Investigation of the (Cu-Li)-related 2.172-eV bound exciton in GaP with optically detected magnetic resonance

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Optically detected magnetic resonance (ODMR) is applied in this work to study the 2.172-eV bound exciton (BE) in GaP, associated with a complex neutral (Cu-Li)-related defect denoted $(Cu\text{-}Li)_V$. The ODMR data are analyzed with a spin-triplet spin Hamiltonian $\mathcal{H}=\mu_B \mathbf{B}\cdot\tilde{\mathbf{g}}_{ex}\cdot\mathbf{S}+\mathbf{S}\cdot\tilde{\mathbf{D}}\cdot\mathbf{S}$, where $\mathbf{S}$ is the effective BE spin. The best fit of this Hamiltonian to the ODMR data gives the values $g_x=1.98\pm0.01$, $g_y=1.97\pm0.01$, $g_z=2.07\pm0.01$; $D_x=(-0.34\pm0.01)\times10^{-5}$ eV, $D_y=(-1.04\pm0.01)\times10^{-5}$ eV, $D_z=(1.38\pm0.01)\times10^{-5}$ eV, where $x\|[001]$, $y\|[1\bar{1}0]$, and $z\|[110]$ are the principal axes of the g and D tensors. The determination of these parameters is much more accurate than in previous work, where neither the principal defect axes nor the sign of the components of the D tensor were given. These improved data establish a C_{2v} symmetry of the defect, with a different atomic and geometrical arrangement than proposed in previous work. With the combined information from the conditions of creation of the defect, the photoluminescence spectra and the ODMR data, it is suggested to be a three-atomic Li_i-Cu_{Ga}-Li_i chain in a bent configuration in a {110} plane. The components of the g tensor for the BE are all close to $g=+2$, consistent with a spinlike character of both electron and hole. It is noted that the fit of the ODMR data with the spin-triplet spin Hamiltonian is quite good, and the influence of the nearby singlet state on the magnetic properties of the triplet state can be regarded as negligible.

I. INTRODUCTION

Optical detection of magnetic resonance (ODMR) has been applied to studies of defects in semiconductors during the last few years, and has in many cases been proven to be a very sensitive technique.[1] In particular, ODMR has recently been extensively used in the detailed characterization of electronic properties of neutral ("isoelectronic") complex defects in semiconductors.[2–11] Such defects often have a triplet-singlet configuration at the lowest energy in the excited (bound exciton) state.[2–13] Strong ODMR signals are in general expected for a triplet-singlet bound-exciton (BE) configuration, related to a large population of the slowly emitting "$M_s=0$" sublevel of the triplet, which can be transferred by microwave-induced transitions to the fast emitting "$M_s=\pm1$" triplet sublevels.

Since the spectral resolution in ODMR measurements is in general at least 2 orders of magnitude better than the resolution in magnetooptical (Zeeman) studies, the ODMR technique (when applicable) is superior in the determination of magnetic properties of defects. In particular, ODMR is capable of resolving the magnetic fine-structure interactions involving the spins of the particles bound at the defect, represented by the D tensor in the spin Hamiltonian. In the case of neutral complex defects the evaluation of the D-tensor elements gives important information on the local interactions on and between the particles (electron and hole) bound at the defect in its excited state.

Recently a detailed evaluation of both the g-tensor and the D-tensor parameters has been demonstrated for the 1.911-eV Cu-related BE complex in GaP.[6] In that case only the triplet BE configuration was analyzed. This was adequate since in that particular case the singlet ($S=0$) BE level is at much higher energy, 91 meV above the triplet, so interaction between these levels is small indeed. A similar good fit has been obtained with a spin-triplet spin Hamiltonian for a number of very deep BE spectra in GaP.[7–9] In the case studied in this work the exchange interaction between the electron and hole in the BE is much smaller, and the singlet is only about 2 meV above the triplet (at 2.172 eV). Although a quite good fit of ODMR data can be obtained in this case with a spin Hamiltonian considering only the triplet state, there may be a non-negligible influence of the singlet state that must be included in a complete evaluation. This problem is of general interest for similar complex neutral defects in semiconductors, but the effect is found to be quite small ($\lesssim0.1\%$ of the evaluated parameter values) in the present case.

The paper is organized in the following way. A brief description of the experimental conditions is presented in Sec. II. The experimental data are displayed in Sec. III. A detailed study of the angular dependence of the ODMR spectrum has been done, with $\mathbf{B}$ rotated in the $(1\bar{1}0)$ and $(1\bar{1}2)$ planes. These data are quite accurate due to the strong ODMR signals obtained, and have been fitted with a spin-triplet spin Hamiltonian. The interaction with the higher singlet BE state is also briefly discussed, in connection with the fitting of the spin Hamiltonian to the experimental data. In Sec. IV the physical interpretation of the g and D tensors is discussed. A new model for the atomic and geometrical structure of the de-

fect is presented. In Sec. V finally a summary of the conclusions obtained for this particular defect is given, i.e., electronic structure, symmetry, and identity.

II. SAMPLES AND EXPERIMENTAL TECHNIQUES

The GaP samples used in this investigation were prepared from single crystalline bulk liquid-encapsulation Czochralski (LEC) -grown material, which was nominally undoped. The samples were doped with Cu and Li by a diffusion procedure, as described elsewhere.[14] Samples were oriented and etched before insertion in the cryostat.

Photoluminescence (PL) spectra with high resolution were obtained with a Spex 1404 0.85-m double monochromator. A Coherent 590 tunable dye laser with a Coumarin-540 dye, pumped by an Ar^+ laser, has been used as excitation source. This setup allowed for below-band-gap excitation, which is advantageous in both PL and ODMR measurements. With such excitation the full volume of the sample contributes to the emission; further, a specific BE system can be selectively excited. The ODMR data shown in this paper were obtained using a modified Bruker 200D-SRC 9-GHz spectrometer, equipped with an Oxford Instruments ESR10 liquid-He continuous-flow cryostat. A cylindrical cavity was employed, with optical access from all directions. The sample temperature could be continuously varied down to 2 K during experiments. Microwave power up to 600 mW was available, but typically much less power was sufficient to obtain a good signal-to-noise ratio for ODMR resonances. The ODMR spectra were taken with an S20 photomultiplier with lock-in techniques, in phase with the chopped microwaves. ODMR spectra could be obtained both in the Faraday and the Voigt configurations. A Jobin-Yvon 0.25-m grating monochromator was used to obtain spectral dependencies of the ODMR signals. Polarization measurements were performed using a Hinds PEM-3 stress modulator operating at 50 kHz. The difference between left- and right-hand circularly polarized components was obtained by lock-in detection at 50 kHz.

III. EXPERIMENTAL RESULTS

Figure 1 shows a high-resolution PL spectrum obtained with above-band-gap excitation. A number of BE spectra are seen, related to nitrogen (N), the Li-Li-O complex,[15] and a range of (Cu-Li)-related complexes,[14,16,17] among which the $(Cu\text{-}Li)_V$ BE at 2.172 eV is of interest here. The $(Cu\text{-}Li)_V$ PL spectrum has been described in detail earlier,[14] and is shown here only for easy reference. Two electronic (no-phonon) lines are seen for the $(Cu\text{-}Li)_V$ BE. The one at the lowest energy (2.1721 eV) has been proved to be a triplet line,[14] and the higher-energy line (2.1742 eV) is a singlet, i.e., the electron-hole exchange splitting is 2.1 meV in this case. A rather strong phonon coupling occurs for both lines, as discussed in more detail separately.[14,18]

In Fig. 2(a) a typical example is shown of an ODMR spectrum related to the 2.172-eV BE emission. Very strong signals can be observed under optimum condi-

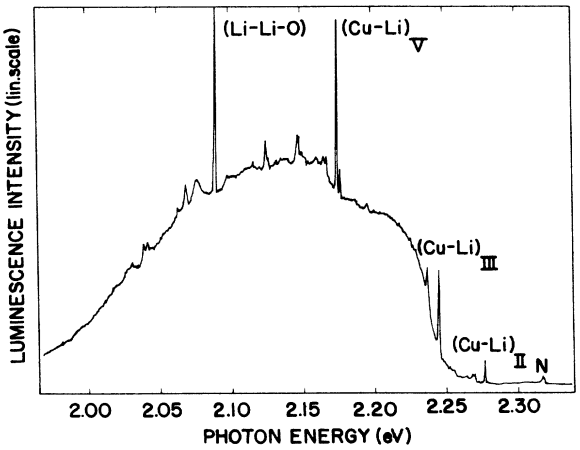

FIG. 1. A high-resolution PL spectrum at 2.1 K for (Cu-Li) co-doped GaP with Ar^+-laser excitation (5145 Å). The spectrum shows emissions related to N, $(Cu\text{-}Li)_{II}$, $(Cu\text{-}Li)_{III}$, $(Cu\text{-}Li)_V$, and Li-Li-O centers.

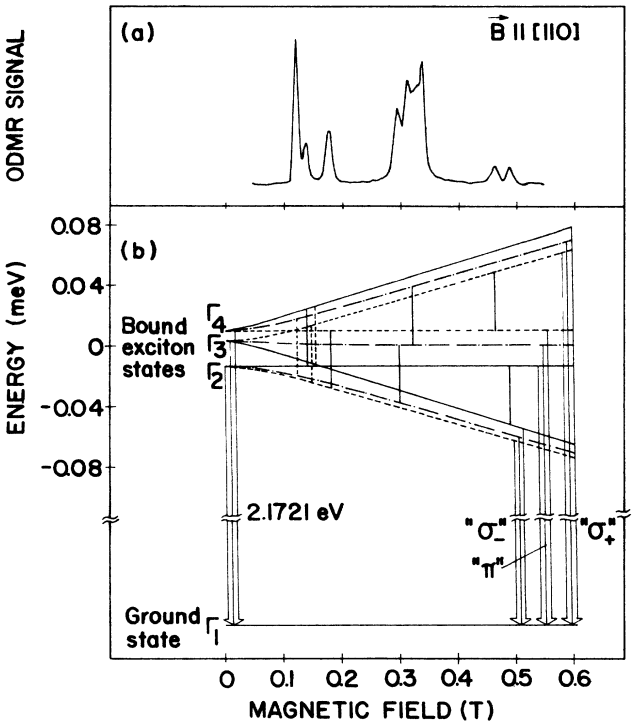

FIG. 2. (a) ODMR spectrum obtained for the $(Cu\text{-}Li)_V$ BE at 4 K at a microwave frequency of 9.23 GHz, with $\mathbf{B}\|[110]$. The ODMR signal from the 2.25-eV BE (Ref. 19) at $B \approx 0.33$ T is also seen. (b) Zeeman-split triplet configuration of the $(Cu\text{-}Li)_V$ BE when $\mathbf{B}\|[110]$, computed with the aid of the spin Hamiltonian with the parameters given in Table I. The three inequivalent sets of defects in this geometry are shown: the solid line represents the one with $\mathbf{B}\|z$, the dashed line the one with $\mathbf{B}\|y$, and the dashed-dotted line represents the other defect geometries where $\mathbf{B}$ is not along any of the principal axes. Also shown are the microwave-induced resonant transitions (vertical lines) and optical transitions to the ground state (arrows). It should be noted that the polarizations shown for the optical transitions are approximately proper only in the high-field limit, when the Zeeman term dominates over the fine-structure interaction. The defect for which $\mathbf{B}\|z$ shows a level crossing at 0.17 T (solid lines), as discussed in the text.

tions, corresponding to a modulation of the total PL intensity of more than 5%. The spectral dependence of the ODMR signal (ODMR-PL) has also been measured. The resulting ODMR-PL spectrum is shown in Fig. 3(a). In Fig. 3(b) the ordinary PL spectrum is shown, measured under the same experimental conditions, but with microwaves off, for comparison. From Figs. 3(a) and 3(b) it is clear that the ODMR resonance being monitored originates from the 2.172-eV triplet BE state, as additionally confirmed by performing ODMR excitation spectroscopy, discussed elsewhere.[19]

By performing such spectral measurements (ODMR-PL), it was established that in the central part of the ODMR spectrum shown in Fig. 2(a) an overlapping resonance spectrum occurs, due to another defect than the 2.172-eV BE,[20] with an electronic triplet line at ≈ 2.25 eV.[19] In order to make a detailed evaluation of the ODMR spectra of the 2.172-eV BE, such spurious resonances must be clearly distinguished. In this case, this can be done by a careful choice of experimental conditions.[19] It is also possible to avoid contributions in the ODMR spectrum from the 2.25-eV defect, by choosing a laser excitation of photon energy lower than 2.25 eV, but higher than 2.172 eV, so that the $(Cu\text{-}Li)_V$ BE is still excited, but the signal-to-noise ratio is then much lower than shown in Fig. 2(a). Other ways to minimize contributions from the 2.25-eV defect in the ODMR spectrum are to choose optimum microwave power and chopping frequency.

The interpretation of the ODMR spectrum in Fig. 2(a) is quite straightforward, and is in agreement with the previous knowledge that the lowest 2.1721-eV BE state is a magnetic triplet.[14] The main resonances are centered around $g=2$ and can be understood as "$\Delta M_s=1$" allowed resonance transitions [Fig. 2(b)]. Several such transitions are expected for a defect of low symmetry. Figure 2(b) shows a triplet level diagram versus a magnetic field, with microwave resonances and optical transitions to the ground state indicated. (This diagram is generated using the spin-triplet spin Hamiltonian, to be described below.) Dashed resonance lines correspond to "$\Delta M_s=2$" resonance transitions. These formally spin-forbidden transitions become allowed and often quite strong for BE triplets in a low symmetry.

Taking proper precautions to eliminate spurious resonances, as described above, an accurate determination of the angular dependence of the 2.172-eV BE ODMR spectrum was possible. In the present investigation, this was done with a rotation of the magnetic field **B** in two different planes, $(1\bar{1}0)$ and $(1\bar{1}2)$, respectively. Figure 4 shows the angular dependence of the ODMR spectrum for rotation of the sample with **B** in this case in the $(1\bar{1}2)$ plane. The data have been fitted with the spin-triplet BE spin Hamiltonian[21]

$$\mathcal{H}=\mu_B \mathbf{B}\cdot\tilde{g}_{ex}\cdot\mathbf{S}+\mathbf{S}\cdot\tilde{D}\cdot\mathbf{S}\ , \tag{1}$$

where **S** is the effective BE spin. The first term describes the linear Zeeman interaction, where μ_B is the Bohr magneton, **B** the external magnetic field, and $\tilde{g}_{ex}$ is the g tensor for the BE. The second term is the magnetic fine-structure term, which has three main contributions. Two of these are induced by spin-orbit interaction, i.e., the usual fine-structure term in ESR,[21] and the anisotropic exchange interaction term. The third term is due to the magnetic dipole-dipole interaction between the electron and the hole bound at the complex defect. This spin Hamiltonian only considers the lowest-energy triplet state of the BE, and neglects interactions with the higher singlet state.

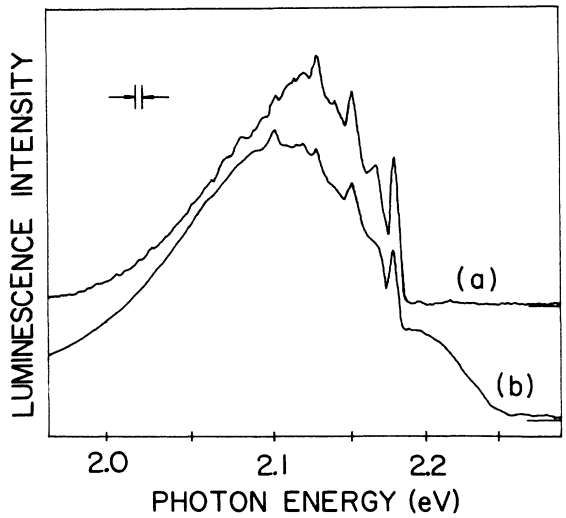

FIG. 3. (a) Spectral dependence of the ODMR signals from the $(Cu\text{-}Li)_V$ BE at 4 K, showing a "fingerprint" of the $(Cu\text{-}Li)_V$-BE emission [as seen in (b) and Fig. 1]. (b) PL spectrum of the same sample as in Fig. 1, but at 4 K and with lower spectral resolution, as a relevant comparison with the spectral dependence of the ODMR measured in the same experimental conditions, as used in (a).

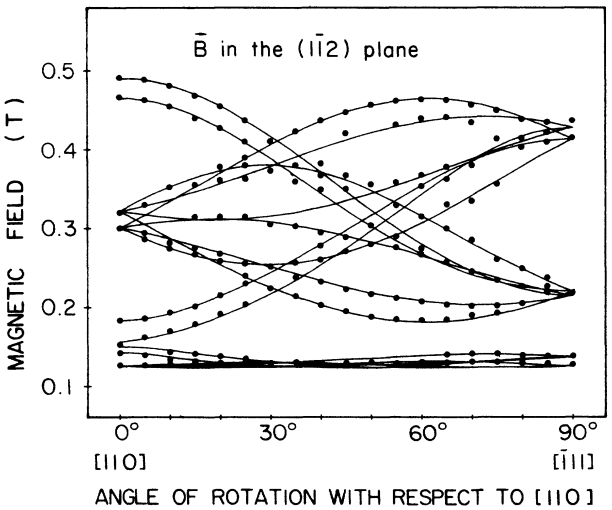

FIG. 4. Angular dependence of the ODMR spectra for the $(Cu\text{-}Li)_V$ BE, for rotation of the sample with **B** in the $(1\bar{1}2)$ plane. Dots show experimental data, while the solid lines are obtained from the fitting with the spin Hamiltonian given in the text with the parameters in Table I.

TABLE I. Spin-Hamiltonian parameters for the 2.172-eV BE in GaP, where $x\|[001]$, $y\|[1\bar{1}0]$, and $z\|[110]$.

Parameter					
	g tensor			D tensor (10^{-5} eV)	
g_x	g_y	g_z	D_x	D_y	D_z
1.98±0.01	1.97±0.01	2.07±0.01	−0.34±0.01	−1.04±0.01	1.38±0.01

The above spin Hamiltonian was diagonalized, with both terms included simultaneously, using a basis set of spinlike wave functions for both electron and hole, and compared with the experimental data (solid lines in Fig. 4). The best fit was obtained with the parameter values listed in Table I, with the axes $x\|[001]$, $y\|[1\bar{1}0]$, and $z\|[110]$ as principal axes of the g_{ex} tensor as well as of the D tensor. The signs of the g- and D-tensor components were determined by measuring the intensity of the right- and left-hand circularly polarized luminescence components separately, with the microwaves off. The measurement monitors the difference between the σ_+ and σ_- components, corresponding to recombination from the $|1,+1\rangle$ and $|1,-1\rangle$ states, respectively. This was done with the aid of a stress modulator operating at 50 kHz and the experiment was performed in the Faraday configuration employing selective excitation to avoid interference with the 2.25-eV BE luminescence.

It was found that the intensity of the σ_- polarized light increased with the magnetic field for all principal directions, suggesting that the $|1,-1\rangle$ magnetic subcomponent is at lower energies for these directions. This is in agreement with a thermalized system with positive g_{ex} components, $g_{x,y,z}$. Further, by detecting the no-phonon line of the BE through a monochromator it was found that the σ_- component was enhanced when the magnetic field was directed along the z axis at a field position corresponding to level crossing. For a positive value of g_z this level crossing establishes a positive value for D_z and consequently a negative sign for D_x and D_y, from the relation $D_z=-(D_x+D_y)$ and the sign of (D_x-D_y) as judged from the pattern of the angular dependence. The sign for D_z is also independently determined by detecting the ODMR signals for $(\sigma_+-\sigma_-)$, using the stress modulator. A positive signal for the low-field $\Delta M_s=1$ resonance and a negative signal for the high-field resonance confirms the positive sign for D_z.

IV. DISCUSSION

A. Identity of the $(Cu\text{-}Li)_V$ defect

Since the components of the g_{ex} and D tensors are all unequal the defect symmetry must be low, as low as C_{2v}. There are six equivalent sets of principal axes in the tetrahedral GaP lattice for C_{2v} overall symmetry of the defect site. The correlation between optical spectra and the doping procedure suggests that the defect is composed of copper and lithium atoms, with Cu_{Ga} as the acceptorlike part of the complex.[14] Since the defect is isoelectronic,[14] a substitutional Cu_{Ga} is compensated for by a pair of interstitial atoms, both here suggested to be Li atoms. A possible model for the defect accounting for these requirements and the details of the ODMR data is given in Fig. 5.

In the model, two interstitial atoms are located along different ⟨111⟩ axes on either site of Cu_{Ga}, which gives the three principal axes x, y, and z of the defect in agreement with the deduced principal axes of the g and D tensors, as shown in the figure. The overall ⟨110⟩ orientation of the defect in the direction of the two interstitial atoms explains the maximum splitting along the z axis in the figure. It can be noted that there are six equivalent defect sites of this kind in the lattice. The point group of the defect shown in Fig. 5 is therefore C_{2v}. Any distortion off the ⟨110⟩ direction for the pair of interstitial atoms would reduce the effective symmetry of the set of principal axes to C_{1h} or C_1, however.

In the previous work a different defect model was suggested, also involving Cu_{Ga} but with two different interstitials, Cu_i and Li_i, in a different geometrical arrangement than deduced from the ODMR data in this work. If the $(Cu\text{-}Li)_V$ defect was composed of Cu_{Ga} and two different interstitial atoms, such as Cu_i and Li_i, the defect symmetry would be C_{1h}, which is lower than observed. Such a C_{1h} symmetry would then be expected to be observed in ODMR data, since the primary particle of the BE (the hole) is fairly localized and should thus be sensi-

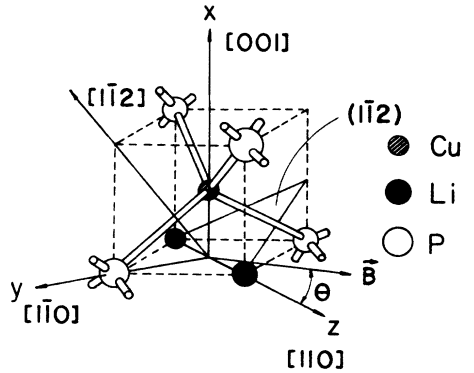

FIG. 5. A possible model of the $(Cu\text{-}Li)_V$ defect studied in this work, as a Li_i-Cu_{Ga}-Li_i complex bent in a {110} plane. The principal axes x, y, and z (which diagonalize the g and D tensors) are indicated in the figure. The set of principal axes in the figure is one of six equivalent ones, and corresponds to the one in Table I.

tive to the defect symmetry. The main reason for the suggestion of only one Li_i interstitial as part of the defect in the previous work was the absence of mixed local-mode phonon replicas in the PL spectrum upon mixed isotope doping with both ^{6}Li and ^{7}Li isotopes.[14] This may be explained by a weak interaction between the vibrations of the two interstitials, when positioned rather isolated from each other, as seen in Fig. 5. It should be noted, though, that the identity of the local-mode defect vibrations corresponding to the observed replica is not well understood at the moment, and consequently no strong arguments about the defect identity can be supported by these observations. In the previous work it was also shown[14] that the so-called COL defect,[12] which is suggested to be a trigonal defect with a Cu_{Ga} and two interstitial Cu atoms, is a precursor to the $(Cu\text{-}Li)_V$ defect discussed in this paper. The latter was previously supported to be formed by an exchange of one Cu_i interstitial for a Li_i interstitial, relaxing to a new position.[14] In the light of the new data presented in this work, it appears like both Cu_i atoms are replaced by Li_i interstitials, both relaxing to new positions (Fig. 5).

B. Electronic structure of the 2.172-eV BE, in relation to ODMR data

The (Cu-Li)-related defect responsible for the 2.172-eV BE is a typical example of a complex defect with a dominantly hole-attractive local potential, as discussed previously.[14] The low symmetry and the strongly localized hole-attractive potential are sufficient conditions to create a spinlike bound-hole state in a material like GaP, where the spin-orbit interaction on bound hole states is usually fairly weak.[13] A spinlike hole together with a spinlike electron gives a triplet-singlet pair as the lowest BE configuration, as observed in this case.

The energy separation between the triplet and the singlet reflects the strength of the isotropic part of the electron-hole exchange interaction in the BE state. The value 2.1 meV is rather low, and a similar (or even smaller) value is found for other (Cu-Li)-related defects in GaP, notably for the 2.307-eV $(Cu\text{-}Li)_I$ BE (0.9 meV),[16] the 2.25-eV BE (3 meV),[19] and for the 2.242-eV $(Cu\text{-}Li)_{III}$ BE (2.3 meV).[17] Other hole-attractive neutral complexes, on the other hand, have much higher values for the triplet-singlet splitting, notably 91 meV for the Cu-related 1.911-eV defect,[3] 21 meV for the Cu-related COL defect,[12] and 8 meV for a shallow (Cu-C)-related defect.[22]

The proximity of the singlet state to the triplet could make the above analysis of the ODMR data in terms of a spin-triplet spin Hamiltonian inaccurate.[6] A proper treatment in that case would be to use a more general effective Hamiltonian of the form[23]

$$\mathcal{H}=\mu_B \mathbf{B}\cdot\tilde{\mathbf{g}}_e\cdot\mathbf{S}_e+\mu_B\mathbf{B}\cdot\tilde{\mathbf{g}}_h\cdot\mathbf{S}_h+\mathbf{S}_e\cdot\tilde{\mathbf{J}}\cdot\mathbf{S}_h\ , \qquad (2)$$

where $\mathbf{S}_e$ and $\mathbf{S}_h$ are the effective spins of bound electrons and holes, respectively, and $\tilde{\mathbf{g}}_e$ and $\tilde{\mathbf{g}}_h$ are the g tensors of these particles. $\tilde{\mathbf{J}}$ is a rank-2 Cartesian tensor describing the mutual interactions between the two particles, including the e-h exchange interaction, as well as the other interactions listed previously for the D tensor.

In the case of large e-h exchange interaction the lowest BE state is decomposed into two parts, the singlet state and the lowest triplet state. The latter can to a good approximation be described by the spin-triplet spin Hamiltonian used in this work [Eq. (1)]. This situation should be compared, e.g., to the case of the 1.911-eV BE in GaP, studied in detail separately.[6] In that case a good fit was obtained with the above spin-triplet spin Hamiltonian [Eq. (1)], as expected when the singlet state is well separated in energy from the triplet, and the triplet-singlet interaction can be neglected.

A fit of the Hamiltonian [Eq. (2)] to the data has been performed, in a similar way as described above for the spin-triplet spin Hamiltonian [Eq. (1)], using the same basis functions for the electron and the hole as for the previous fit. It was possible to obtain quite a good fit of Eq. (2) to the data with parameters corresponding to those listed in Table I, using the relation $\tilde{\mathbf{g}}_{ex}=(\tilde{\mathbf{g}}_e+\tilde{\mathbf{g}}_h)/2$, and assuming that the electron g value is isotropic, $g_e=2.00$, typical for shallow donorlike electrons in GaP.[24] The deviations between the two fits were less than 0.1%. This result reassures that the spin-triplet spin Hamiltonian [Eq. (1)] still gives a sufficiently adequate description of the experimental data for the $(Cu\text{-}Li)_V$ BE. This is because the e-h exchange interaction term is still much larger than the Zeeman term which is coupling the triplet to the singlet state $[\approx\frac{1}{2}\mu_B\mathbf{B}\cdot\Delta\tilde{\mathbf{g}}\cdot(\mathbf{S}_e-\mathbf{S}_h)]$ where $\Delta\tilde{\mathbf{g}}\equiv\tilde{\mathbf{g}}_e-\tilde{\mathbf{g}}_h$, which was true in our ODMR experiments performed at 9 GHz.

The anisotropy $\Delta\tilde{\mathbf{g}}$ of the g tensor is accurately resolved in the data, although its magnitude is limited to $\pm3\%$. If $\tilde{\mathbf{g}}_e$ is taken as isotropic, $g_e=+2.00$, as evident from ESR work on shallow donor electrons in GaP, the residual anisotropy of g_{ex} is supposed to be related to $\tilde{\mathbf{g}}_h$, due to the incomplete quenching of the orbital angular momentum of the bound hole.[13] Also, $\tilde{\mathbf{g}}_h$ is deduced to have positive components, consistent with the observed positive components of $\tilde{\mathbf{g}}_{ex}$, all quite close to $g=2$. The D-tensor elements are in this case of about the same magnitude as for the Cu-related 1.911-eV defect in GaP,[6] as well as for the recently studied (P_{Ga}-Cu)-related antisite complexes in GaP.[7,9] The elements of the D tensor are not directly proportional to the elements of the Δg tensor ($\Delta\tilde{\mathbf{g}}=\tilde{\mathbf{g}}_{ex}-2.0023\times1$), although the g and D tensors are diagonalized by the same principal axes. This observation allows the conclusion that the D tensor does not originate from spin-orbit-induced effects only, for which case direct proportionality between D and Δg components is expected.[21] Thus the electron-hole magnetic dipole-dipole interaction appears to be an important contribution to the D tensor. This situation is similar to the one found for other neutral complex defects studied in GaP.[6-9] It should be noted that the magnitude of the D-tensor components is consistent with an approximately 2.5-Å separation between two localized magnetic dipoles, which is quite close to the 2.4-Å nearest-neighbor separation in the GaP lattice. The above result should, however, not be considered as a proof for the domination of the magnetic dipole-dipole mechanism, since it was obtained using the point-charge approximation. This approximation might be of limited value for the case of BE's, partic-

ularly when one of the carriers is rather delocalized.

The width of the ODMR resonance lines in this case is about 100 G, which is narrower than for other shallow triplet systems in GaP.[4-6,25] The natural ESR linewidth in GaP, in the absence of central hyperfine (CHF) interactions, is about 50–60 G.[26] The slightly increased linewidth in this case could be due to an unresolved CHF interaction from Cu_{Ga}, believed to introduce the dominant potential in the defect, due to a quite strong overlap between the bound hole wave function and the Cu_{Ga} nucleus. Resolved CHF interaction due to Cu_{Ga} has not been observed amongst several complex defects in GaP studied with ODMR,[4-9,25] and has in fact only been observed in one case in GaP.[27] Certainly other broadening mechanisms, such as, e.g., excitation transfer,[28] exist to explain the observed ODMR linewidth for the $(Cu\text{-}Li)_V$ defect. The linewidth of ODMR resonances from shallow Li donors in GaP is of the same order as observed in this case, 100–150 G.[20]

V. CONCLUSIONS

Accurate 9-GHz ODMR data are presented in this work for the 2.172-eV BE in GaP, related to the $(Cu\text{-}Li)_V$ defect.[14] The intensity of the ODMR signals is quite large in this case, with $>5\%$ modulation of the PL signal at magnetic resonance. The data are analyzed with a spin-triplet spin Hamiltonian $\mathcal{H}=\mu_B \mathbf{B}\cdot\tilde{\mathbf{g}}\cdot\mathbf{S}+\mathbf{S}\cdot\tilde{\mathbf{D}}\cdot\mathbf{S}$. This defect is a typical case of a hole-attractive neutral complex defect, which binds a hole in a very localized state as the primary particle of the BE. This hole is then essentially spinlike, as confirmed by the deduced values of the g tensor in this work (all principal components of $\tilde{g}_h$ are positive and close to $g=+2$). The electron is bound as a secondary particle, in a rather delocalized state. This explains a rather weak isotropic part of the *e-h* exchange interaction, which is directly measured as the separation between the lowest BE triplet state and the higher singlet state (2.1 meV). The magnetic dipole-dipole interaction of the electron-hole pair is deduced to be an important contribution to the D tensor. Additional contributions from the spin-orbit interaction (direct spin-orbit term or spin-orbit-induced anisotropic exchange interaction) are also present. The angular dependence of the ODMR signals is consistent with six equivalent defect sites in the GaP lattice. The defect is tentatively identified as a three-atomic chain Li_i-Cu_{Ga}-Li_i, with a bent configuration in a $\{110\}$ plane.

It is noted that the spin-triplet spin Hamiltonian used in this work is sufficient to give a good fit to ODMR data, just as in the separately studied case of the 1.911-eV defect in GaP, where the triplet-singlet splitting is 91 meV and the singlet therefore is far removed from the triplet state. The Hamiltonian in which the singlet BE state is included does not significantly change the parameters in the fitting to experimental data.

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