Optical properties of a neutral Cu-C complex defect in GaP

H. P. Gislason,* B. Monemar, and P. Bergman
Department of Physics and Measurement Technology, University of Linköping, S-581 83 Linköping, Sweden

M. E. Pistol
Department of Solid State Physics, University of Lund, Box 118 S-221 00, Lund, Sweden
(Received 7 December 1987)

A bound-exciton (BE) spectrum with a lowest electronic line at 2.2383 eV at 2 K is reported in GaP doped with both C and Cu. This BE has an electronic structure composed of two pairs of magnetic singlet-triplet states. The triplets are at lower energy and separated by about 0.9 meV. The corresponding pair of singlet states is split towards higher energies by 8 meV. This unusual electronic structure can be explained if an electron-hole pair is bound to a spin-free complex defect with a dominantly hole-attractive central-cell potential and symmetry only slightly distorted from trigonal symmetry. The identity of the defect is suggested to be Cu_{Ga}-C_i. The involvement of interstitial C is evidenced by local modes in the phonon side band of the BE emission spectrum.

I. INTRODUCTION

Cu in GaP gives rise to deep acceptor levels[1-4] as well as a large number of neutral complex defects. Detailed optical studies have been presented for bound excitons associated with such complexes, notably the so-called characteristic orange luminescence (COL) defect,[5,6] believed to be a trigonal Cu_{Ga}-Cu_i-Cu_i complex, and the 1.91-eV center, assigned to be a Cu_{Ga}-Ga_i complex.[7] Co-doping with Li also gives rise to a large number of neutral complex (Cu-Li) defects, involving both Cu and Li atoms.[8-10] A rather good understanding of the electronic structure of electron-hole pairs bound to such defects has been obtained.[11,12] The microscopic identity is much less certain, but consistent models for the geometrical structure of these complexes have in most cases been derived from optically detected magnetic resonance (ODMR) experiments on the triplet-bound-exciton (BE) states characterizing most of the cases mentioned above.[7-10,13-16]

C in GaP is known to be a shallow hydrogenic acceptor when substituted on P site,[17-19] the binding energy being about 54 meV.[19] C substituting on Ga sites has so far not been positively identified. Theoretical calculations using the Green's-function formalism indicate that C_{Ga} should be a deep midgap donor in GaP.[20] In our data from the present work we see no trace of such a donor in C-doped GaP.

When C-doped GaP is Cu-diffused, a new previously unreported strong bound-exciton spectrum is observed, with a lowest electronic transition at 2.2383 eV at 2 K.[11] This defect appears to involve both C and Cu and is attributed to a neutral spin-free complex from the electronic configuration of the associated BE lines. It will be demonstrated that C is most probably involved in interstitial form in this case, i.e., neither C_{Ga} nor C_P is likely to be a part of this complex defect.

II. SAMPLES AND EXPERIMENTAL PROCEDURE

As starting material solution-grown C-doped GaP samples of good photoluminescence (PL) efficiency were used. For Cu doping a diffusion source of Cu was first evaporated on the samples. These samples were subsequently placed in evacuated sealed quartz ampoules, and diffused in these ampoules for approximately 1 h. Typical diffusion temperatures employed in this study were 850–900 °C. After diffusion the ampoules were rapidly quenched in water.

Cu diffusion at lower temperatures than 850 °C was not successful in creating the 2.238-eV spectrum reported in this work, while in the interval 850–900 °C the spectrum appeared with intensity comparable to other BE lines generally observed under these conditions (e.g., the N, S, and COL bound-exciton spectra). Correlation was found between the intensities of the 2.238-eV emission and the shallow bound-exciton lines related to C_P,[21] under these diffusion conditions.

Photoluminescence measurements were performed in the temperature range 1.5–50 K. Temperatures below 4.2 K were obtained by pumping at the sample chamber of a He immersion cryostat. For temperatures above 4.2 K a variable-temperature cryostat was used, in which the sample temperature was controlled through thermal contact with a Cu heater, which was cooled by cold He gas. The temperature of the heater was electronically regulated and monitored with calibrated Si-diode sensors.

Above-band-gap excitation was provided by the 5145-Å Ar^+ laser line. The photoluminescence spectrum was dispersed either with a 0.75-m Jarrell-Ash or a 0.6-m Jobin-Yvon double-grating monochromator, with 600-lines/mm gratings blazed at 1 μm.

The cw PL signal was detected with an S-20 photomultiplier (PM) tube and recorded with lock-in techniques.

In addition, photon-counting techniques were employed, using a GaAs PM tube (Hamamatsu R943-02).

For time-resolved measurements a pulsed N_2 laser (Lambda Physik M1000) with a tunable dye laser (FL 2002) was the excitation source. The transients were detected with a GaAs PM tube (Hamamatsu R943-02) and recorded with a transient recorder (Biomation Model 6500 waveform recorder). Zeeman measurements were made in Linköping using a 7-T Oxford Spectromag 4 superconducting magnet system, in which the sample temperature could be varied. Such measurements were also performed at Royal Signals and Radar Establishment, employing a 3-T Varian electromagnet and an immersion cryostat, pumped below 2 K.

III. EXPERIMENTAL RESULTS

A. Photoluminescence measurements

In Fig. 1 a typical photoluminescence (PL) spectrum of Cu-C–doped solution-grown GaP is shown. The near-band-gap region is dominated by PL lines related to the shallow C_P acceptor, together with the N BE spectrum[22] [Fig. 1(a)]. In the ir region (not shown) the spectrum is dominated by oxygen-related emissions,[23,24] and no evidence for an isolated deep C_{Ga} donor is seen in photoluminescence in these samples. The interesting new features related to Cu diffusion occur in the spectral region 2.15–2.25 eV [Fig. 1(b)].

Partly overlapping with the COL BE emission with a zero-phonon line at 2.1774 eV,[5] a new emission [Fig. 1(b)] with a no-phonon line $L1$ at 2.2383 eV at 2 K is observed. Actually, two closely spaced electronic lines can be resolved at a slightly higher temperature, the higher-energy one, $L2$, at 2.2392 eV at 4 K. The relative intensities of these two lines thermalize so that the 2.2392-eV line has about half the intensity of the 2.2383-eV line above about 5 K, as shown in Fig. 2.

When the temperature is raised above 10 K two additional closely spaced electronic lines $L3$ and $L4$ are observed at photon energies 2.2463 and 2.2475 eV, respectively (Fig. 2). The thermalization between the latter pair of lines is similar to that of lines $L1$ and $L2$. All four lines belong to the same PL spectrum and show phonon coupling similar to that observed for the lowest PL line at 2.2383 eV (Fig. 3) (see also Fig. 5 of Ref. 11). The high-energy lines $L3$ and $L4$ are observed in PL through thermal population at 15–40 K, but they are both of much higher oscillator strength than the low-energy lines $L1$ and $L2$, as the time-resolved measurements (to be presented below) show. The absorption strength of all these lines is rather low, however, and the concentration of the 2.238-eV center is concluded to be well below 10^{15} cm^{-3}, since it was not possible to observe the total electronic spectrum of this bound exciton in absorption, neither transmission nor dye-laser–excited excitation spectra.

As was observed for the COL BE,[5,25] a rich spectrum

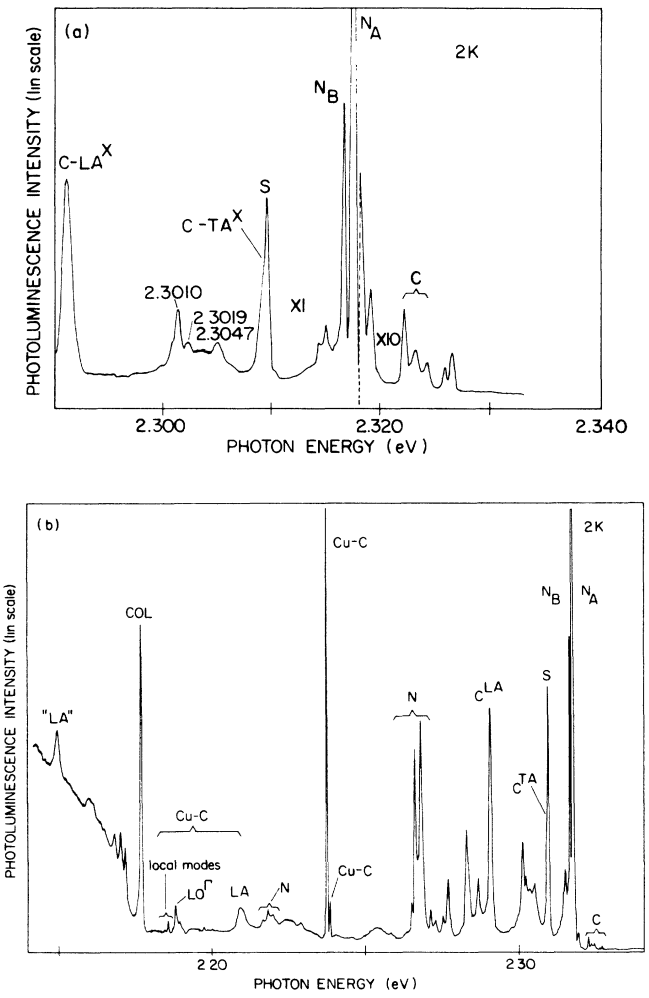

FIG. 1. (a) Near-band-gap photoluminescence spectrum at 2 K of a (Cu-C)-doped solution-grown GaP platelet. The bound-exciton lines related to the C_P acceptor are clearly shown, as well as N- and S-related bound excitons. (b) Extension of the spectrum in (a) towards lower photon energies. The (Cu-C)-related spectrum is clearly shown with sharp electronic lines at 2.2383 and 2.2392 eV, respectively. The Cu-related COL emission (Ref. 5) is also seen at the low-energy end of the spectrum.

of phonon replicas, representing both GaP lattice modes and defect-related phonon modes, is observed in the spectrum of the 2.2383-eV $L1$ line (Fig. 3). The most prominent sharp features in the one-phonon-assisted part of the spectrum are listed in Table I, together with a suggestion for the identification of the corresponding phonon modes.

A rather strong coupling is observed to the low-energy acoustic-phonon wing, although weaker than in the case of the COL spectrum, as can be seen in Fig. 1(b). A phonon mode is observed at 8.7 meV, followed by a band of several such features at 10–13 meV, resonant in energy with the high-density-of-states region just below the TA (X)-phonon energy of 13.1 meV in GaP.[26] A strong,

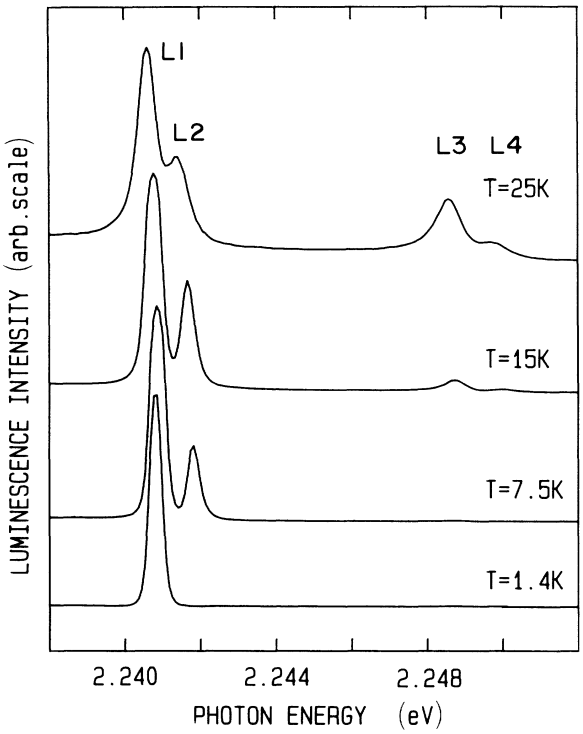

FIG. 2. No-phonon part of the Cu-C bound-exciton spectrum, measured in photoluminescence at four different temperatures. Four electronic lines are observed above ≈ 12 K, labeled $L1$–$L4$. The high-energy lines ($L3$,$L4$) appear weak, due to thermalization, but have a much higher oscillator strength than the lower-energy pair ($L1$,$L2$).

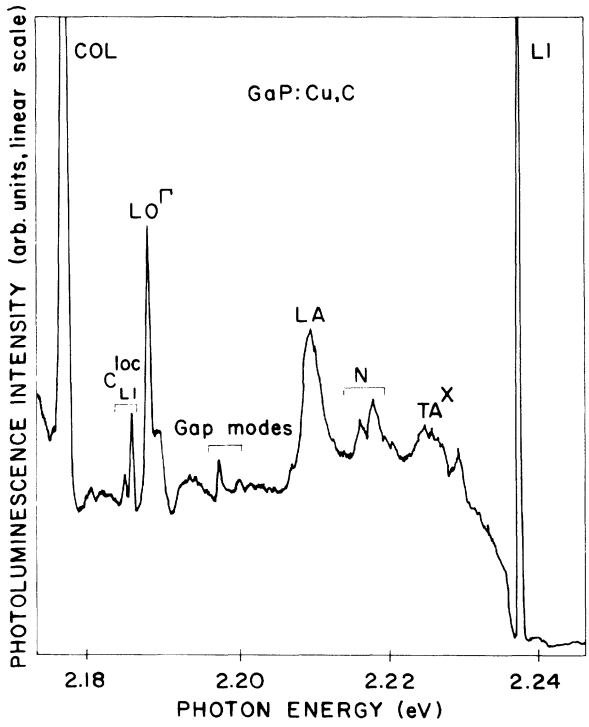

FIG. 3. The photoluminescence spectrum of the lowest-energy Cu-C bound-exciton line $L1$ at very low temperature ($T<2$ K), showing the electronic line at 2.2383 eV, together with a phonon-assisted spectrum, mainly in the one-phonon range. Several phonon replicas are observed and identified in Table I. Lines marked N are 2LO replicas of the N-bound exciton at 2.317 eV.

broad peak is observed in the spectrum at 29.7 meV, which is close in energy to the LA(L) phonon. A similar mode is strong in the COL spectrum,[5,25] where it was attributed to a Ga-site–localized motion, and shown to involve Cu.[25] Two sharp modes at 38.0 and 41.1 meV occur in the gap of the phonon density of states in GaP,[26] and may be interpreted as defect modes perturbed either from the LA band, or the optical-phonon branch. The latter phonon-energy range is dominated by the LO(Γ) replica (Fig. 3).

Two sharp local modes occur in the 2.238-eV spectrum with phonon energies 52.3 and 53.5 meV, respectively (Fig. 3). These modes are so-called true local modes with phonon energies above the high-energy cutoff of the GaP host lattice, which proves the involvement of a light element such as C in the defect complex,[27] which we henceforth refer to as the Cu-C center. The presence of two local modes is similar to the case of Cu-Li defects in GaP reported previously,[8–10] where they were attributed to interstitial Li. Isotope doping with C was not attempted in this work. Therefore we cannot establish whether more than one C atom are involved in the defect. It should be noted that the Cu atoms, being rather heavy, are not expected to give rise to true local modes, and no such modes are observed in the COL (Ref. 5) and 1.91-eV (Ref. 7) Cu-related BE spectra in GaP. The 2.238-eV complex was observed to be thermally instable at room temperature. Thus its photoluminescence intensity decreased compared to other emissions in the same samples that were kept at room temperature for about 2 yr. In our opinion this suggests the participation of an interstitial species in the defect, in agreement with similar observations for Cu-related defects in ZnTe.[28]

The Zeeman splitting at 2 K of the electronic lines of the Cu-C BE was measured at 2.8 T. The two lowest electronic lines at 2.2383 and 2.2392 eV ($L1$ and $L2$)

TABLE I. Phonon replicas in the Cu-C bound-exciton spectrum.

Energy (eV)	Energy difference from no-phonon line (meV)	Interpretation
2.2383	0	no-phonon line
2.2296	8.7	in-band resonance
2.2252	13.1	TA(X)
2.2085	29.7	perturbed LA mode
2.2003	38.0	gap mode
2.1972	41.1	gap mode
2.1888	49.5	LO(Γ)
2.1860	52.3	local mode, C-related
2.1848	53.5	local mode, C-related

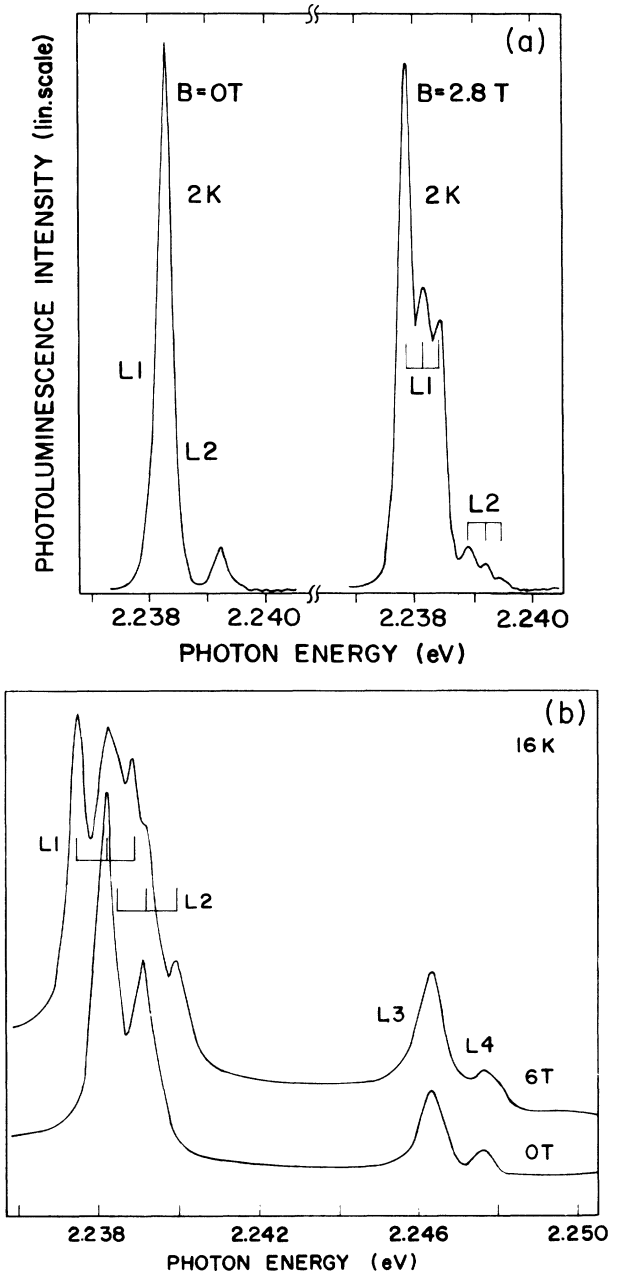

FIG. 4. (a) Zeeman splitting in photoluminescence at 2 K of the two lowest-energy Cu-C bound-exciton lines $L1$ and $L2$. Both split as approximately isotropic triplets. The g value $g_{\text{eff}}=\frac{1}{2}(g_e+g_h)$ is close to $g_{\text{eff}}=2$ for both lines. (b) Zeeman splitting at about 16 K for all four lines. No splitting is observed for $L3$ and $L4$ at 6 T, whereas the triplet nature of $L1$ and $L2$ shown in (a) is confirmed. Thermal broadening at this temperature reduces the resolution somewhat.

were both observed to split into three lines, i.e., they originate from magnetic triplet states [Fig. 4(a)]. The observed thermalization between the magnetic subcomponents is consistent with the triplet state being the excited BE state. The Zeeman splitting is approximately isotropic for both lines, with an effective g value $g_{\text{eff}}=\frac{1}{2}(g_e+g_h)$ close to 2. If the electron g value of the BE is supposed to have the normal value for shallow donors in GaP, i.e., $g_e\approx 2.00$,[29,30] the hole g value g_h is also close to $g_h=2$, and the hole is effectively a spin particle. This is expected in the case of a hole bound to a complex defect with a strongly-hole-attractive potential, as discussed in Sec. IV. In order to determine the magnetic degeneracy of the high-energy lines $L3$ and $L4$, it is necessary to raise the temperature to about 12–15 K, where all lines can be observed with reasonable linewidths. Figure 4(b) shows the splitting at 6 T for an arbitrary direction of the magnetic field. It is clear that no splitting of either line $L3$ or $L4$ is observed, whereas both $L1$ and $L2$ split into three overlapping components, as shown more clearly in Fig. 4(a). Hence, it is established that the Cu-C BE has the unusual electronic configuration of two pairs of singlet-triplet states.

Optically detected magnetic resonance experiments were attempted for this BE emission in a 9-GHz equipment. No ODMR resonance could be detected in these experiments, similar to the case of the COL emission,[5] where ODMR experiments also failed. As mentioned before, ODMR data have been recorded for excitons bound to several other complexes of similar type in GaP,[13–16] however. The reasons for the failure of ODMR in this case might be connected with details of the electronic structure of the BE, as discussed below.

B. Decay-time measurements

The exchange splitting, 8 meV, between the singlet and the triplet components of the Cu-C bound exciton is of intermediate value among the reported such splittings in GaP,[5–10] and is large enough that both components can be studied well separated at elevated temperatures in a rather wide temperature range, before thermal ionization of the bound exciton quenches the photoluminescence.

Figure 5 shows the experimentally measured decay

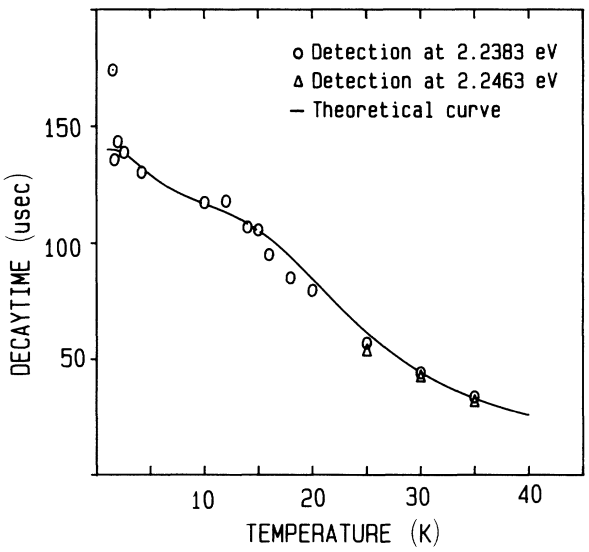

FIG. 5. The decay of the Cu-C BE at different temperatures, measured at $L1$ (dots) and $L2$ (squares). The curve represents a fit of Eq. (1) to the data with $\tau_{L1}=140$, $\tau_{L2}=80$, and $\tau_{L3}=\tau_{L4}=1$ μsec.

time as a function of temperature. A theoretical fit to the experimental values is included in the figure. The analysis assumes that the spin-lattice relaxation time between the different states is much shorter than any of the radiative recombination times involved. A value of 25 ps has been reported for the relaxation time in a similar isoelectronic system, GaP:N.[31] Because of the fast relaxation time all four components of the Cu-C BE show the same experimental decay time, since they interact to form a canonical distribution of states at all times after excitation. Using simple statistics the resulting experimental decay time at temperature T, $\tau_{\text{expt}}(T)$, can be expressed as

$$\tau_{\text{expt}}(T)=\frac{1+e^{(-\Delta_{12}/kT)}+g_S/g_T(e^{(-\Delta_{13}/kT)}+e^{(-\Delta_{14}/kT)})}{1/\tau_{L1}+1/\tau_{L2}e^{(-\Delta_{12}/kT)}+g_S/g_T(1/\tau_{L3}e^{(-\Delta_{13}/kT)}+1/\tau_{L4}e^{(-\Delta_{14}/kT)})} . \quad (1)$$

The four states are labeled Li, where $i=1,2$ denotes the triplets and $i=3,4$ the singlets with degeneracies g_T and g_S, respectively. τ_{Li} is the radiative recombination time for state i and Δ_{ij} denotes the energy separation between states i and j. A good fit of Eq. (1) to experimental data is obtained with $\tau_{L1}=140$, $\tau_{L2}=80$, and $\tau_{L3}=\tau_{L4}=1$ μs.

It should be pointed out that a four-parameter fit to a limited number of experimental points is somewhat arbitrary, and the result should not be interpreted too literally. The decrease of τ_{expt} with increased temperature is, however, a clear demonstration of the change in the population distribution between the triplet and singlet states. The slow spin-forbidden recombination from the triplets dominates at low temperatures, while the allowed and consequently faster recombination from the singlet states is thermally favored at higher temperatures. The observed difference between the singlet and triplet lifetimes (about a factor of 100) agrees with other singlet-triplet systems both in GaP (Ref. 32) and Si (Ref. 33).

The sizable exchange splitting of the Cu-C BE makes this system more suitable for dynamical studies than BE systems with either smaller or larger such splitting.[5–10] With a splitting of about 2 meV, a common value in GaP,[8–10] the two components are observed simultaneously only in a very narrow temperature interval. In cases where the splitting is much larger, on the other hand, thermal ionization may prevent the singlet from being observed.[5] In the present case, however, both the singlet and triplet components of the Cu-C BE show strong luminescence lines at temperatures above some 25 K, well before thermal quenching. It is therefore possible to measure separately the decay time of the singlet and triplet lines at the same temperature [at the actual temperatures it is not possible to resolve the small splitting (~ 1 meV) between the two singlets or the two triplets]. The decay time was found to be identical for both components, which supports the model presented above.

A detailed analysis of the dynamics of singlet-triplet BE systems in GaP, including the present one, will be given elsewhere.[32,34]

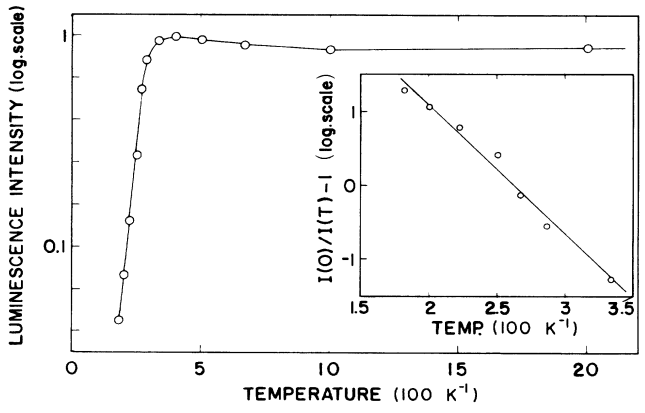

FIG. 6. The integrated intensity of the Cu-C photoluminescence, taken as the area under the PL band, as a function of $100/T$. The inset shows that to a good approximation the rapid quenching above 30 K can be described by a single nonradiative process with activation energy 35 meV.

C. Thermal quenching of the photoluminescence

The integrated intensity of the 2.238-eV Cu-C PL band was measured as a function of temperature as illustrated in Fig. 6. The sharp decrease in the intensity above about 30 K can be described by the equation[35]

$$y(T)=I(0)/I(T)-1=W_{\text{NR}}(T)/W_R , \quad (2)$$

where W_R is the radiative recombination rate, taken to be temperature independent, and $W_{\text{NR}}(T)$ is the combined nonradiative recombination rate. The latter is well described by a single thermally activated process in our case as shown in the inset, $W_{\text{NR}}(T)=W_0e^{-E_a/kT}$ with $E_a=35$ meV and the preexponential factor $W_0=4\times10^4$ sec^{-1}. The quenching behavior was measured with above-band-gap excitation (5145 Å), since it was found that extrinsic excitation was a very ineffective excitation source for the Cu-C BE.

IV. DISCUSSION

A. Electronic structure of the 2.238-eV (Cu-C)-related bound exciton

From the above analysis of bound-exciton spectra, we assign the Cu-C defect to a neutral "isoelectronic" center. For such a center there is an electron-hole pair bound to the defect in its excited state, while no particle is bound in the ground state. A strong argument for this assump-

tion is the relatively strong radiative intensity observed for this rather deeply bound exciton (114 meV), which is not expected if the center were a neutral donor or acceptor, with an additional particle present in both excited state and ground state. Indeed, in the latter case competing Auger effects upon BE recombination are quite strong in GaP,[21,36] which quenches the photoluminescence. In addition, the observed electronic singlet-triplet structure of the defect is inconsistent with an odd number of electronic particles in either the excited state or the ground state.

The mechanism for obtaining a magnetic triplet as the lowest-energy configuration of an electron-hole pair bound to a neutral complex defect has been discussed previously, e.g., for the case of Cu-related complexes in GaP.[9,11] A necessary condition is a rather strong local strain field at the defect site, acting more strongly on the hole states than the spin-orbit interaction. If the defect potential is hole attractive and of low symmetry, an orbitally nondegenerate state with a quenched orbital angular momentum can result as the lowest-energy bound-hole state at the defect. Such a hole, i.e., essentially a spinlike hole $s_h=\frac{1}{2}$, once bound, attracts an electron ($s_e=\frac{1}{2}$) to form a BE with either a spin singlet ($S=0$) or spin triplet ($S=1$) configuration, for antiparallel or parallel spins, respectively. Usually, the spin-triplet state has the lowest energy for bound excitons.[5]

An electronic structure similar to the double singlet-triplet pairs of the 2.238-eV BE was encountered in recent work on (Cu-Li)-doped GaP.[9] In that case, however the singlet-triplet splitting was much smaller, or about 2 meV, and only one of the two triplets could unambigously be identified as such in magnetic field.[9]

In a simple model a small splitting of either hole states or electron states seems to be required to explain a corresponding small splitting of the bound-exciton states. Such a splitting cannot be easily understood for the highly localized A_1-like hole states, which are a necessary condition for orbitally nondegenerate holes.[5,11,12] The bound-electron states, on the other hand, offer such possibilities. These states derive from multivalley degenerate conduction-band states. They are rather delocalized in nature and predominantly effective-mass-like for the class of hole-attractive centers discussed here.

An evidence for this is the activation energy for the thermal quenching of the BE, which was shown to be 35 meV from the data in Fig. 6. We attribute this activation energy to the thermal release of the electron from the BE, its binding energy thus being of the order expected from effective-mass theory (actually lower, but Coulomb repulsion from the electron-repulsive core of the complex must be taken into account). We note that the reverse, a thermal ionization of a hole, seems very unlikely. Judging from the spin-only behavior of the hole, it is highly localized.

However, it should be pointed out that despite this evidence for effective-mass properties of the electron, the large exchange splitting between the singlet and triplet states, which is related to the overlap between electron and hole wave functions, suggests a considerable overlap of these. Here the *e-h* exchange splitting for each triplet-singlet pair is about 8 meV. This value is larger than for most (Cu-Li)-related complex BE's in GaP [where Δ_{ex} is typically 2 meV (Refs. 8–10)] but smaller than for other Cu-related complexes in GaP, such as the COL defect [$\Delta_{ex}=23$ meV (Ref. 5)] or the 1.91-eV defect [$\Delta_{ex}\approx 90$ meV (Ref. 7)]. This is inconsistent with an extended effective-mass-like electron wave function. Another evidence for the same is the absence of effective-mass-like diamagnetic shift in magnetic fields up to 6 T. Hence, both particles of the Cu-C BE seem to have quite localized character, the hole presumably more so, however.

The symmetry of shallow donor electron states in GaP has been discussed by Morgan for tetrahedral symmetry,[37] neglecting the small "camel's-back" effect of the conduction-band structure. In this approximation the electron wave function contains contributions from three equivalent conduction-band minima at the X points of the Brillouin-zone boundaries.[37] For symmetries lower than tetrahedral, this equivalency is broken, which results in a splitting between wave functions with nodes and antinodes of the donor sites.[38]

Trigonal symmetry is an exception, however, since the $\langle 100\rangle$-oriented conduction-band valleys remain equivalent with respect to trigonal $\langle 111\rangle$ strain. There-

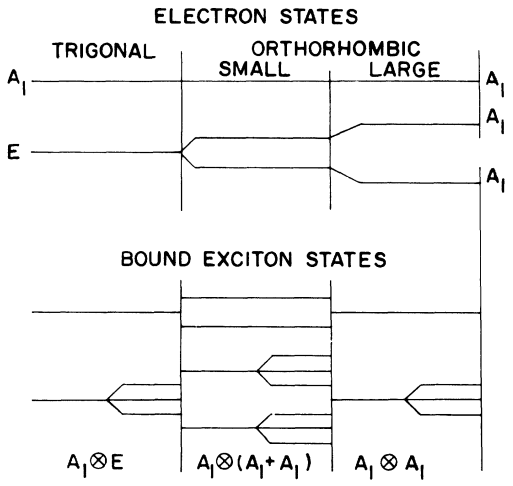

FIG. 7. Schematic representation of the electronic structure of bound states for the Cu-C defect in GaP (center), compared with other similar complex defects. For a hole-attractive center the lowest bound-electron state is an orbitally degenerate E state in trigonal symmetry, which splits further upon lowering the symmetry. (All symmetry notations refer to orbital degeneracy.) The bound-hole state is assumed to be an orbital singlet in symmetry lower than T_d, for a strongly hole-attractive defect potential. The bound-exciton states shown below the corresponding bound-electron states are spin triplet-singlet pairs in all cases. The case of trigonal symmetry is, in practice, realized with the COL defect (Refs. 5 and 6), and the case of small orthorhombic distortion is found for the Cu-C defect discussed in this work, but also for the $(\text{Cu-Li})_{\text{III}}$ defect (Ref. 9). The case of large orthorhombic distortion is found in the majority of cases, such as the 1.91-eV defect (Ref. 7), and the $(\text{Cu-Li})_{\text{I}}$ (Ref. 8) and $(\text{Cu-Li})_{\text{V}}$ defects (Ref. 10).

fore C_{3v} symmetry does not split the A_1 and E states of tetrahedral symmetry further. This is shown to the left in Fig. 7. For a hole-attractive defect the E state has lower energy, since the symmetric A_1 state has an antinode at the electron-repulsive central cell. This splitting is expected to be sizable by analogy with the central-cell shift of donors at tetrahedral P sites in GaP.[37] Hence a bound exciton at a hole-attractive site in trigonal symmetry would have the orbital degeneracy $A_1 \times E$ as shown in Fig. 7, given that the hole states are orbitally nondegenerate, transforming as A_1 in C_{3v}. This results in a single spin singlet-triplet pair of BE lines as has been encountered for the 2.177-eV COL bound exciton in GaP.[5,6]

Any lowering of the symmetry beyond trigonal splits the orbitally-twofold-degenerate E state as shown in Fig. 7. A strong deviation from trigonal symmetry causes a large splitting of the electron states as shown to the right, resulting in a single nondegenerate electron state A_1 and a corresponding single $A_1 \times A_1$ pair of BE states, for a similarly orbitally nondegenerate hole. This is the prevailing situation for low-symmetry hole-attractive defects in GaP, such as the $(\text{Cu-Li})_{\text{I}}$ (Ref. 8), $(\text{Cu-Li})_{\text{V}}$ (Ref. 10), and 1.91-eV (Ref. 7) defects.

For a small perturbation of the trigonal symmetry, such as a minor orthorhombic distortion, we envisage a situation where the trigonal E state splits into two closely spaced orbitally nondegenerate A_1 states. This would explain the particular electronic structure of the bound exciton in the present case, as shown in the central part of Fig. 7, that is, two spin singlet-triplet pairs. The same argument holds for the $(\text{Cu-Li})_{\text{III}}$ complex previously discussed.[9] This observed electronic structure is therefore taken as evidence for a defect with a symmetry close to trigonal.

The failure to observe ODMR resonances for either of the lowest two triplet lines in this study might be explained by the suggested electronic structure of the BE. If the bound-exciton state is an orbitally degenerate E state, it is sensitive to random strain fields in the crystal, which are known to broaden microwave resonances for orbitally degenerate levels in semiconductors to an extent that resonances may not be observed. The observed small splitting of the E state might not be sufficient to remove completely the interaction between these states, so that they may still cause sufficient broadening of ODMR resonances to make ODMR unobservable. The situation would then be analogous to the COL BE,[5,6] where the bound-electron state in the BE is an E state, and where no ODMR signals can be observed.[5,6]

B. Possible identity of the Cu-C complex defect

In the absence of symmetry information from magneto-optical or ODMR data, the geometrical structure of the complex has to be deduced from the information on sample preparation, as well as the electronic structure discussed above. The doping experiments discussed in Sec. II demonstrate that the Cu-C defect reported here appears only when GaP is doped with both C and Cu, and should therefore involve both. As noted in Sec. II, the strength of the Cu-C emission correlates with the intensity of the shallow C_P-related bound-exciton lines; further, the observed local modes in PL spectra are naturally interpreted as C related.

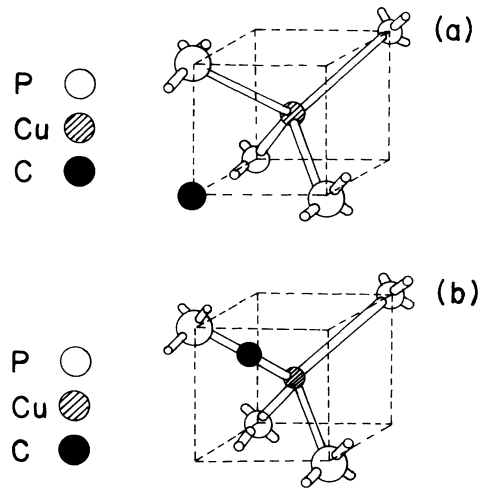

FIG. 8. Two possible configurations of the geometrical structure of the Cu-C defect studied in this work. (a) The possibility of a C atom in a tetrahedral interstitial position is shown. Small deviations from trigonal symmetry are not shown. (b) The case of bond-centered interstitial C atom, having a substitutional Cu_{Ga} nearby, is illustrated.

The electronic structure discussed in Sec. IV A rules out several possibilities for defect configurations. Thus the requirement of an overall hole-attractive defect potential strongly argues against C_P as the acceptorlike core of the defect. C_P is a shallow acceptor, probably shallower than interstitial donors such as Cu_i or C_i, and would not be the dominating part of complex defect comprising of a donorlike and an acceptorlike part. We consequently assume that Cu_{Ga} is the hole-attractive part of the complex, knowing that isolated Cu_{Ga} gives rise to deep bound hole states.[1-4]

In what follows, we shall assume that the Cu-C defect has a symmetry close to trigonal, in view of the observed electronic configuration. The requirement that the defect be neutral and isoelectronic greatly restricts the possible defect configurations. Since Cu_{Ga} is a double acceptor, it requires two electrons to complete its local bonds for a neutral defect in an ionic model. If C_P is involved as well, the center would be a triple acceptor instead. A logical conclusion is therefore the participation of interstitial atoms in the Cu-C center.

From the sample preparation and the presence of local modes in the BE spectrum, we feel confident that C_i is involved in the defect complex, as in Fig. 8(a). An interstitial C has four valence electrons, two of which might compensate for the missing electrons when Cu replaces Ga. The remaining two electrons of the C_i would thus be required to remain in a paired configuration, not affecting the magnetic properties of the Cu-C complex in either its ground or excited state.

Another possible configuration would be a bond-centered C, adjacent to Cu_{Ga} [Fig. 8(b)]. In such a configuration two electrons are needed for bonding purposes in addition to the two compensating the double-acceptor Cu_{Ga}. The symmetry in this case would be trigonal with a possible slight distortion off the ⟨111⟩ bond direction, thus in agreement with the above predictions. We tentatively suggest either of the two Cu_{Ga}-C_i complexes in Fig. 8 as the identity of the 2.238-eV Cu-C complex.

C. Lattice sites for C and the problem of C_{Ga} in GaP

The electronic structure of the C_{Ga} donor in GaP has been treated theoretically in recent Green's-function calculations,[20] where a deep midgap A_1 state was suggested for this donor. Such a state would be observable in the ir region via donor-acceptor (D-A) pair spectra at low temperature. The presence of an isolated deep C_{Ga} donor in GaP is not established experimentally, however. On the other hand, recent ODMR measurements on a PL band at 1.4 eV in crystals containing the 2.238-eV center may suggest the existence of a neutral complex containing C_{Ga} as a donorlike part.[39] Careful experimental work on C-doped GaP is necessary to examine the possibility of the existence of the isolated C_{Ga}.

Our conclusions from the present work is that C may occupy interstitial sites in GaP in addition to the well-known C_P shallow acceptor site. It is not clear, however, whether the interstitial C atoms are present in the as-grown GaP, or occur as a result of a defect reaction taking place during Cu diffusion at elevated temperatures ($T > 850\,^{\circ}C$), when the Cu-C defects are formed. More detailed future work is necessary to understand the defect reactions governing the behavior of C in GaP.

---

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

[1]B. Monemar, J. Lumin. **5**, 472 (1972).
[2]E. Fabre and R. N. Bhargava, Appl. Phys. Lett. **24**, 322 (1974).
[3]B. Wessels, J. Appl. Phys. **47**, 1131 (1976).
[4]P. O. Fagerström, H. G. Grimmeiss, and H. Titze, J. Appl. Phys. **49**, 3341 (1978).
[5]B. Monemar, H. P. Gislason, P. J. Dean, and D. C. Herbert, Phys. Rev. B **25**, 7719 (1982).
[6]M. J. Kane, P. J. Dean, M. S. Skolnick, and W. Hayes, J. Phys. C **17**, 6127 (1984).
[7]H. P. Gislason, B. Monemar, P. J. Dean, D. C. Herbert, S. Depinna, B. C. Cavenett, and N. Killoran, Phys. Rev. B **26**, 827 (1982).
[8]H. P. Gislason, B. Monemar, M. E. Pistol, P. J. Dean, and D. C. Herbert, Phys. Rev. B **31**, 3774 (1985).
[9]H. P. Gislason, B. Monemar, M. E. Pistol, P. J. Dean, D. C. Herbert, S. Depinna, A. Kana'ah, and B. C. Cavenett, Phys. Rev. B **32**, 3958 (1985).
[10]H. P. Gislason, B. Monemar, M. E. Pistol, A. Kana'ah, and B. C. Cavenett, Phys. Rev. B **33**, 1233 (1985).
[11]H. P. Gislason, B. Monemar, P. J. Dean, and D. C. Herbert, Physica **117&118B**, 269 (1983).
[12]B. Monemar, U. Lindefelt, and M. E. Pistol, J. Lumin. **36**, 149 (1986).
[13]S. Depinna, B. C. Cavenett, N. Killoran, and B. Monemar, Phys. Rev. B **24**, 6740 (1981).
[14]M. Godlewski, W. M. Chen, M. E. Pistol, B. Monemar, and H. P. Gislason, Phys. Rev. B **32**, 6650 (1985).
[15]A. Kana'ah, B. C. Cavenett, H. P. Gislason, B. Monemar, and M. E. Pistol, J. Phys. C **19**, 1239 (1986).
[16]W. M. Chen, B. Monemar, H. P. Gislason, M. Godlewski, and M. E. Pistol, Phys. Rev. B **37**, 2558 (1988).
[17]P. J. Dean, C. J. Frosch, and C. H. Henry, J. Appl. Phys. **39**, 5631 (1968).
[18]A. T. Vink, R. L. A. van der Heyden, and J. A. W. van der Does de Bye, J. Lumin. **8**, 105 (1973).
[19]M. D. Sturge, A. T. Vink, and F. P. J. Kuijpers, Appl. Phys. Lett. **32**, 49 (1978).
[20]M. Scheffler, J. Bernholc, N. O. Lipari, and S. T. Pantelides, Phys. Rev. B **29**, 3269 (1984).
[21]P. J. Dean, R. A. Faulkner, S. Kimura, and M. Ilegems, Phys. Rev. B **4**, 1926 (1971).
[22]D. G. Thomas and J. J. Hopfield, Phys. Rev. **150**, 680 (1966).
[23]P. J. Dean, C. H. Henry, and C. J. Frosch, Phys. Rev. **168**, 812 (1968).
[24]B. Monemar and L. Samuelson, Phys. Rev. B **18**, 809 (1978).
[25]H. P. Gislason, B. Monemar, P. O. Holtz, P. J. Dean, and D. C. Herbert, J. Phys. C **15**, 5467 (1982).
[26]R. M. Hoff and J. C. Irwin, Can. J. Phys. **51**, 63 (1973).
[27]P. J. Dean, Phys. Rev. B **4**, 2596 (1971).
[28]P. O. Holtz, B. Monemar, H. P. Gislason, and N. Magnea, J. Lumin. **34**, 245 (1986).
[29]F. Mehran, T. N. Morgan, R. S. Title, and S. E. Blum, Phys. Rev. B **6**, 3917 (1972).
[30]M. Godlewski, W. M. Chen, and B. Monemar, Phys. Rev. B **33**, 8246 (1986).
[31]L. W. Molenkamp and D. A. Wiersma, Phys. Rev. B **32**, 8008 (1985).
[32]P. Bergman and B. Monemar, Proceedings of the 6th International Conference on Dynamical Processes of Excited States in Solids, Tsukuba, Japan, 1987 [J. Lumin. **38**, 87 (1987)].
[33]E. C. Lightowlers, L. T. Canham, G. Davies, M. L. W. Thewalt, and S. P. Watkins, Phys. Rev. B **29**, 4517 (1984).
[34]P. Bergman and B. Monemar (unpublished).
[35]M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).
[36]P. J. Dean and D. C. Herbert, in *Excitons,* Vol. 14 of *Topics in Current Physics,* edited by K. Cho (Springer-Verlag, Berlin, 1979), p. 55.
[37]T. N. Morgan, Phys. Rev. Lett. **21**, 819 (1968).
[38]In Morgan's analysis (Ref. 37) a distinction is made for donors on tetrahedral P and Ga sites, the former experiencing a valley-orbit interaction, which splits the electron wave function into A_1 and E states already in tetrahedral symmetry. This distinction is not necessary in trigonal or lower symmetry, and Fig. 7 is thus valid for both P and Ga site substitutes.
[39]W. M. Chen, B. Monemar, and M. Godlewski (unpublished).