

## Optically detected magnetic resonance studies of the 1.911-eV Cu-related complex in GaP

W. M. Chen, B. Monemar, H. P. Gislason,\* M. Godlewski,<sup>†</sup> and M. E. Pistol<sup>‡</sup>

*Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden*

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A detailed study of optically detected magnetic resonance (ODMR) in photoluminescence is reported for the 1.911-eV Cu-related neutral complex defect in GaP. By excitation with a tunable dye laser directly in an excited state at around 2.002 eV associated with the 1.911-eV bound exciton (BE), quite strong ODMR signals are obtained. Separate recordings of differently polarized components of the ODMR spectra at 9 GHz give a considerably more accurate angular dependence of the ODMR spectrum than previously reported. The triplet 1.911-eV BE state can be described by the spin Hamiltonian  $\mathcal{H} = \mu_B \mathbf{B} \cdot \vec{g}_{ex} \cdot \mathbf{S} + \mathbf{S} \cdot \vec{D} \cdot \mathbf{S}$  with the parameter values  $g_x = 1.99 \pm 0.01$ ,  $g_y = 2.06 \pm 0.01$ ,  $g_z = 2.03 \pm 0.01$ ,  $D_x = (-7.40 \pm 0.05) \times 10^{-6}$  eV,  $D_y = (-0.70 \pm 0.05) \times 10^{-6}$  eV, and  $D_z = (8.10 \pm 0.05) \times 10^{-6}$  eV, where  $x \parallel [1\bar{1}0]$ ,  $y \parallel [110]$ , and  $z \parallel [001]$  are the axes diagonalizing both  $g_{ex}$  and  $D$  tensors. The defect has the low  $C_{1h}$  symmetry, i.e., lower than previously deduced from less accurate ODMR data. It is tentatively identified as a substitutional-interstitial pair  $\text{Cu}_{\text{Ga}}\text{-Ga}_i$ , probably with an additional interstitial  $\text{Cu}_i$  attached. The magnetic properties of the 1.911-eV BE triplet state are discussed in detail, and are found to be consistent with a strongly hole-attractive local defect potential, causing a nearly complete quenching of the angular momentum of the bound hole, so that its  $g$  tensor  $\vec{g}_h$  is quite isotropic. The residual anisotropy of the  $g$  tensor is explained as due to spin-orbit interaction on the bound hole, while the  $D$  tensor is found to be mainly derived from the magnetic dipole-dipole interaction between the electron and the hole bound at the defect. The rather large linewidth for the ODMR resonances is tentatively explained as due to an unresolved hyperfine interaction involving the  $\text{Ga}_i$ , consistent with the evidence that the electron is also strongly localized to the defect.

### I. INTRODUCTION

The 1.911-eV photoluminescence (PL) line associated with a Cu-related complex defect in GaP is an example of a triplet bound exciton (BE) in a semiconductor, as established in previous work.<sup>1,2</sup> Such triplet states are common for BE's related to neutral complex defects with a hole-attractive local potential,<sup>1,3,4</sup> and are characterized by a nearly isotropic  $g$  factor  $g_h \approx +2$  for the bound hole, in sharp contrast to effective-mass-like bound-hole states.<sup>3,4</sup> The degree of quenching of the orbital angular momentum for the bound hole determines how close the hole  $g$  value  $g_h$  is to the ideal isotropic case of  $g_h = +2$ . This can only be studied approximately by Zeeman splitting of the BE triplet line,<sup>1</sup> since the linewidth of the BE usually disguises the deviations from the ideal  $g = 2$  case for the effective  $g$  value of the BE.

Optical detection of magnetic resonance (ODMR) has been established as a very useful technique for the study of magnetic properties of bound excitons in semiconductors.<sup>5,6</sup> This is true in particular for triplet states associated with neutral complex defect BE's. EPR is not applicable in this case, since the ground state of the defect has no spin. For the 1.911-eV defect studied in this work, preliminary ODMR data have previously been reported.<sup>1,2</sup> These data suggested a  $\langle 001 \rangle$  linear orientation of the defect, and a rather large anisotropy ( $\approx 10\%$ ) of the  $g$  tensor for the BE. Due to a considerable width of the resonance lines ( $\approx 500$  G), the data were not sufficiently accurate for a definite analysis of the defect symmetry and the detailed magnetic properties of the bound-hole state, however. These details are important

for the understanding of the electronic properties of the defect, as will be shown below.

In this work a more accurate ODMR study of the 1.911-eV triplet BE state has been undertaken. The experimental conditions for ODMR in photoluminescence have been optimized by using extrinsic tunable-dye-laser excitation and separate detection of circularly and linearly polarized  $\sigma$  and  $\pi$  components of the emitted light. This procedure enabled a decomposition of the overlapping broad resonance lines, and hence more reliable data were obtained. The angular dependence of the ODMR resonances has been obtained for rotations in two different crystallographic planes. A quite satisfactory fit of the data for the angular dependence of ODMR resonances to a spin Hamiltonian for triplet states has been obtained for both planes. Therefore, sufficiently accurate parameters for a detailed evaluation of the magnetic properties of the primary bound hole for a neutral complex defect have been obtained for the first time. A discussion of the observed small anisotropy of the hole  $g$  factor is given, considering the general magnetic properties of excitons bound at neutral defects in semiconductors. The accurate ODMR data obtained in this work lead to a microscopic model for the complex defect that has a lower symmetry from the one previously reported.<sup>1</sup>

In Sec. II below a brief description of samples and experimental procedure is given. Section III contains a detailed exposition of the ODMR data, together with the evaluation of parameters in the spin Hamiltonian for a complete description of the magnetic properties of bound particles. Section IV contains a discussion of the magnetic properties of the bound exciton, with reference

to the evaluated anisotropy of the hole  $g$  factor. The origin of the  $D$  tensor for a tightly bound exciton is also discussed. The main conclusions from the present work are collected in Sec. V.

## II. EXPERIMENT

Cu-doped GaP crystals showing the 1.911-eV BE PL emission were prepared by a high-temperature diffusion

process (1000–1100°C, 1 h), as previously reported.<sup>1</sup> Photoluminescence spectra were obtained with a Spex 1404 0.85-m double monochromator, and the same setup was used for photoluminescence excitation spectra (PLE), employing a Coherent 590 tunable dye laser as excitation source, pumped by an Ar<sup>+</sup> laser. For the ODMR work a modified Bruker 200D-SRC 9-GHz spectrometer was used with an Oxford ESR 10 liquid-He

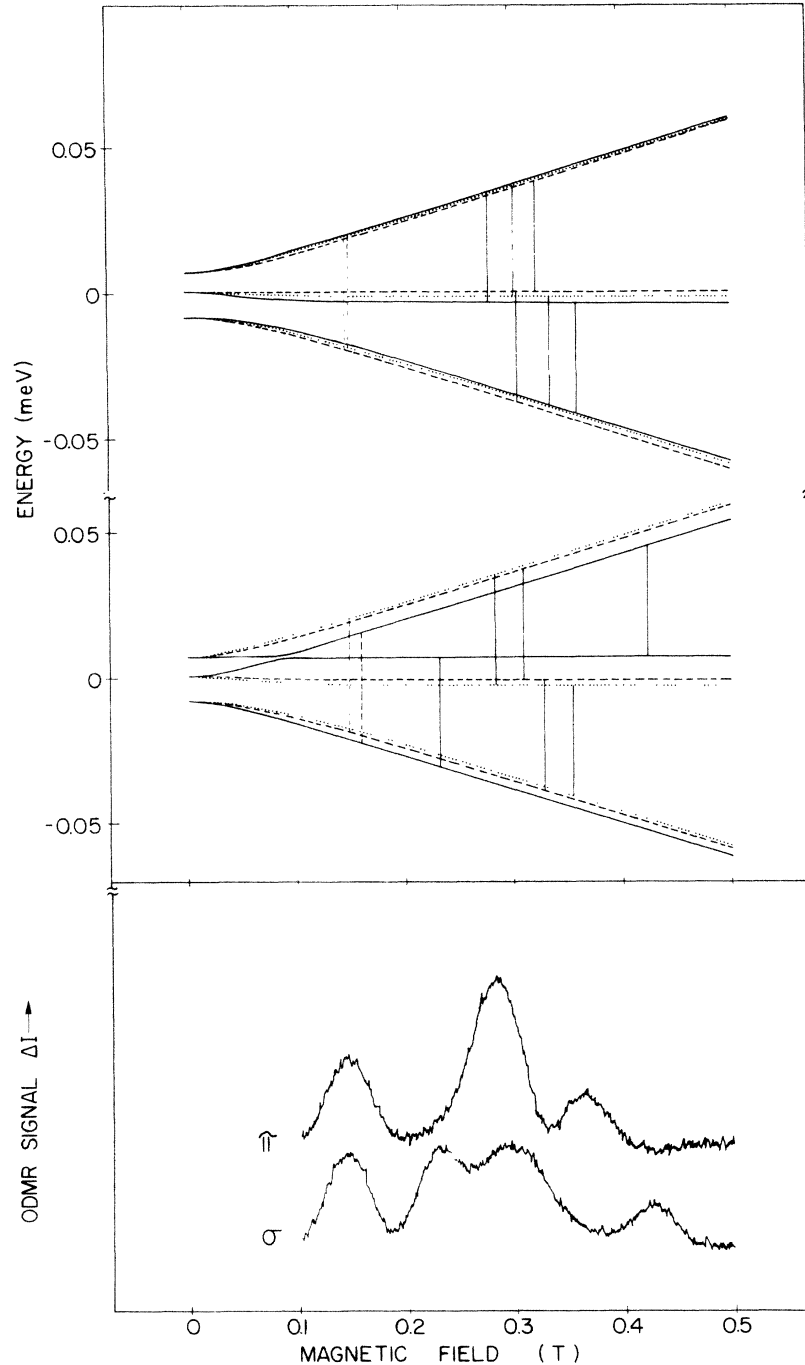


FIG. 1. ODMR spectra obtained for the 1.911-eV triplet at  $\approx 4$  K at a microwave frequency of 9.23 GHz when  $\mathbf{B}$  is about  $6^\circ$  off  $[1\bar{1}0]$  in the (112) plane. The Voigt configuration was employed, and spectra obtained in both  $\sigma$  and  $\pi$  polarizations are shown. The two figures in the top part, each with three separate sets of Zeeman-split triplets, represent the triplet configuration for the six inequivalent sets of defects in this geometry computed with the aid of the spin Hamiltonian derived below for the 1.911-eV BE. Microwave transitions are also indicated in the top part, for comparison with the spectra below.

continuous-flow cryostat and a cylindrical cavity with optical access from all directions. Sample temperatures could be continuously varied down to 2 K. Microwave power up to 500 mW could be employed, but typically much less power was sufficient. Optical detection was done with an S20 photomultiplier, with lock-in technique in phase with the chopped microwave excitation.<sup>5</sup> Experiments could be performed in both the Faraday and Voigt configurations. For the spectral dependence of the ODMR signal a Jobin-Yvon 0.25-m grating monochromator was used.

### III. EXPERIMENTAL RESULTS

The PL spectrum for the 1.911-eV BE has been published previously.<sup>1</sup> As shown in the inset of Fig. 1 of Ref. 1, the 1.911-eV line is a magnetic triplet from Zeeman data, and it has a completely isotropic angular dependence of the Zeeman splitting up to 6 T, as far as can be resolved.<sup>1</sup> The oscillator strength of the 1.911-eV triplet line is quite weak, and the line is not seen in transmission spectra. It can be seen in PLE, however,<sup>1</sup> but the PLE spectrum is dominated by the strong higher-energy transition at 2.002 eV (Fig. 7 of Ref. 1), believed to be due to the singlet BE line (i.e., the electron and hole have opposite spins). As mentioned in the introduction and elsewhere,<sup>1,7</sup> photoexcitation in this excited state is a very efficient way of achieving a large population of the 1.911-eV triplet state throughout the volume of the sample, which is particularly useful for the ODMR studies reported here. The PLE spectrum obtained for the ODMR signal is identical to the ordinary PLE spectrum for the luminescence signal.<sup>1,7</sup> This proves that the ODMR resonances reported below are actually derived from the 1.911-eV triplet, and transfer effects from other defects, which are sometimes important for ODMR studies in GaP,<sup>8</sup> are not important in this work.

A typical ODMR resonance spectrum obtained at 2 K with detection of the 1.911-eV PL emission is shown in Fig. 1. It contains a low-field line at  $\approx 0.15$  T and a number of higher-field lines centered around "g=2," i.e.,  $\approx 0.33$  T. The low-field line is the " $\Delta M=2$ " transition of the triplet, while the higher-field manifold constitute the " $\Delta M=1$ " resonances (see the top part of Fig. 1). ODMR spectra were recorded in the Voigt configuration in both polarizations,  $\sigma$  and  $\pi$ , as shown in Fig. 1. This is important since the state of polarization of the PL transitions affected by the " $\Delta M=1$ " resonances depends on the direction versus the magnetic field. Although the state of polarization for a particular PL transition is mixed in general, the recordings of ODMR spectra for both polarizations allow the resolution of individual resonances that may be orientationally degenerate, or overlapping due to the rather large natural width of typically  $\approx 500$  G for each individual resonance in Fig. 1 may be due to an unresolved hyperfine splitting for one of the atoms in the defect complex (such as Ga<sub>i</sub>), but other contributions to the broadening are certainly possible. The strong localization of both electron and hole to this defect, evident from the large value (91 meV)

of the electron-hole exchange interaction,<sup>1</sup> is certainly consistent with a substantial hyperfine broadening from the donorlike part of the complex, in this case believed to be dominated by a deep Ga<sub>i</sub> donor.<sup>1</sup>

The full angular dependence of the ODMR resonance spectrum is shown in Figs. 2(a) and 2(b) for rotation of the magnetic field in two different planes, i.e., **B** in the (110) plane [Fig. 2(a)] and **B** in the (112) plane [Fig. 2(b)]. The spin Hamiltonian,<sup>9</sup> fitted to the data in both planes, is

$$\mathcal{H} = \mu_B \mathbf{B} \cdot \vec{g}_{\text{ex}} \cdot \mathbf{S} + \mathbf{S} \cdot \vec{D} \cdot \mathbf{S} . \quad (1)$$

This Hamiltonian is accurate if the energy distance to the singlet state ( $S=0$ ) is large, as is the case here: 91 meV.<sup>1</sup> The first term in Eq. 1. describes the linear Zeeman interaction, and the second term the fine structure part, introducing zero-field splittings of the triplet state.  $\mu_B$  is the Bohr magneton, and **B** is the external magnetic field.  $\vec{g}_{\text{ex}}$  is the g tensor for the bound exciton and  $\vec{D}$  is the fine-structure tensor reflecting both the spin-orbit

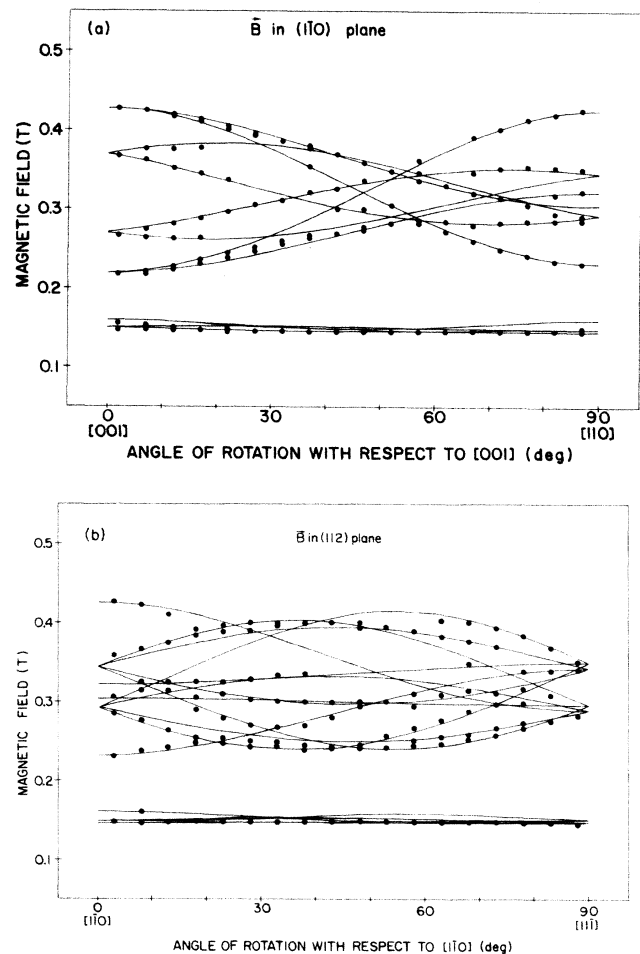


FIG. 2. (a) Angular dependence of ODMR spectra such as those shown in Fig. 1, for rotation of the sample with **B** in the (110) plane. Solid lines are obtained from the fitting to the spin Hamiltonian described in the text. (b) Similar angular dependence as in (a), but with the sample rotated with **B** in the (112) plane.

induced interactions (mainly for the hole) in the BE, and the electron-hole magnetic dipole-dipole interaction,<sup>9,10</sup> as will be discussed below. The values of the traceless  $D$  tensor along three principal axes, i.e.,  $D_x$ ,  $D_y$ , and  $D_z$ , are in general unequal for a symmetry lower than tetrahedral, and are equal to zero for  $T_d$  symmetry. The labels  $x$ ,  $y$ , and  $z$  refer to the principal axes of the  $g_{ex}$  and  $D$  tensors, which depend on the symmetry of the defect.

The above spin Hamiltonian was diagonalized with both terms included simultaneously, and compared with the data for the angular dependence of Fig. 2, in order to evaluate the parameters for best fit. In this procedure a simple basis set with spinlike wave functions for both electrons and holes was employed. The computer fit of the ODMR spectrum employing these parameters is included in Figs. 2(a) and 2(b) as solid lines. The deduced values of the principal components of the  $\vec{g}_{ex}$  and  $\vec{D}$  tensors are listed in Table I. It is noted that the  $g_{ex}$  and  $D$  tensors are diagonalized by the same set of axes, and the  $D$  tensor is traceless. Since the components of  $\vec{g}_{ex}$  and  $\vec{D}$  are all unequal, the symmetry must be either  $C_{2v}$  or  $C_{1h}$ . The symmetry  $C_{1h}$  is used further on since it is consistent with the presence of two different interstitials in the defect, as proposed in Sec. IV C.

The signs of the principal components of the  $\vec{D}$  tensor in the spin Hamiltonian have been determined as shown in Table I from the ODMR experiment in the Faraday configuration, where both the  $\sigma^+$  and  $\sigma^-$  components of the ODMR signal could be separately recorded. The resulting spectra are similar to the results in Fig. 2 of Ref. 12.

#### IV. DISCUSSION

##### A. The $g$ tensor, its residual anisotropy, and quenching of hole orbital angular momentum

The anisotropy of the  $g$  tensor for the BE contains important information, mainly related to the theoretical description of the bound-hole state for this hole-attractive neutral defect. It has recently been pointed out<sup>1,3,4</sup> that for hole-attractive complex defects of a low symmetry the orbital angular momentum of a hole localized at such a defect is expected to be quenched. This means that the bound hole has spinlike properties, and an isotropic  $g$  factor  $g_h = +2$  is expected.

The Zeeman interaction term for an exciton (electron-hole pair) bound to a complex neutral defect can be described as

$$\mathcal{H}_Z = \mu_B (\mathbf{L} + g_h \mathbf{S}_h) \cdot \mathbf{B} + \mu_B g_e \mathbf{S}_e \cdot \mathbf{B}. \quad (2)$$

Here the orbital angular momentum contribution to the  $g$  factor for the electron has been neglected, as appears to be relevant from several studies of donor states in GaP.<sup>8,11-14</sup> In addition the  $g$  value for such donors is

generally found to be quite close to  $g_e = 2$ , between 1.99 and 2.01.<sup>11-14</sup> If we note that the orbital angular momentum for the bound hole must be quenched to a large degree in this case (otherwise the  $g_{ex}$  tensor would be much more anisotropic in  $C_{1h}$  symmetry<sup>9</sup>) we can rewrite Eq. (2) as

$$\mathcal{H}_Z = \mu_B g_h \mathbf{S}_h \cdot \mathbf{B} + \mu_B g_e \mathbf{S}_e \cdot \mathbf{B}. \quad (3)$$

As a perturbation on this picture, we now turn to the discussion of the residual orbital angular momentum contribution to the bound-hole magnetic moment. The amount of quenching of the orbital angular momentum for localized hole states at a complex defect with a hole-attractive potential is critically dependent on the spin-orbit coupling the bound hole experiences within the extent of the bound-hole wave function.<sup>4,10</sup> In the absence of spin-orbit coupling the angular momentum is expected to be perfectly quenched in low symmetry.<sup>4</sup> On the other hand weak effects of spin-orbit coupling can be treated by perturbation theory, and will induce a small amount of angular momentum back into the bound-hole magnetic moment.<sup>4</sup> Since the size of the spin-orbit (s.o.) perturbation for a defect may be dominated by the defect potential, it may differ from the intrinsic value  $\Delta_{s.o.}$  for the host semiconductor, and may also vary between different defects. In general, however, the spin-orbit (s.o.) matrix elements are expected to be rather weak in GaP, since the s.o. splitting  $\Delta_{s.o.}$  of the valence-band top is quite small, only 82 meV.<sup>15</sup> Thus the energy denominator may easily dominate in the perturbation expressions for the spin-orbit coupling,<sup>4</sup> and only a small contribution to angular momentum is admixed back into the bound-hole state.<sup>4</sup> As a consequence of the resulting anisotropy of  $\vec{g}_h$ , Eq. 3 should be rewritten as

$$\mathcal{H}_Z = \mu_B \mathbf{S}_h \cdot \vec{g}_h \cdot \mathbf{B} + \mu_B g_e \mathbf{S}_e \cdot \mathbf{B}. \quad (4)$$

In the case of large electron-hole exchange interaction, which is often two orders of magnitude larger than the Zeeman term, it is more convenient to describe the Zeeman interaction in terms of the total angular momentum  $\mathbf{S} = \mathbf{S}_h + \mathbf{S}_e$ . By applying the Wigner-Eckart theorem,<sup>16</sup>  $\mathbf{S}_e$  and  $\mathbf{S}_h$  can be expressed in terms of  $\mathbf{S}$  as

$$\langle S, M_s | \mathbf{S}_e | S, M_s' \rangle = \frac{\langle S | \mathbf{S} \cdot \mathbf{S}_e | S \rangle}{S(S+1)} \cdot \langle S, M_s | \mathbf{S} | S, M_s' \rangle, \quad (5)$$

$$\langle S, M_s | \mathbf{S}_h | S, M_s' \rangle = \frac{\langle S | \mathbf{S} \cdot \mathbf{S}_h | S \rangle}{S(S+1)} \cdot \langle S, M_s | \mathbf{S} | S, M_s' \rangle, \quad (6)$$

where  $|S, M_s\rangle$  stands for the bound-exciton state in the usual notation.<sup>17</sup> The scalars  $\mathbf{S} \cdot \mathbf{S}_e$  and  $\mathbf{S} \cdot \mathbf{S}_h$  in Eqs. (5) and (6) have matrix elements independent of  $M_s$ :

TABLE I. Parameter values for the best fit to the spin Hamiltonian, where  $x \parallel [1\bar{1}0]$ ,  $y \parallel [110]$ , and  $z \parallel [001]$ .

Parameter	$g_x$	$g_y$	$g_z$	$D_x$ ( $10^{-6}$ eV)	$D_y$ ( $10^{-6}$ eV)	$D_z$ ( $10^{-6}$ eV)
Value	1.99±0.01	2.06±0.01	2.03±0.01	-7.40±0.05	-0.70±0.05	8.10±0.05

$$\mathbf{S} \cdot \mathbf{S}_e = \frac{1}{2}(\mathbf{S}^2 - \mathbf{S}_h^2 + \mathbf{S}_e^2), \quad (7)$$

$$\mathbf{S} \cdot \mathbf{S}_h = \frac{1}{2}(\mathbf{S}^2 + \mathbf{S}_h^2 - \mathbf{S}_e^2). \quad (8)$$

Consequently the observed  $g$  tensor  $\vec{g}_{\text{ex}}$  for the BE can be described as

$$\mathcal{H}_Z = \mu_B \mathbf{S} \cdot \vec{g}_{\text{ex}} \cdot \mathbf{B} \quad (9)$$

with  $\vec{g}_{\text{ex}} = \frac{1}{2}(g_e \cdot \vec{1} + \vec{g}_h)$  and  $\mathbf{S} = \mathbf{S}_e + \mathbf{S}_h$ . This is obviously consistent with the observed components of  $\vec{g}_{\text{ex}}$  in this work; they are all quite close to +2, as are both  $g_e$  and the components of  $\vec{g}_h$ .

We believe that this situation is quite typical for bound-hole states for hole-attractive complex defects in GaP, where virtually isotropic triplet states with  $g_{\text{ex}} = 2$  have been observed for many such defects.<sup>1-3,18-20</sup> If the strain splitting of bound-hole states is of a typical value, 300 meV, as concluded from PLE spectra for the 1.911-eV defect,<sup>1</sup> a reduced value of the spin-orbit matrix element at the defect would result; i.e., typically much less than the 82 meV found for the host material itself. This is evident since the total amount of  $L$  observed from the small anisotropy of the  $g$  tensor  $\vec{g}_{\text{ex}}$  (which is believed to reflect the anisotropy of  $\vec{g}_h$  only) is only  $\approx 2\%$  from the data in this work.

#### B. The $D$ tensor and its relation to the $g$ tensor for the BE triplet state

The description of the spin Hamiltonian [Eq. (1)] used in this work is partly taken over from a discussion of single-particle electron states associated with ions embedded in crystalline solids.<sup>9</sup> For the case of an electron-hole pair bound to a defect in a semiconductor the origin of the fine-structure tensor  $\vec{D}$  is different, however. It originates mainly from two different sources of interaction: the spin-orbit interaction (for both electron and hole) and the magnetic dipole-dipole interaction between the electron and the hole.

The contribution to the  $D$  tensor from the spin-orbit interaction (including spin-orbit-induced anisotropic exchange interaction) may be important for either or both particles of the BE. For a triplet BE in GaP discussed here the bound electron can normally be assumed to be spinlike with an isotropic  $g$  value. The bound hole usually experiences some spin-orbit interaction, as evidenced from the deviation of the  $g$  tensor from the spin-only value  $g_h = 2$ . The magnitude of the spin-orbit-induced contributions  $\vec{D}_{\text{s.o.}}$  to the  $D$  tensor is proportional to the spin-orbit-induced  $g$  shift.<sup>10</sup>

It appears, however, that the different components of the tensors  $\Delta g \approx (\vec{g}_{\text{ex}} - 2.00 \times \vec{1})$  and  $\vec{D}$  evaluated from experimental data in this work are not proportional, which, as explained above, would be expected if they were both of the same origin; the deviation from such proportionality is quite large. We therefore conclude that the main contribution to the  $D$  tensor in the case of the 1.911-eV BE comes from the  $e$ - $h$  magnetic dipole-dipole interaction, and not from spin-orbit interaction.

The magnitude of the contribution to the  $D$  tensor from the magnetic dipole-dipole interaction can be cal-

culated directly, e.g., for a pair of point charges, such as two closely separated transition-metal atoms in a solid.<sup>9</sup> A similar evaluation is in general unreliable for a BE in a semiconductor, since in that case the point-charge approximation is in general inappropriate. It is noticed, however, that the values of the  $D$ -tensor elements observed correspond to about 4 Å separation between two localized magnetic dipoles for a magnetic dipole-dipole interaction mechanism,<sup>9,10</sup> a value which is not far from the nearest-neighbor separation in the GaP lattice (2.4 Å), which equals the (unrelaxed) distance between  $\text{Cu}_{\text{Ga}}$  and  $\text{Ga}_i$  in Fig. 3 below. As noted before, both carriers are believed to be strongly localized for this BE. A strong contribution of the magnetic dipole-dipole interaction to the  $D$  tensor is therefore reasonable for the 1.911-eV BE. More detailed calculations are not warranted until wave functions for the bound electron and hole are available.

#### C. Possible identity of the 1.911-eV complex defect

In our previous work several possible models for the geometrical structure of this defect have been discussed.<sup>1,2</sup> The more accurate data derived in this work permit a more precise prediction of the defect symmetry, and consequently its possible identity. We recall that the primary defect axes are [001], [ $\bar{1}\bar{1}0$ ], and [110], i.e., the set that diagonalizes both the  $g$  tensor and the  $D$  tensor. In addition it is known from previous work<sup>1</sup> that the isotropic  $e$ - $h$  exchange interaction is quite large, 91 meV,<sup>1</sup> meaning that both hole and electron must be strongly localized. This is most naturally understood if the defect has one strongly hole-attractive (acceptorlike) part and also one strongly electron-attractive (donorlike) part. The former is naturally identified as  $\text{Cu}_{\text{Ga}}$ , being a deep (0.51 eV) acceptor in GaP.<sup>21,22</sup> The deep donor is most naturally identified as a Ga interstitial, as previously discussed,<sup>1</sup> but other possibilities cannot be ruled out. A  $\text{Ga}_i$  interstitial may contribute one or more donor electrons. If only one electron is provided, which seems most likely, another single donorlike part is needed in the complex to make an overall neutral core together with  $\text{Cu}_{\text{Ga}}$ , which is supposed to have a filled  $d$  shell. A natural suggestion here is an interstitial Cu atom,  $\text{Cu}_i$ . (It has previously been concluded that foreign impurities except Cu are not active in the complex.<sup>1,2</sup>)

The ODMR data presented in this work give more reliable information about the symmetry of the defect than was previously obtained.<sup>1</sup> Clearly the  $C_{1h}$  symmetry is inconsistent with the previous tentative conclusion of an axial  $\langle 001 \rangle$ -oriented defect. For this configuration the components  $D_x$  and  $D_y$  of the  $D$  tensor would have to be the same, for symmetry reasons, while they are found to be very different in this work. Previous work on uniaxial stress spectroscopy for this defect allows the conclusion that the defect is approximately a  $\langle 110 \rangle$ -oriented  $\pi$  oscillator.<sup>23</sup> The stress data also appear to be inconsistent with a linear  $\langle 001 \rangle$  orientation.

Figure 3 shows one of 12 equivalent centers of  $C_{1h}$  symmetry, which can explain the ODMR data. In this model the three-atomic defect lies in a  $\{110\}$  plane, with

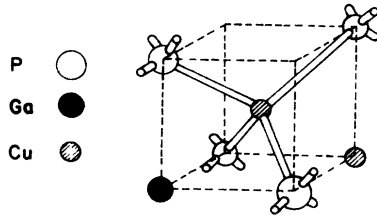


FIG. 3. A possible model of the 1.911-eV Cu-related complex defect studied in this work. The defect is bent in a  $\{110\}$  plane.

the central Cu atom on a Ga site and the two interstitials ( $\text{Cu}_i$ ,  $\text{Ga}_i$ ) located along two different  $\langle 111 \rangle$  axes with respect to  $\text{Cu}_{\text{Ga}}$ . This configuration can account for the  $\langle 001 \rangle$  and  $\langle 110 \rangle$  principal axes of the defect. Two interstitials along two adjacent  $\langle 111 \rangle$  axes lead to an overall  $\langle 110 \rangle$  defect axis. The defect potential is dominated by  $\text{Cu}_{\text{Ga}}$  (hole-attractive part) and  $\text{Ga}_i$  (electron-attractive part), which would explain the maximum splittings observed along the  $z$  ( $\langle 001 \rangle$ ) and  $y$  ( $\langle 110 \rangle$ ) axes in Fig. 2. This is therefore suggested as a possible geometrical model for the defect (Fig. 3). It should be emphasized, however, that it is only one of several possible configurations consistent with the low  $C_{1h}$  symmetry and the involvement of two interstitial sites. A more definite assignment of the defect identity requires information from both central and ligand hyperfine interaction in ODMR spectra, which were not resolved in this case.

## V. SUMMARY AND CONCLUSIONS

A detailed study is reported on the magnetic properties of the 1.911-eV bound exciton in GaP, from ODMR data in the photoluminescence mode. With the aid of below-band-gap tunable-dye-laser excitation directly into the excited (singlet) BE state of the defect, ODMR spectra could be recorded with good sensitivity in a standard 9-GHz microwave system at 4 K. The 1.911-eV triplet BE spectrum gives ODMR of both " $\Delta M = 1$ " and " $\Delta M = 2$ " character, and using both  $\sigma$  and  $\pi$  polarizations in the Voigt configuration all resonance components could be spectrally resolved. The relevant spin Hamiltonian contains the usual  $\vec{g}_{\text{ex}}$  and  $\vec{D}$  tensors, the values of which could be determined with an accuracy of about 1%.

With the aid of these data, and a theoretical fit of the spin Hamiltonian, several properties of the defect may be firmly established. The symmetry of the defect is found to be  $C_{1h}$ , i.e., a defect consisting of three atoms (such as  $\text{Ga}_i$ - $\text{Cu}_{\text{Ga}}$ - $\text{Cu}_i$  bent in a  $\{110\}$  plane). The symmetry is lower than the one previously deduced from less accurate ODMR data. The angular momentum of the bound hole is nearly completely quenched, which is typical for hole-attractive defects of low symmetry. In this work the small anisotropy of the hole  $\vec{g}$  tensor  $\vec{g}_h$  ( $\approx 2\%$ ) can be accurately resolved, however, which allows a discussion of the relevance of spin-orbit induced perturbations on the properties of such bound-hole states. It is also concluded that the  $D$  tensor is not dominated by the spin-orbit interaction, but rather by the magnetic dipole-dipole interaction between the electron and the hole.

\*Permanent address: Science Institute, University of Iceland, Dunhaga 3, 107 Reykjavik, Iceland.

†Permanent address: Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Al. Lotnikow 32/46, Poland.

††Permanent address: Department of Solid State Physics, Box 118, University of Lund, S-220 07 Lund 7, Sweden.

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