Neutral (Cu-Li) complexes in GaP: The $(Cu\text{-}Li)_{III}$ bound exciton at 2.242 eV

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A photoluminescence study is reported in order to identify a new radiative center in GaP co-doped with Cu and Li. This center, denoted $(Cu\text{-}Li)_{III}$, binds an exciton with binding energy 110 meV. The bound-exciton spectrum shows sharp electronic lines and a structured phonon sideband with well-resolved replicas. The group of electronic transitions consists of spin-only-like singlet-triplet pairs, which are characteristic of tightly bound holes in a strong compressive axial crystal field. Two such singlet-triplet pairs are observed for the $(Cu\text{-}Li)_{III}$ center, instead of the usual one pair. A model taking into account the splitting of electron states as well as hole states is proposed to explain this additional splitting. The experimental work includes photoluminescence spectroscopy and time-resolved and Zeeman measurements as well as optically detected magnetic resonance measurements. The careful doping procedure includes isotope doping with both ^{63}Cu,^{65}Cu and ^{6}Li,^{7}Li. The Li-isotope doping was clearly reflected in the phonon sideband. A neutral molecular associate of isoelectronic nature is suggested, with the $(Cu\text{-}Li)_{III}$ center involving Cu_{Ga} and a pair of interstitial atoms, Cu_i and Li_i.

I. INTRODUCTION

Isoelectronic centers occur not only as simple, single substitutional impurities, but also as associated donor-acceptor pair complexes. Such electrically neutral complexes are easily formed during diffusion at high temperatures due to Coulomb attraction between species of opposite charge.[1]

A small but significant proportion of neutral associate centers cause a perturbation strong enough to bind excitons with associated sharp-line photoluminescence spectra at low temperature. The Hopfield-Thomas-Lynch (HTL) model for isoelectronic point defects in semiconductors has successfully been extended to electron-attractive associate defects, such as nitrogen pairs in GaP where the separation of the atoms is much less than the Bohr radius of the exciton.[2]

Recently, there has been growing interest in the neglected case of neutral complexes dominated by acceptorlike central cells. A generic model for such defects, accounting for the splitting of the tightly bound hole states in the reduced symmetry, has been discussed previously.[3,4] The model has been used to explain the electronic structure of excitons bound to complexes of Cu in GaP. These excitons are subject to a strong axial field which causes a large binding energy for the electron as well as the hole, and consequently, a large electron-hole exchange interaction. Hence, the HTL model is not applicable to these bound-exciton systems.

New Cu-Li centers appear as a result of Li diffusion of the Cu-doped samples. Both these dopants are fast interstitial diffusers and being singly ionized at the diffusion temperature they are expected to be attracted to either Li_{Ga} or Cu_{Ga}. Neither of these substitutional impurities has been positively identified, but at least five complexes involving Cu and Li in GaP have been observed in bound-exciton (BE) spectra so far.[5–7] In a separate paper[5] we have reported on a center denoted as $(Cu\text{-}Li)_I$ with the lowest bound-exciton line at 2.306 eV. Another defect, referred to as the $(Cu\text{-}Li)_V$ center, which binds an exciton at 2.172 eV, will be discussed in a forthcoming paper.[6] The $(Cu\text{-}Li)_{III}$ complex discussed in the present paper binds an exciton with the lowest electronic transition at 2.242 eV.

In Sec. II we describe the doping procedure necessary to produce a strong $(Cu\text{-}Li)_{III}$ luminescence. Also, we outline the experimental techniques used in the optical measurements. In Sec. III A we present photoluminescence data for this center, including spectra measured in a magnetic field of 6 T. In Sec. III B we describe the results from the Li-isotope doping, in Sec. III C results from photoluminescence excitation measurements are given, and in Sec. III D the optically detected magnetic resonance data are summarized. In the discussion section (Sec. V) we correlate the observations with a model for the electronic structure as well as with a possible structural model of the defect. We pay particular attention to the results of the Li-isotope doping, which causes substantial shifts of the

local-mode replicas in the strong phonon sideband of this defect.

II. EXPERIMENTAL

A. Sample preparation

The Cu- and Li-doped GaP samples were prepared from liquid-phase-epitaxial (LPE) wafers, solution-grown material, and liquid-encapsulated Czochralski bulk material (LEC). The starting material was either *n* doped, *p* doped, or nominally undoped. It was found that the $(Cu\text{-}Li)_{III}$ spectrum is most easily produced from the purest starting material. It was found necessary to perform the diffusion in the samples in two steps. First a Cu diffusion was made at high temperature with a subsequent Li diffusion at lower temperatures. The reverse order produced no Cu-Li spectra. Li doping alone only caused the shallow Li_A and Li_B excitons to appear[8] along with the corresponding shallow donor-acceptor pair (DAP) emissions.

The Cu diffusion was performed in the temperature range 900—1100 °C for 1 h. The samples were diffused in an evacuated quartz ampoule. All samples were quenched in water to room temperature. This procedure, which has been described elsewhere,[3] gives rise to the characteristic orange Cu luminescence (COL) at 2.177 eV. Separately we prepared samples with both ^{63}Cu and ^{65}Cu isotopes.

The Li-diffusion step was performed at 400—1000 °C for from 40 min to 4 h in an evacuated quartz ampoule. A pellet of natural Li metal (92.6% ^7Li, 7.4% ^6Li) was placed in the ampoule. Separately, crystals were diffused with the ^6Li isotope and with a mixture of approximately equal amounts of ^6Li and ^7Li. The natural metal represented the ^7Li isotope.

After the Li doping in this temperature interval the COL luminescence always disappears completely. At the same time several new spectra appear. At least three of these appear regularly [$(Cu\text{-}Li)_I$ (Ref. 5), $(Cu\text{-}Li)_{III}$, and $(Cu\text{-}Li)_V$ (Ref. 6)] with relative intensities depending on starting material and diffusion procedure.

The $(Cu\text{-}Li)_{III}$ luminescence is strongest in nominally undoped epitaxial samples, Li diffused at 600° for 1 h. This spectrum is also easily produced in solution-grown material, at lower Li-diffusion temperatures for longer times, typically 400 °C for 4 h. However, the $(Cu\text{-}Li)_I$ luminescence at 2.306 eV always dominates in the solution-grown samples.[5] It was found that only the purest bulk material was useful for studying the $(Cu\text{-}Li)_{III}$ luminescence. The spectra are generally broader in the bulk material, and in the region 2.17—2.25 eV DAP spectra usually appear in GaP unless very pure.

In bulk material a third center, $(Cu\text{-}Li)_V$, was easily produced at lower Li-diffusion temperatures with longer diffusion times. In nominally undoped samples it was found that the relative strength of the $(Cu\text{-}Li)_{III}$ luminescence increased as the Li-diffusion temperature increased from 400—800 °C with a corresponding decrease of the diffusion time in order to avoid damage of the sample surface.

We found no correlation between the $(Cu\text{-}Li)_{III}$ center and other dopants often present in the samples. The most abundant ones were N, S, O, Te, S, Zn, and Ba, which could often be detected in the samples through their corresponding bound excitons.

B. Experimental techniques

Photoluminescence (PL) measurements were performed with Ar^+ cw laser excitation at 5145 Å with typical intensity 100 mW. The sample temperature could be varied from 1.8 K to room temperature. The PL spectra were recorded through a Jarrell-Ash 0.75-m double-grating monochromator employing a Nicolet 1170 signal averager. The magneto-optical experiments were made at the University of Hull with a superconducting magnet at fields up to 6 T. The lifetime measurements were made at the Royal Signals and Radar Establishment using cathodoluminescence, and at Hull University with conventional pulsed-laser measurements as well as frequency-response-spectroscopy measurements. Optically detected magnetic resonance results were obtained at a microwave frequency of 9 GHz using a superconducting magnet system.[9] The microwaves were chopped at approximately 300 Hz. The luminescence in the ODMR measurements was also excited at 5145 Å. The luminescence intensity changes were measured either for all light or selected wavelengths using a suitable choice of bandpass filters or a monochromator. An S20 photomultiplier was used for photoluminescence detection.

Photoluminescence excitation (PLE) measurements used cw dye-laser excitation with narrow-band detection through the Jarrell-Ash monochromator. The signals were extremely weak. Broadband detection, collecting the whole of the luminescence, did not improve the signal-to-background ratio.

III. EXPERIMENTAL RESULTS

A. Photoluminescence spectra

In Fig. 1 a typical low-temperature PL spectrum is shown for a Cu-Li—co-doped epitaxial wafer. Three

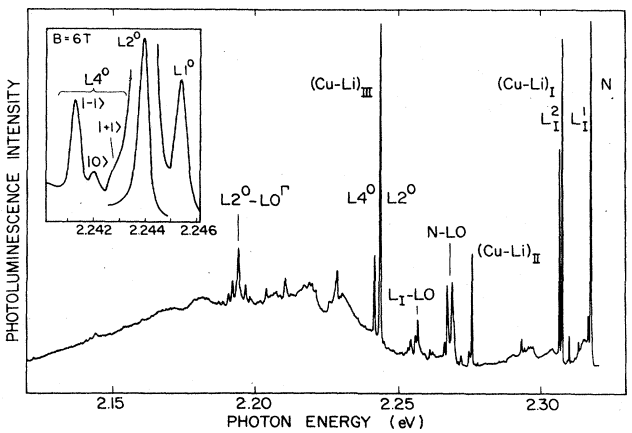

FIG. 1. Low-temperature PL spectrum of a typical epitaxial GaP wafer, co-doped with Cu and Li. Three independent Cu-Li centers are seen, $(Cu\text{-}Li)_{I-III}$. The electronic lines $L\,2^0$ at 2.2440 eV and $L\,4^0$ at 2.2419 eV are observed at 4 K for the $(Cu\text{-}Li)_{III}$ bound exciton. As shown in the inset, $L\,4^0$ splits into three subcomponents in a magnetic field of 6 T, while $L\,2^0$ remains unsplit. A third electronic line, $L\,1^0$, at 2.2454 eV is also a singlet as shown in the inset.

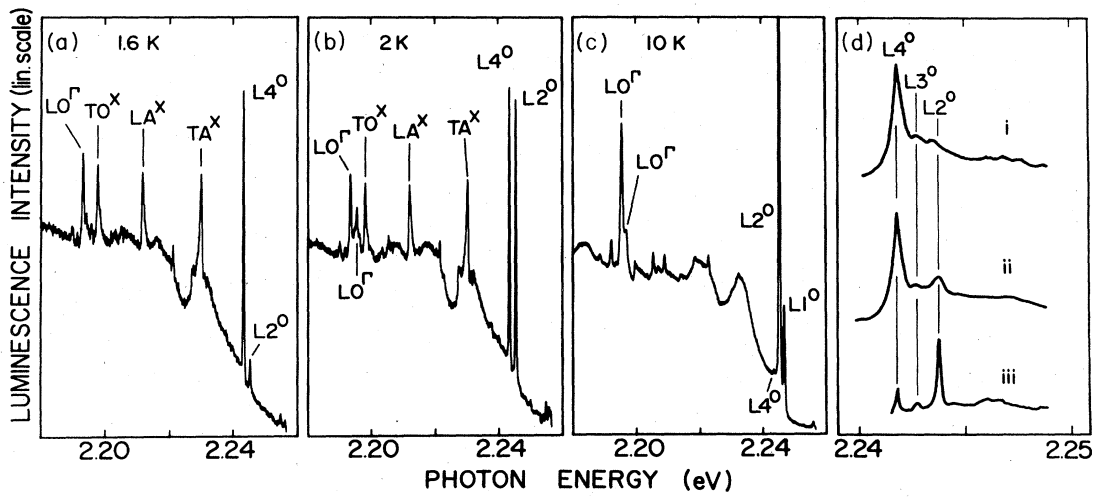

FIG. 2. Low-temperature PL spectra of the $(Cu\text{-}Li)_{III}$ luminescence. The magnetic triplet $L4^0$ dominates the spectrum at the lowest temperatures in (a). The strong phonon coupling to the X zone-boundary phonons is clearly seen for this line. At slightly higher temperature the singlet $L2^0$ grows stronger, panel (b). This line does not couple to the X zone-boundary phonons, but both lines show similar coupling to LO^Γ. At higher temperatures (c) $L4^0$ disappears whereas a second singlet $L1^0$ appears. Both singlets show a similar phonon coupling. In (d) is finally shown a blowup of the three electronic lines $L2^0$—$L4^0$ at three different low temperatures (1.6—3 K), also showing weakly the second triplet $L3^0$.

independent BE spectra are observed in Fig. 1, labeled $(Cu\text{-}Li)_{I-III}$. The $(Cu\text{-}Li)_I$ center is described elsewhere,[5] while the $(Cu\text{-}Li)_{II}$ spectrum has not been investigated in detail, since it is usually weak.

The $(Cu\text{-}Li)_{III}$ PL spectrum exhibits four electronic lines as shown in Fig. 2. The lowest line $L4^0$ occurs at 2.2419 eV, and it has a small relative oscillator strength. Therefore it is strong only when thermally favored at the very lowest temperatures [Fig. 2(a)]. The other two lines appear at 2.2440 eV ($L2^0$), and at 2.2454 eV [$L1^0$, Fig. 2(c)]. A close inspection in high resolution [Fig. 2(d)] reveals a weak component between the $L4^0$ and $L2^0$ lines. This line is denoted by $L3^0$ and is always of negligible strength in our spectra. The $L4^0$ line is a magnetic triplet according to Zeeman measurements up to 6 T. This is shown in the inset of Fig. 1, where the lowest magnetic subcomponent is strongest due to thermalization. Neither $L2^0$ nor $L1^0$ splits in a magnetic field of 6 T. The decay time for the $L4^0$ triplet is very long, about 500 μs, whereas the singlet $L2^0$ has a decay time of about 5 μs, also unusually long.

The phonon coupling to the $(Cu\text{-}Li)_{III}$ center is stronger than for the more shallow centers such as $(Cu\text{-}Li)_I$,[5] and it is different for the different electronic states. This is illustrated in Fig. 3 as well as in Table I, which contains a list of all phonon replicas observed in the $(Cu\text{-}Li)_{III}$ spectrum. The phonon coupling of $L4^0$ is characterized by three sharp peaks at the energies of the dominant phonons close to the X point of the Brillouin zone in the GaP reciprocal lattice.[10] They are $L4^{TA}$ (TA phonon energy 13.2 meV), $L4^{LA}$ (LA phonon energy 31.5 meV), and $L4^{TO}$ (TO phonon energy 45.3 meV). In addition, coupling of $L4^0$ to LO^Γ is represented by a peak $L4^{LO}$ at phonon energy 49.9 meV.

The most striking difference in the phonon coupling to the $L4^0$ triplet and the $L2^0$ singlet is that the strong

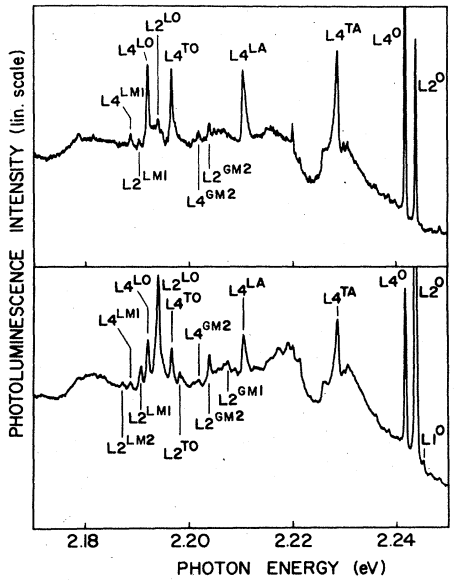

FIG. 3. A detailed PL spectrum of the $(Cu\text{-}Li)_{III}$ luminescence at two slightly different temperatures (compare Fig. 2). Unrelated peaks superimposed on the spectrum are not labeled. The phonon replicas related to the $(Cu\text{-}Li)_{III}$ center are listed in Table I. $L1^0$, $L2^0$, and $L4^0$ are the electronic lines, while the phonon replicas of the different lines are labeled similarly. $L4^{TA}$, $L4^{LA}$, and $L4^{TO}$ are the TA^X, LA^X, and TO^X zone-boundary phonon replicas of the $L4^0$ triplet. $L2^{LO}$ and $L4^{LO}$ are the LO^Γ replicas of $L2^0$ and $L4^0$, respectively. Localized phonon modes falling in the gap between the acoustical and optical branches of GaP are labeled GM1 and GM2, for the two different gap modes, respectively. Similarly, the two different true local modes with phonon energies above the cutoff frequency of the LO bands are labeled LM1 and LM2. For details see Table I.

TABLE I. Energy positions of the electronic transitions and the strongest phonon replicas in the $(Cu\text{-}Li)_{III}$ PL spectrum. Phonon energies are also listed for phonons coupling to the three lines $L1^0$, $L2^0$, and $L4^0$.

Notation	Photon energy (eV)	ΔE (meV) ^{7}Li	^{6}Li	Interpretation
$L1^0$	2.2454			$S=0$ singlet
$L2^0$	2.2440			$S=0$ singlet
$L3^0$	2.2430			$S=1$ triplet
$L4^0$	2.2419			$S=1$ triplet
$L4^{TA}$	2.2287	13.2		TA^X
$L4^{TA}$	2.2104	31.5		LA^X
$L2^{GM1}$	2.2075	36.5		gap mode 1
$L2^{GM2}$	2.2039	40.1		gap mode 2
$L4^{GM1}$	2.2018	40.1		gap mode 2
$L2^{TO}$	2.1982	45.8		TO^X
$L4^{TO}$	2.1966	45.3		TO^X
$L1^{LO}$	2.1954	50.0		LO^Γ
$L2^{LO}$	2.1940	50.0		LO^Γ
$L4^{LO}$	2.1920	49.9		LO^Γ
$L1^{LM1}$	2.1921	53.3		local mode 1 (^{7}Li)
$L1^{LM1}$	2.1886		56.8	local mode 1 (^{6}Li)
$L1^{LM2}$	2.1884	57.0		local mode 2 (^{7}Li)
$L1^{LM2}$	2.1854		60.0	local mode 2 (^{6}Li)
$L2^{LM1}$	2.1907	53.3		local mode 1 (^{7}Li)
$L2^{LM2}$	2.1872		56.8	local mode 1 (^{6}Li)
$L2^{LM1}$	2.1870	57.0		local mode 2 (^{7}Li)
$L2^{LM2}$	2.1840		60.0	local mode 2 (^{6}Li)
$L4^{LM1}$	2.1886	53.3		local mode 1 (^{7}Li)
$L4^{LM1}$	2.1851		56.8	local mode 1 (^{6}Li)

zone-boundary phonon replicas TA^X, LA^X, and TO^X observed in the phonon sideband of $L4^0$ are virtually absent for $L2^0$. The LO^Γ interaction is of similar strength for both states, however, as shown in Fig. 3.

It was difficult to study the phonon coupling to the highest $(Cu\text{-}Li)_{III}$ singlet-state $L1^0$ in detail, but the absence of strong coupling to the X zone-boundary phonons indicates a phonon coupling similar to that of the $L2^0$ line.

B. Isotope measurements

Figure 4 shows in detail the two local modes in the $(Cu\text{-}Li)_{III}$ spectrum, a rather strong one at 53.3 meV and a weaker one at 57 meV for ^{7}Li, and at 56.8 and 60 meV, respectively, for ^{6}Li. The abundances of ^{6}Li and ^{7}Li were approximately reflected in the relative intensities of the local modes after doping with natural Li, indicating that there is only one Li atom vibrating in the $(Cu\text{-}Li)_{III}$ center. Similar but better-resolved local-mode spectra were obtained for the $(Cu\text{-}Li)_I$ center.[5]

Mixed-isotope doping using approximately equal amounts of ^{6}Li and ^{7}Li in the ampoule reveals no new peaks. As will be discussed below, the simplest interpretation of these results is a model of the $(Cu\text{-}Li)_{III}$ center involving only one Li atom.

C. PLE measurements

The broad phonon wing in the PL spectrum of the $(Cu\text{-}Li)_{III}$ center allows a direct detection of PLE spectra. The result of such a measurement is shown in Fig. 5. A strong background from dominant exciton or carrier capture via two-step excitation had to be subtracted from the spectrum in order to display the weak signal.

Three strong transitions are positively identified in the PLE spectrum of Fig. 5. The two lines $A1^0$ at 2.2454 eV and $A2^0$ at 2.2440 eV correspond to the two singlets $L1^0$ and $L2^0$, respectively. The transition to the weak magnetic triplet ground state at 2.2419 eV does not appear in the PLE spectrum; neither is the second triplet state, $L3^0$, observable.

In addition to these lines a sharp line appears in the PLE spectrum at 2.2510 eV. This line is 9 meV above $L4^0$ and is thus never thermally populated in PL measurements. We do not know whether it belongs to the $(Cu\text{-}Li)_{III}$ center or to another unidentified center. A slightly wavy background is present in the PLE spectrum from stray light, but LA and TA density-of-states maxima are identified.

D. Optically detected magnetic resonance (ODMR) measurements

The optically detected magnetic resonance results will be published in detail separately[11] and so only a brief summary will be given here. The ODMR results for the $(Cu\text{-}Li)_{III}$ center confirm triplet-exciton recombination at axial centers and the $\langle 111 \rangle$ symmetry of the centers was deduced by detailed angular-dependence measurements of the ODMR signals fitting the data into the well-known

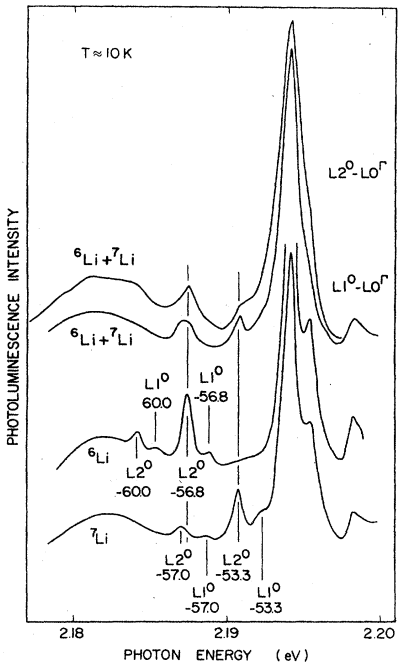

FIG. 4. A selected part of the PL spectrum of the $(Cu\text{-}Li)_{III}$ center showing the LO-phonon replicas and the true local modes of the electronic lines $L1^0$ and $L2^0$ (phonon energies in meV). The two topmost curves are results from mixed isotope doping with approximate equal concentrations of ^6Li and ^7Li. The remaining two curves at the bottom in the figure show spectra for pure isotope doping with ^6Li and ^7Li (actually 92.6% ^7Li in natural abundance). Two modes appear for each isotope, 53.3 and 57.0 meV for ^7Li, but 56.8 and 60.0 meV for ^6Li. No additional modes appear when both isotopes are present, neither with the natural abundancies nor in other ratios.

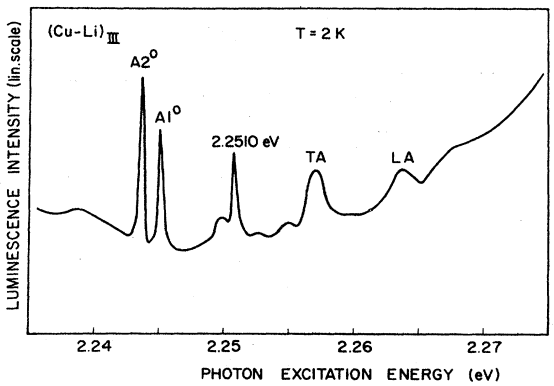

FIG. 5. PLE spectrum of the $(Cu\text{-}Li)_{III}$ luminescence measured with tunable dye-laser excitation at low temperature. The detection was set to 2.2 eV. The very weak signal is superimposed on a strong background (suppressed in the figure) due to low concentration of the center in the material. Only the two singlets $A2^0$ at 2.2440 eV and $A1^0$ at 2.2454 eV are observed ($L2^0$ and $L1^0$ in PL) with comparable strength. No signs of the triplets are detectable. The line at 2.2510 eV is possibly related to the $(Cu\text{-}Li)_{III}$ spectrum.

spin Hamiltonian

$$H=\mu_B \mathbf{S}\cdot\mathbf{g}\cdot\mathbf{B}+D[S_z^2-\tfrac{1}{3}S(S+1)]\,,$$

where $S=1$, $g_{||}=2.00$, $g_\perp=1.95$, and $D=0.04\ \mathrm{cm}^{-1}$.

IV. DISCUSSION

A. Electronic structure of the $(Cu\text{-}Li)_{III}$ bound exciton

The $(Cu\text{-}Li)_{III}$ center is characterized by a set of four electronic BE lines. The lowest line $L4^0$ is a magnetic triplet with $g\approx 2$. The weak component $L3^0$ is never strong in PL and not detectable in PLE, which suggests a forbidden triplet configuration. Both high-energy components, $L2^0$ and $L1^0$, are singlets. The lowest singlet-triplet pair, $L4^0$,$L2^0$, of this BE has a JJ splitting of 2.1 meV, which is of the order of magnitude usually found in GaP.[1,7] The second pair, $L3^0$,$L1^0$, has a similar JJ splitting.

A common feature for previously studied BE singlet-triplet pairs is the combination of a dominating central cell, attractive for holes, and a strong compressive strain field from the local arrangement of the defect atoms.[2,4,5] This field splits the hole states, giving the observed BE states through a combination of two spin ($S=\frac{1}{2}$) particles.[3–5] In this scheme transitions between the $S=0$ ground state and the triplet are forbidden by the spin selection rule $\Delta S=0$. When the triplet is heavily favored by thermalization at low temperatures, transitions violating this selection rule are observed. This was first realized in the study of Cu-related defects in GaP.[3–5]

The $(Cu\text{-}Li)_{III}$ spectrum differs from other Cu- and Cu-Li–related spectra since it involves two singlet-triplet pairs of BE states instead of only one. We present here a generic scheme for the formation of two pairs of singlet-triplet BE states and propose an explanation for the $(Cu\text{-}Li)_{III}$ center in this scheme.

In Fig. 6 we summarize the effect of a compressive axial crystal field on the p-like hole states derived from the topmost valence band of GaP. The crystal-field splitting is assumed to be large, exceeding the spin-orbit splitting of GaP. A necessary condition for this is that the hole wave function be localized at the defect. Therefore the hole must be tightly bound by an overall hole-attractive associate center. The ground state of the holes is then the orbital singlet $|\,|l_z|j_z\rangle=|0\pm\frac{1}{2}\rangle$. It will be at lowest energy only for a compressive sign of the crystal field.[12] If the electron wave function were orbitally nondegenerate there would be a single singlet-triplet pair. The possibility of two such pairs is based on the fact that the lowest electron state may be multivalley degenerate. Then a local stress can cause an additional splitting of the BE states. This requires a nonattractive central cell for electrons.[12]

GaP is an indirect semiconductor with a set of equivalent conduction-band minima near the X point of the Brillouin zone. It is well known that the pseudopotential difference between Ga and P splits the X minima into X_1 and X_3 subminima.[14] (In this description it is assumed that the conduction-band minima coincide with the Brillouin-zone boundaries X.) Depending on the origin of coordinates, the lower conduction band is labeled X_3 (Ga

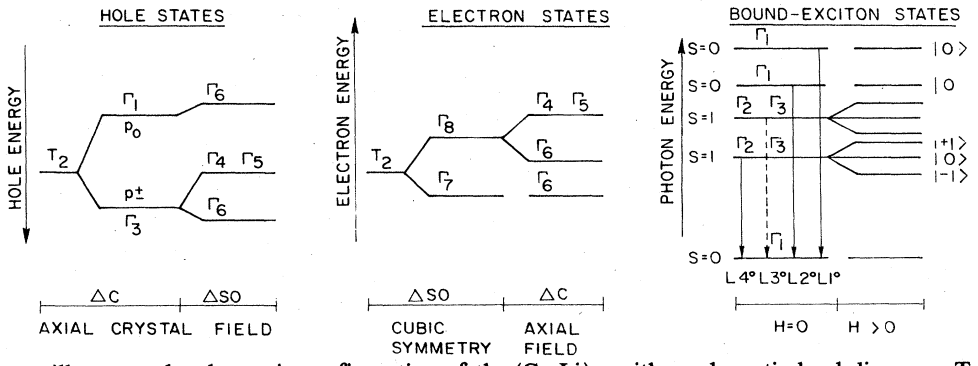

FIG. 6. The figure illustrates the electronic configuration of the $(Cu\text{-}Li)_{III}$ with a schematic level diagram. To the left the hole states are shown with the spin-only-like $|0\pm\frac{1}{2}\rangle$ state as the ground state of the holes. The electron states in the middle are shown to split in a qualitatively similar way. The spin-orbit splitting (ΔSO) is assumed to be of similar order of magnitude as the crystal-field splitting (ΔC) for the electron. The general hypothesis is that two closely spaced spin states ($\Delta E=1$ meV) result because of the local strain field. Both these states couple to the hole ground state to give the two sets of BE singlet-triplet states shown to the right. The spacing between the two sets is determined by the splitting of the electron states, while the exchange interaction governs the splitting within each set as usual.

site) or X_1 (P site).[15] For electrons bound at the electron-attractive group-V sites the $1s$ ground state derived from the X_1 minima splits into a lower $1s$ A_1 state and a higher $1s$ E state because of the valley-orbit splitting. With spin included, the notations are Γ_6 and Γ_8, respectively, in cubic symmetry.

For electrons bound at the less electron-attractive group-III site the wave function possesses nodes in the Bloch component instead of antinodes on the group-V sites. Therefore the orbitally-threefold-degenerate $1s$ T_2 ground state derived from the X_3 conduction-band minima is unaffected by the valley-orbit splitting. When spin is included, a Γ_7 ground state and a higher Γ_8 state result (this spin-valley interaction is likely to be a negligible feature for a strong axial field). The orbital degeneracy of the Γ_8 electron state can be lifted in a uniaxial strain field. For a direction of the axial field other than $\langle 111\rangle$ the state splits into two spin doublets, since the equivalence of the conduction-band valleys is destroyed. Only the $\langle 111\rangle$ direction is equivalent for the set of $\langle 100\rangle$ conduction-band minima.

The $(Cu\text{-}Li)_{III}$ associate center is likely to be dominated by a hole-attractive Ga-site substituent with local symmetry reduced by interstitial Cu or Li atoms giving charge neutrality at the defect. The trigonal symmetry of the $(Cu\text{-}Li)_{III}$ defect is not expected to split the electron states. However, if a small perturbation is superimposed on the major trigonal strain field a small splitting of the multivalley degenerate electron states may be produced. The magnitude of such a strain-field component should be much smaller than the strain field acting on the above-mentioned Cu defects. (In fact, such a component was not resolved in the ODMR data.[11]) Two closely spaced Γ_6 orbital singlets will be produced in this model (as well as a Γ_4,Γ_5 orbital singlet at higher energy), as schematically illustrated in Fig. 6. We propose that the observed two sets of single-triplet BE states result upon taking the triplet product of the symmetric envelope functions, the nondegenerate hole state, and the pair of Γ_6 orbital singlet electron states.[13]

Thus, we argue that the singlet-triplet pair $L4^0$ and $L2^0$ derive from the lowest electron state while the $L1^0$ state is the singlet component of a second pair $L1^0$,$L3^0$ resulting from a higher, moderately split-off electron state. The $L3^0$ component is shown to the right in Fig. 6, characterized by a broken arrow. We have no explanation for the fifth line which appears in PLE measurements at 2.2510 eV. In this scheme, possible explanations are split-off hole states and higher electron states. In the absence of magneto-optical data on this component we do not speculate further in its origin.

B. Models for the identity of the $(Cu\text{-}Li)_{III}$ center

The different experimental results from this study do not result in an unequivocal microscopic model of the $(Cu\text{-}Li)_{III}$ center. Nevertheless, we propose a model of the defect from the existing data, considering different possibilities.

The observed magnetic multiplicity of the BE lines is consistent with spin-free final states for the PL emission. A model of two or more particles in the ground state pairing off to give $S=0$ is not attractive due to strong Auger processes, which should severely weaken the corresponding luminescence. For the same reason complexes containing a Cu atom with an open d-shell configuration seem improbable.[16] The long radiative lifetime of this BE luminescence further supports the hypothesis of an isoelectronic molecular center, with no electronic particle in the ground state.[17]

Both of the group-I interstitial species Li and Cu are expected to act as single donors. As substitutional ions on Ga sites both would be double acceptors, but neither of these has so far been shown to exist isolated. Both Li_{Ga} and Cu_{Ga} are, on the other hand, found as parts of complexes, such as Li_i-Li_{Ga}-O_P (Ref. 7) and the COL complex (Ref. 3).

Given the diffusion procedure described above, several possibilities for forming neutral complexes of Cu and Li atoms exist. Either Cu or Li may occupy a Ga site to

provide the hole-attractive central cell of the $(Cu\text{-}Li)_{III}$ complex. The mobile Li_i^+ donors (ionized at the diffusion temperatures) may combine with a charged acceptorlike complex of Cu atoms influenced by the Coulomb attraction. Similarly the Cu_i^+ donors may pair with an acceptorlike Li complex.

It is evident that the Li-isotope experiments are consistent with one Li atom present in the complex. If the local modes result from a coupled motion of more than one Li atom, modes of mixed Li isotopes would be reflected in the spectrum. If there are two coupled Li atoms in a defect, either on equivalent sites or not, combinations of both isotopes result in three or four modes, respectively. The above-mentioned arguments are not valid if the complex involves inequivalent uncoupled Li atoms. For these reasons we cannot completely rule out the possibility of more than one Li atom in the complex.

For the $(Cu\text{-}Li)_{III}$ complex we favor a model involving a Cu_{Ga} acceptorlike central cell and tentatively assign this center to a neutral complex of Li_i-Cu_{Ga}-Cu_i. In the $\langle 111 \rangle$ direction in a zinc-blende lattice there are two adjacent interstitial sites, a cubic and a hexagonal.[18] Since it may be unlikely that both the donorlike species of the complex sit on the same side of the acceptorlike species, we propose that there is a bond-centered unbonded Li_i present on one side of Cu_{Ga}, while the second interstitial (presumably Cu_i) occupies either of the interstitial sites. We believe that a slight perturbation of the trigonal symmetry caused by a small relaxation of the linear configuration would be sufficient to explain the splitting of the electronic states suggested in Sec. IV A.

We consider a model involving Li_{Ga} unlikely. Two Cu_i (instead of a Cu_i and a Li_i) would then be needed for reasons of charge neutrality, since a Li_{Ga}-Li_i pair would certainly be expected to give rise to coupled vibration of Li atoms, as in the Li_i-Li_{Ga}-O_P system.[7] A bond-centered Cu_i (which would be necessary in view of the $\langle 111 \rangle$ orientation) may be more difficult to realize owing to the large radius of Cu_i, even though such a configuration may be probable for the smaller Li_i.

C. Symmetry and origin of the local modes

From Figs. 3 and 4 we note the important fact that both local modes in the $(Cu\text{-}Li)_{III}$ spectrum couple equally strongly to the electronic singlet and triplet lines. The LO^{Γ} phonon has similar coupling to both components while the transverse phonons TA^X, LA^X, and TO^X all show a strong coupling to the triplet alone. In cubic symmetry the LO^{Γ} phonon involves the A_1 representation of T_d (origin of coordinates taken at a Ga site). In the C_{3v} symmetry deduced for the $(Cu\text{-}Li)_{III}$ center from the ODMR data, the symmetric A_1 representation is compatible with Γ_1, which represents motion along the defect axis.

We conclude from the comparison with band phonons that both local modes of the $(Cu\text{-}Li)_{III}$ complex have the same symmetry, presumably Γ_1 of C_{3v}. The motion is thus longitudinal LO-like motion and involves the neighboring atoms as well. Since the selection rules for the band phonons agree with an origin of coordinates at a Ga site (only this origin gives a symmetric LO^{Γ} phonon), the neighboring atoms are phosphorus atoms. We suggest that the two local modes of the $(Cu\text{-}Li)_{III}$ complex are introduced by a coupled motion of Li and P in a linear defect involving Cu and Li, centered on a Ga site.[19] A bond-centered interstitial Li between a P atom and a Ga-site substituent (presumably Cu_{Ga}) may give rise to such a mixed motion.

Summarizing, both local modes may be perturbed LO modes as is reasonable from symmetry arguments. It may be argued that mixing into TO modes in higher-order perturbation theory splits the local mode into the two observed modes LM1 and LM2. This requires that the symmetry remain overall Γ_1-like (LO-like) despite this perturbation. On the other hand, a splitting of a T_2-like local mode into a longitudinal and a transverse mode seems unphysical. Firstly, we do not observe different symmetry for the two modes. Secondly, such modes are generally observed to have widely different energies, with the transverse vibration at lower energy. Thus we do not consider this suggestion as probable.

V. CONCLUSIONS

Th $(Cu\text{-}Li)_{III}$ BE center is shown to involve Cu and Li from doping experiments. The involvement of Li is explicitly proved by Li-isotope doping which gives a substantial shift of the local-phonon-mode energies. From mixed isotope doping it is concluded that probably only one Li atom is present in the defect.

The electronic lines of the BE luminescence are suggested to result from a small splitting of the multivalley degenerate bound electron states. They couple to the more tightly bound holes to form two sets of partly overlapping singlet-triplet BE states. The characteristic singlet-triplet configuration is a generic result of a hole-attractive central cell dominating a defect associate. The compressive strain field created locally at such a defect splits the tightly bound hole states, with an orbital-singlet ground state as a result. Only very few cases of splitting of the electron states have been demonstrated.[13] Usually the electron binding results in an isolated lowest orbital singlet, giving only one pair of singlet-triplet states under the above circumstances. The additional splitting of the $(Cu\text{-}Li)_{III}$ BE states indicates a small splitting of the electron states caused by a weak perturbation of the trigonal symmetry deduced from the ODMR measurements. It is suggested that the small magnitude of this perturbation renders it possible for both pairs of singlet-triplet BE states to be observable, in contrast to the cases where a strong strain field of symmetry other than trigonal causes a larger splitting of the electron states, separating one singlet electron state from the rest. The latter case is found for (Cu-Li) centers of lower symmetry, such as the orthorhombic $(Cu\text{-}Li)_I$ center[5] and the $(Cu\text{-}Li)_V$ center.[6] A model for the microscopic identity of the $(Cu\text{-}Li)_{III}$ defect associate is suggested on the basis of the information collected from the doping experiments, the electronic configuration of the BE lines, and the local-mode structure in the phonon sideband. The overall hole-attractive central cell of the neutral isoelectronic $(Cu\text{-}Li)_{III}$ associate is pro-

posed to be caused by the double acceptor Cu_{Ga}. To ensure charge neutrality a pair of group-I interstitial donors may pair with the Cu_{Ga} substituent. Since the defect is oriented along the ⟨111⟩ direction the small Li atom is assumed to be bond centered between the Cu_{Ga} and a P host atom. This configuration is proposed to account for the sharp Li-related local modes in the $(Cu\text{-}Li)_{III}$ spectrum. Thus we suggest a model for the identity of the $(Cu\text{-}Li)_{III}$ center as a ⟨111⟩-oriented Li_i-Cu_{Ga}-Cu_i defect associate, of the molecular isoelectronic type.

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