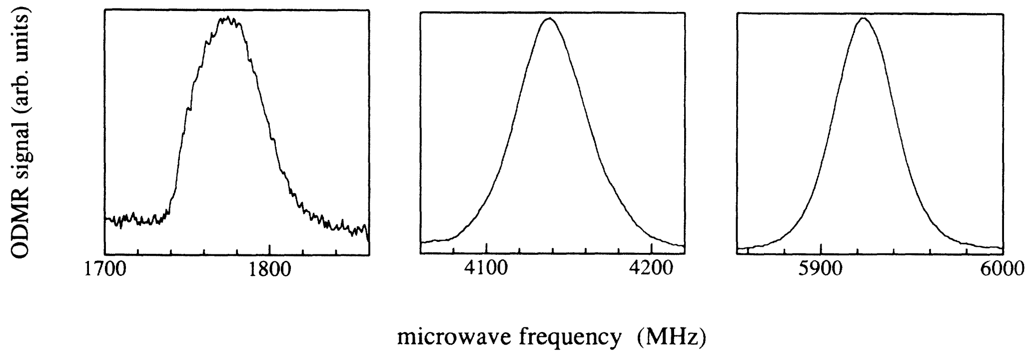

FIG. 3. The three zero-field ODMR transitions obtained for the $(Cu\text{-}Li)_V$ defect. The transition at 1780 MHz corresponds to an increase in phosphorescence intensity of 0.9%; the other two transitions both correspond to an increase of about 9%.

From a comparison of the linewidth of the zero-field and X-band ODMR transitions, the hyperfine coupling constant is estimated to have a value between 50 and 250 MHz. Since in the case of a complex isoelectronic defect such as the $(Cu\text{-}Li)_V$ defect the hole and the electron are more or less tightly bound to the defect, this large value might be interpreted in terms of a significant Fermi contact contribution to the hyperfine splitting of the atoms making up the defect.

B. Microwave-induced delayed phosphorescence

The MIDP experiments were carried out at 5920 and 4140 MHz because at these frequencies much stronger signals were obtained than at 1780 MHz. For both of these transitions the MIDP signal was recorded for different values of t_d.

In Fig. 4(a) the result of the MIDP experiment is shown obtained with a microwave pulse resonant with

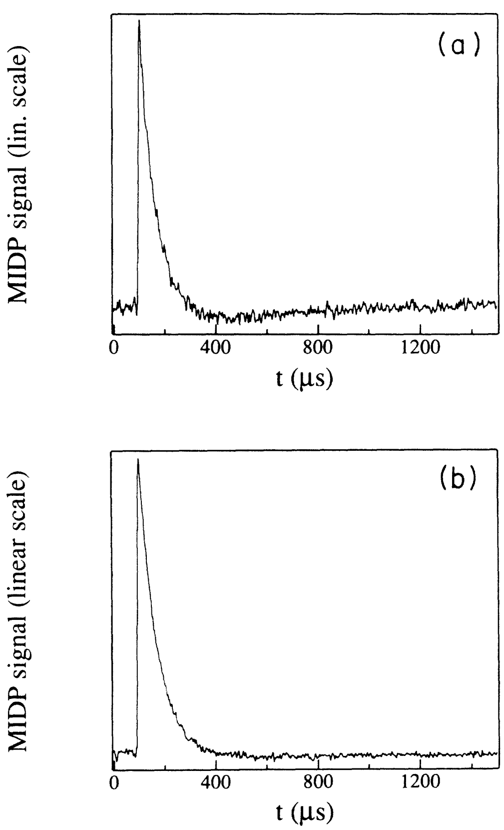

FIG. 4. Typical MIDP signals for (a) the xz transition at 4140 MHz and (b) the yz transition at 5920 MHz. Both signals were obtained by substraction of a decay curve of the type indicated in Fig. 2(a) from one of the types indicated in Fig. 2(b). The resonant microwave pulse with a duration of 5 μs is applied at a time $t_d = 100$ μs after shutting off the optical excitation.

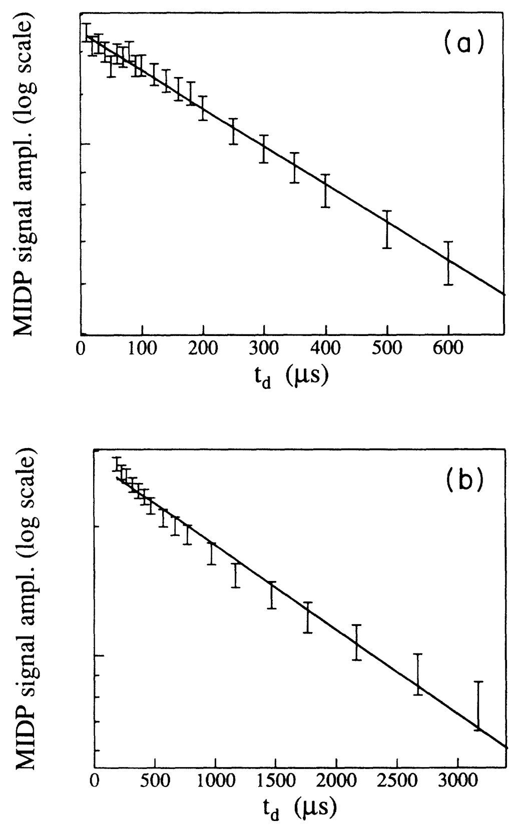

FIG. 5. Semilogarithmic plot of the MIDP signal height at $t = t_d$ for (a) the xz transition at 4140 MHz shown in Fig. 4(a) and (b) the yz transition at 5920 MHz shown in Fig. 4(b). The solid lines are monoexponential functions fitted to the data points according to Eq. (5). The fitting parameters are given in Table I.

TABLE I. The decay rates k_i and the relative radiative decay rates k_i^r, steady-state populations N_i, and populating rates P_i of the T_0 sublevels as determined in the MIDP experiments.

	k_i (s^{-1})	k_i^r	N_i	P_i
T_x	1515±70	0.09	≥ 10	≥ 1
T_y	480±50	≤ 0.1	≥ 10	≥ 0.3
T_z	13 900±400	1	1	1

the 4140-MHz transition at a time $t_d = 100$ μs after shutting off the laser. As expected from Eq. (4), this signal can be fitted to the difference of two exponentials, yielding $k_z^{-1} = 71(\pm 3)$ μs, $k_x^{-1} = 660(\pm 30)$ μs, and $(k_z^r/k_x^r) = 11(\pm 1)$.

The height of the MIDP signal at t_d is plotted in Fig. 5(a) as a function of t_d. Contrary to what one expects from Eq. (5), these data can only be fitted to one exponential with a time constant of $600(\pm 70)$ μs. This implies that the prefactor of one of the exponentials dominates. Taking into account the errors in the signal height, we conclude that $N_x(0) \geq 10 N_z(0)$.

A typical MIDP signal for the 5920-MHz zero-field transition is shown in Fig. 4(b). This signal can also only be fitted to one exponential with a time constant $k_z^{-1} = 72(\pm 2)$ μs, in contrast to what one would expect on the basis of Eq. (4). Thus the radiative decay rate of one sublevel is at least 10 times larger than the other: $k_z^r \geq 10 k_y^r$. The plot of the signal height at $t = t_d$ as a function of t_d for the MIDP experiments on the 5920-MHz transition shown in Fig. 5(b) also yields a single exponential from which we can extract $k_y^{-1} = 2100(\pm 200)$ μs. Again, using the same arguments as above, we can conclude that one sublevel has a steady-state population that is at least 10 times larger than the other: $N_y(0) \geq 10 N_z(0)$.

Combining the results of the time-resolved experiments described above, we find the values as indicated in Table I. The significant difference between k_x, k_y, and k_z justifies the assumption that the spin-lattice-relaxation rate is slow compared to the decay rates at 1.2 K. If the triplet sublevels would not be thermally isolated, the different decay channels of the sublevels would be connected and the decay rates would be nearly equal.

Also shown in Table I are the relative populating rates P_i calculated from the decay rates k_i and the relative steady-state populations N_i with the aid of Eq. (1). These results indicate that the difference in populating rates is much smaller than the difference in the decay rates. This nearly complete lack of spin selectivity in the population of the triplet sublevels is hardly surprising in view of the fact that the $(Cu\text{-}Li)_V$ defect was excited via the conduction band. Consequently several processes such as the energy transfer reported previously[14] can contribute to the formation of the lowest excited triplet state of the defect.

From the relative radiative decay rates k_i^r it is clear that the T_z sublevel is much more radiative than the T_x sublevel, while the decay from the T_y sublevel is nearly completely nonradiative. This means that in particular the T_z sublevel is mixed with the excited singlet states through spin-orbit coupling. To understand this result, a detailed model of the defect and its electronic structure is needed. Unfortunately, this model of the $(Cu\text{-}Li)_V$ defect is still a matter of speculation.

V. CONCLUSION

Studying the $(Cu\text{-}Li)_V$ neutral defect complex in GaP by zero-field ODMR we have demonstrated the usefulness of this technique to obtain new results which might be helpful in the understanding of this type of defect in semiconductors. The cw experiments enable a direct determination of the zero-field splitting of the lowest excited triplet state T_0 from which the defect symmetry can be deduced. In the case of the $(Cu\text{-}Li)_V$ defect the degeneracy of the T_0 sublevels is completely lifted and thus the defect symmetry must be C_{2v} or lower.

From time-resolved MIDP experiments the dynamic properties of the T_0 substates are obtained. Similar to the situation in molecular triplet states, we find a large difference in the decay rates of the three spin levels. Moreover the phosphorescence from T_0 is mainly due to the T_z spin level. Thus far we cannot interpret these results because the detailed electronic structure of the $(Cu\text{-}Li)_V$ defect is not yet known. However, when more information on the microscopic defect geometry becomes available, these data can be of importance in the interpretation of the electronic structure.

Surprisingly, in contrast to the decay rates, the populating rates are nearly equal. This observation leads us to the conclusion that the creation of the bound exciton at the $(Cu\text{-}Li)_V$ complex is likely to be composed of several processes with different or no spin selectivity.

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