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Neutral (Cu-Li) complexes in GaP: The $(\text{Cu-Li})_{\text{I}}$ bound exciton at 2.306 eV

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Several new emissions due to excitons bound at neutral complexes are observed in GaP upon diffusion with Cu and subsequently with Li. Here we report work on the most shallow of these centers, with lowest electronic transition at 2.306 eV. This center, which we denote as $(\text{Cu-Li})_{\text{I}}$, is studied by means of photoluminescence, photoluminescence excitation, and magneto-optical work. The luminescence spectrum exhibits a pair of electronic lines of singlet-triplet multiplicity as revealed by magnetic field measurements. This configuration has been shown to be characteristic of certain defect complexes in cubic semiconductors. These centers are dominated by a compressive local strain field combined with a hole-attractive central cell of the neutral complex. Optically detected magnetic-resonance measurements determine the symmetry of the $(\text{Cu-Li})_{\text{I}}$ complex as orthorhombic with the z axis $\langle 111\rangle$-oriented. The phonon sideband of the luminescence is richly structured and the well-resolved phonon spectra contain two true local modes and a gap mode in addition to the usual zone-boundary modes of GaP. The local modes show substantial energy shift when replacing ^{7}Li with ^{6}Li, thus proving the presence of Li in the complex. No new local modes appear after mixed isotope doping indicating the presence of only one Li atom. Lifetime measurements reveal a very long decay time for the triplet line of $\tau=1$ ms, whereas the singlet has a more allowed character with $\tau=20\ \mu\text{s}$. The long radiative lifetime is consistent with no free spin in the final state of the transition. This agrees with the observed thermalization between the magnetic subcomponents of the triplet, proving that the splitting in magnetic field occurs in the initial state of the transition. The compiled data suggest an orthorhombic $\langle 111\rangle$-oriented complex consisting of Cu_{Ga} in combination with a pair of interstitial atoms, of which one is known to be Li, as the identity of the $(\text{Cu-Li})_{\text{I}}$ center.

I. INTRODUCTION

Properties of defects in semiconductors and their identification are problems of great current interest. Such defects are well understood only in a few cases such as substitutional point defects. Even in this case problems still exist in identifying the so-called deep-level substitutional defects.[1] Unfortunately, high-temperature chemical reactions during growth or heat treatment and the subsequent cooldown seem to favor the creation of various complexes of impurity atoms and other point defects, in particular for compound semiconductors.[2] The electronic properties of such complex of even more difficult to predict. Yet, these defects may be very important as persistent recombination centers in semiconductors, for the reason that they often can capture and bind both kinds of carriers.[3] In addition, they may transform into electrically active centers via defect reactions during various processing steps, such as device fabrication.

Some of the most successful cases of characterization of defect complexes in semiconductors have been carried out with optical spectroscopy, notably for those centers where bound excitons (BE) can be observed.[3] For the reason of charge neutrality and Coulomb attraction during defect formation at high temperature the most abundant type of complex is are believed to be the electrically neutral associates, often referred to as molecular isoelectronic defects.[3] The atoms forming such complexes are arranged to compensate for all valence electrons of the host lattice sites they occupy, so as to give neutral substitutes. Both an electron and a hole (a bound exciton) may be bound to each of these centers at low temperature. This type of defect has been studied in some detail in materials such as GaP. Good examples are the Zn-O and Cd-O complexes occupying nearest-neighbor sites,[4,5] and the so-called NN pairs consisting of two N atoms substituted at P sites separated by various distances.[6] Electronically these particular cases are reasonably well understood in terms of the so-called Hopfield-Thomas-Lynch model.[7] Here one particle is deeply bound in a localized potential (the electron in the above-mentioned examples) while the second particle is bound in a shallow state by the Coulomb-type potential of the primary particle.[7] The electronic properties of the bound exciton thereby formed can usually be understood in terms of the expected electron-hole (J-J) splitting and internal strain field of the defect.[3,8]

A more complicated class of complexes arises when interstitial atoms also are involved. A good example of such a case is the linear Li_i-$\mathrm{Li}_{\mathrm{Ga}}$-$\mathrm{O}_{\mathrm{P}}$ $\langle 111 \rangle$-oriented defect in GaP, which has been studied via its bound-exciton spectra.[9] In this case all observed electronic states of the excitons are within a few meV of the lowest state (at 2.087 eV at 2 K). The splittings are again explained in a satisfactory way by a moderate *J-J* splitting and a weak axial strain field.[9] A recent study of the characteristic-orange-luminescence (COL) defect in GaP with the lowest BE state at 2.1774 eV (concluded to be a Cu_i-$\mathrm{Cu}_{\mathrm{Ga}}$-$\mathrm{Cu}_i$ complex), on the other hand, reveals a case with a much stronger effect of the strain field and also a very strong *J-J* splitting.[10] Similar but even stronger effects of axial field and exchange interaction are observed for the bound exciton at 1.911 eV in GaP, ascribed to a $\langle 100 \rangle$-oriented complex.[11] Both these luminescence bands have been found to disappear upon Li diffusion for diffusion temperatures larger than 350 °C, while new emissions are introduced.[12,13]

As a continuation of these studies we report here the results of an investigation with optical spectroscopy on neutral complexes of isoelectronic character formed by the interaction of Cu and Li in GaP. Both these group-I species are fast interstitial diffusers, and as an isolated impurity Li has so far only been found to occupy interstitial sites while the case of Cu is more uncertain. In complexes both should be able to occupy Ga sites.[9,10] Doping with Li and Cu is therefore expected to create neutral associates involving both Ga sites and interstitial sites. Several different complexes may be expected, depending on which of the atoms (Cu or Li) occupies a Ga site, the number of each species involved, and which interstitial sites they occupy. We have observed at least five different Cu-Li spectra appearing in GaP after a subsequent Li diffusion into Cu-doped material. These centers labeled $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}, \ldots, (\mathrm{Cu\text{-}Li})_{\mathrm{V}}$ are characterized by their different BE luminescence spectra, all of them being neutral molecular associates. The subject of this paper, $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$, is the most shallow center, binding an exciton with lowest electronic transition at 2.306 eV. The $(\mathrm{Cu\text{-}Li})_{\mathrm{II}}$ center binds an exciton at 2.276 eV, $(\mathrm{Cu\text{-}Li})_{\mathrm{III}}$ at 2.242 eV (Ref. 12), $(\mathrm{Cu\text{-}Li})_{\mathrm{IV}}$ at 2.116 eV, and the $(\mathrm{Cu\text{-}Li})_{\mathrm{V}}$ center has the lowest BE line at 2.170 eV.[13] Besides the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ center, $(\mathrm{Cu\text{-}Li})_{\mathrm{III}}$ and $(\mathrm{Cu\text{-}Li})_{\mathrm{V}}$ show particularly strong and persistent photoluminescence (PL) bands and are the subject of separate unpublished works.[12,13] The $(\mathrm{Cu\text{-}Li})_{\mathrm{III}}$ center has been shown to have a trigonal $\langle 111 \rangle$-oriented symmetry from optically detected magnetic resonance (ODMR) data. A model for its identity as a linear Li_i-$\mathrm{Cu}_{\mathrm{Ga}}$-$\mathrm{Cu}_i$ neutral associate is proposed.[12]

In this study we present PL spectra for the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ center. Also, the splitting of the electronic lines in a magnetic field is reported. To achieve information on all electronic states, photoluminescence excitation (PLE) spectra were recorded with a cw dye-laser excitation. It appears that the observed electronic states are fairly close together for this center (*J-J* splitting only 1.0 meV). This indicates a moderate exchange interaction for the bound exciton. The BE spectra are consistent with an exciton binding at a center with reduced local symmetry rather than at a point-defect site. The local strain field is deduced to have a compressional sign, and its symmetry is determined as orthorhombic from ODMR measurements.

In Sec. II below the procedure of crystal preparation and doping is described. The experimental techniques for measuring optical spectra are also outlined. Section III A contains detailed photoluminescence data at low temperatures. PL spectra taken at various temperatures slightly above 2 K reveal differences in phonon coupling for the two electronic states. Section III A also includes Zeeman data for the electronic lines which show that the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ center exhibits a magnetic triplet-singlet structure, often observed as a consequence of a compressional noncubic strain field interacting with BE states. In Sec. III B excitation spectra for the center are shown, giving the relative oscillator strengths of the electronic states. In Sec. III C a summary of the ODMR results for the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ center is presented. Section IV contains a more detailed discussion on the possible identity of the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ complex, suggested from both electronic and vibrational properties, ODMR data and Li-isotope doping as well as comparison with other previously studied neutral complexes involving Cu and Li.[12,13]

II. EXPERIMENTAL

A. Crystal preparation

The starting material used in these investigations was mostly *n*-type or *p*-type liquid-encapsuled Czochralski-grown bulk material. Epitaxial wafers and solution-grown material were also used. Luminescence studied on the solution-grown starting material showed the presence of C, S, Si, and N in various concentrations, usually low, and often the corresponding BE lines were barely detectable. No correlation with the spectra described in this paper was found for any of these impurities. The impurity concentration was generally higher in the bulk material. In such crystals the $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ luminescence was always weak or absent for all types of shallow doping. It was very strong in solution-grown crystals, however. This spectrum also appeared strongly in epitaxial wafers, although the $(\mathrm{Cu\text{-}Li})_{\mathrm{III}}$ luminescence (Ref. 12) (with lowest electronic transition at 2.242 eV) is always of comparable strength in these samples. This is in contrast to the solution-grown crystals where $(\mathrm{Cu\text{-}Li})_{\mathrm{I}}$ always dominates.

For the initial Cu diffusion Cu was evaporated on the surface of the crystal to a thickness of 600-1400 Å. The crystals were then placed in a fused SiO_2 ampoule together with a protective GaP-Ga melt. The ampoules were evacuated and sometimes backfilled with dry N_2 gas. The crystals were diffused at temperatures between 900 and 1100 °C followed by a rapid quenching in water to room temperature. Residual Cu was cleaned from the GaP surface with 40% HCl and the crystals were washed in distilled water. This diffusion procedure causes the COL center to appear strongly in luminescence,[10] thus proving the presence of Cu in the samples. Samples were doped either with natural Cu or with the pure isotopes $^{63}\mathrm{Cu}$ and $^{65}\mathrm{Cu}$.

In the Li-doping step the crystals were placed in a quartz ampoule together with a small pellet of metallic Li. For high diffusion temperatures the Li metal was often placed on a piece of quartz. This reduced the risk of Li reacting with the tube wall due to chemical reactions with SiO_2.

Isotope doping was made by using separately natural Li metal representing the ^7Li isotope and enriched Li metal for the ^6Li isotope. The natural abundance of Li is 92.6% ^7Li and 7.4% ^6Li. The commercially available enriched metal used had 95.5% ^6Li and 4.5% ^7Li. We also performed a series of mixed isotope doping with approximately equal quantities of each isotope in the ampoule. We could not account for the possibility of different diffusion rates of the Li isotopes. Judging from the local-mode spectra, however, we found that both isotopes were present in the defect. (See below under Sec. III.)

The Li diffusion was performed at temperatures between 250 and 1000 °C. The diffusion time varied from 20 min at 1000 °C to 4 h at 250 °C. After the diffusion the ampoules were quenched to room temperature in water or air with similar results. It was found that $T = 450\,^\circ\mathrm{C}$ produced the best $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ spectra, but the spectrum appears after diffusion at all temperatures between 250 and 850 °C. For all diffusion temperatures above 350 °C the strong Cu-related COL emission (as well as other Cu-related emissions when present) always disappeared completely, while new Cu-Li spectra appeared strongly. Sometimes the well-known Li_i-Li_Ga-O_P spectrum (Ref. 9) with electronic ground state at 2.087 eV also appeared indicating the presence of O in those samples. None of the spectra assigned to Cu and Li showed any shift with changes in O isotope, however. Thus the corresponding complexes are unlikely to involve O. Li doping alone produced only the shallow donor-acceptor pair spectra involving the two inequivalent Li_i donors and their corresponding BE spectra close to the band gap.[14] None of the new Cu-Li BE spectra and particularly not the $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ spectrum described in this paper are found with Li doping alone. This further proves their association with both Cu and Li.

B. Optical measurements

Photoluminescence measurements were performed either with Ar^+ or Kr^+ cw laser excitation at temperatures varying from 1.8 K up to 30 K. PL spectra were obtained with a Jarrell-Ash 0.75-m double-grating monochromator and with a 2-m Bausch & Lomb single-grating spectrograph. The signals were recorded with a Nicolet 1170 signal averager. Magneto-optical data were obtained with a Varian electromagnet at fields up to 3.5 T and a superconducting magnet at fields up to 6 T. Excitation spectra were performed with cw dye-laser excitation, mostly with narrow-band detection through the 0.75-m double monochromator to select out a suitable part of the spectrum. Sometimes broadband detection with a filter was employed. Lifetime measurements were performed at Royal Signals and Radar Establishment using cathodoluminescence at about 10 K and at Hull University employing conventional pulsed-laser techniques.

III. EXPERIMENTAL RESULTS

A. Low-temperture photoluminescence spectra

A typical low-temperature photoluminescence spectrum from Cu-Li co-doped GaP is shown in Fig. 1. It is dominated by the $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ spectrum involving sharp electronic lines with a phonon-assisted wing at lower energies. The shallow $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ center occurs with two electronic lines L_I^1 and L_I^2 at 2.3072 and 2.3062 eV, respectively. The sharpness and energy positions of the lines indicate that they are electronic transitions from a bound-exciton complex.[3] Investigation in a magnetic field of 3.5 T shows that the lower-energy line L_I^2 is a magnetic triplet ($J = 1$) with an isotropic g value. The higher-energy component L_I^1 does not split in a magnetic field, see inset in Fig. 1. Thermalization between the magnetic subcomponents is observed in luminescence. Thus it is concluded that the splitting occurs in the initial state of the transition which is evidence for the identification as a BE transition to a spin-free final state.

A rich phonon spectrum occurs with the $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ exciton. The coupling strength is rather weak, however. In contrast with many deeper centers the small exciton localization energy for the $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ center results in a luminescence spectrum which clearly reveals the one-phonon density of states of the GaP host. This coupling is induced by delocalization of the electron wave function in k space.

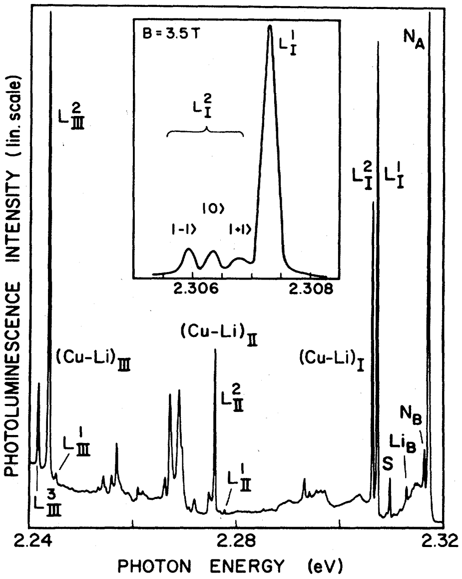

FIG. 1. Low-temperature PL spectrum of an epitaxial GaP wafer diffused with Cu and Li and excited with the 5145-Å Ar^+ laser line. The group of electronic lines labeled $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ are consistently present in this type of material after such doping. In the inset the electronic lines of the $(\mathrm{Cu\text{-}Li})_\mathrm{I}$ spectrum are shown in magnetic field $B = 3.5$ T. The L_I^1 line does not split while the L_I^2 line splits into three magnetic subcomponents, corresponding to an isotropic g value.

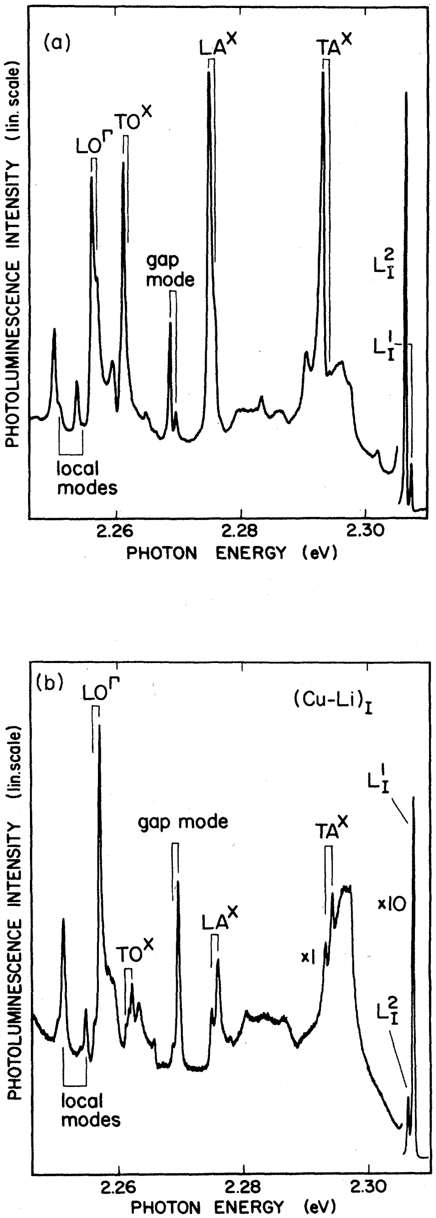

FIG. 2. (a) Low-temperature PL spectrum of a solution-grown GaP sample doped with Cu and Li. Below 2 K, thermalization favors the $L_{\rm I}^2$ transition, which dominates in this spectrum. The phonons at the X point of the Brillouin zone show a strong coupling to this forbidden line, as does LO$^\Gamma$. Note in particular the strong localized modes present in the (Cu-Li)$_{\rm I}$ spectrum. Both a sharp gap mode of 37.7 meV is found as well as two distinguished true local modes. This crystal was doped with the ^{6}Li isotope. (b) PL spectrum of the same crystal as in (a) at a slightly higher temperature. Here the electronic singlet state is thermally populated and the $L_{\rm I}^1$ singlet transition dominates due to the forbidden character of the triplet $L_{\rm I}^2$. Observe that the LO$^\Gamma$ shows similar coupling strengths to both electronic components. This is also the case for all localized phonon modes. The zone-boundary phonons, on the other hand, clearly couple more strongly to the triplet line.

In Figs. 2(a) and 2(b) the phonon sideband of the (Cu-Li)$_{\rm I}$ luminescence is shown in detail. Phonon energies and interpretations of the most prominent peaks are listed in Table I. Phonon coupling to the X zone-boundary phonons is present as expected for the case of a forbidden triplet transition. At a phonon energy of 13.1 meV we observe the TA^X phonon replicas of both singlet and triplet BE components. The coupling is stronger to the triplet $L_{\rm I}^2$ as a consequence of the selection rules. This can be clearly seen at elevated temperature, where the electronic singlet line dominates, but both TA^X replicas have comparable strength, in spite of the weak triplet line [Fig. 2(b)], illustrating the different photon coupling to the components as commonly observed for such systems.[3,12]

The LA^X components are partly overlapping with an independent electronic BE transition labeled (Cu-Li)$_{\rm II}$ in Fig. 1. It occurs at 2.2758 eV in epitaxial layers under the same doping conditions as the (Cu-Li)$_{\rm I}$ center. However, the LA^X component of the triplet line is clearly observed. In solution-grown samples the (Cu-Li)$_{\rm II}$ center is weak or absent (Fig. 2). At lower energies TO^X components are found in the spectrum with phonon energy 45.2 meV. As before the triplet $L_{\rm I}^2$ shows stronger coupling to this mode. On the other hand, both electronic components have similar coupling strength to LO$^\Gamma$, which is represented by a pronounced peak at a phonon energy of 50.2 meV. A weak coupling to TO$^\Gamma$ is also present, 45.7 meV below the electronic lines. All these zone-boundary phonon energies agree well with earlier data from BE measurements in GaP.[3,5]

Localized phonon modes can give important clues for the identification of defect complexes for which the exact chemical identities are not known. Such localized modes can be classified as true local modes of energy higher than the host lattice vibrations, gap modes with energy between the optical and acoustic bands, and in-band resonance modes. A rather striking example of the last type of mode in the (Cu-Li)$_{\rm I}$ spectrum is the occurrence of a broad band of what seems to be sharp replicas peaking at about 2.296 eV. Since this band of quasilocalized modes with energies about 10—12 meV is strongest at temperatures where the singlet $L_{\rm I}^1$ is dominating, this phonon coupling seems to be related to the singlet.

A prominent gap mode occurs at a phonon energy of 37.7 meV (Fig. 2). This phonon couples equally to both components of the electronic line. True local modes also appear in the (Cu-Li)$_{\rm I}$ spectrum, stronger than usually found in BE spectra. There are two local modes present, each coupling with similar strength to both electronic components. The weaker phonon mode has the energy 51.2 meV and the stronger one 52.8 meV (Fig. 2). These local peaks are relatively sharp and their intensities make it possible to perform isotope doping in order to reveal the nature of the corresponding vibrational modes. The result is shown in Fig. 3 and Table I.

Upon doping with ^{6}Li a marked shift occurs in both local-mode energies. The 51.2-meV mode shifts to 52.4 meV, which is not to be confused with the 52.8-meV mode of ^{7}Li. The resolution in Fig. 3 clearly resolves the 0.4-meV energy difference. The 51.2-meV replica of the $L_{\rm I}^1$ singlet is only detectable at higher temperatures when

TABLE I. Photon energies of the electronic transitions in the $(\text{Cu-Li})_\text{I}$ photoluminescence spectrum. The energies of the most significant phonon replicas of L_I^1 and L_I^2 are listed in separate columns.

Notation	Photon energy (eV)	Energy from L_I^1 (meV)	Energy from L_I^2 (meV)	Interpretation
L_I^1	2.3072	0		$S=0$ singlet
L_I^2	2.3062	1.0	0	$S=1$ triplet
	2.2941	13.1		TA^X
	2.2931		13.1	TA^X
	2.2768	30.4		LA mode
	2.2746		31.6	LA^X
	2.2695	37.7		gap mode
	2.2685		37.7	gap mode
	2.2620	45.2		TO^X
	2.2610		45.2	TO^X
	2.2615	45.7		TO^Γ
	2.2605		45.7	TO^Γ
	2.2570	50.2		LO^Γ
	2.2560		50.2	LO^Γ
	2.2560	51.2		Local ^7Li mode
	2.2550		51.2	Local ^7Li mode
	2.2548	52.4		Local ^6Li mode
	2.2538		52.4	Local ^6Li mode
	2.2544	52.8		Local ^7Li mode
	2.2534		52.8	Local ^7Li mode
	2.2516	55.6		Local ^6Li mode
	2.2506		55.6	Local ^6Li mode

the L_I^2 triplet has vanished since it overlaps its LO^Γ replica.

The 52.8-meV mode shifts in energy to 55.6 meV with ^6Li doping. This shift is larger than for the lower-energy local mode. When doping with natural Li a small peak is observed at 55.6 meV. The relative ratio of this peak to the strong 52.8-meV mode approximately agrees with the abundance of ^6Li in natural Li (7.4% ^6Li).

The mixed isotope doping did not reveal any new local modes in addition to the pure ones, as can be seen in Fig. 3. Judging from the relative strength of the ^7Li and ^6Li local modes, which are now observed in the same spectrum, we conclude that both isotopes are present in the complexes in approximately equal concentrations. Some variation is observed in different experiments, though. The good resolution in these experiments rules out the possibility that any replicas of the same order of magnitude could remain unrevealed in the PL spectra. This result is important since the absence of new local modes for approximately equal amounts of both Li isotopes evidently means that there is only one Li atom vibrating in the $(\text{Cu-Li})_\text{I}$ complex in the simplest model. As discussed below in Sec. IV two or more Li atoms would give rise to mixed modes involving both isotopes simultaneously if they are not vibrationally isolated from each other.

A slight increase in temperature has a profound effect on the relative intensities of the two electronic lines in the $(\text{Cu-Li})_\text{I}$ spectrum. Thermal population causes the higher singlet state to become much stronger at elevated temperature at the same time as the triplet gradually disappears. Apparently the $J=0$ singlet has an appreciably higher oscillator strength than the lower-energy triplet. This is also shown by the PLE measurements reported in the next section.

B. Excitation spectra

To gain information on the existence of further electronic excited states beyond the range of obtainable thermal population in PL spectra, absorption spectra for the $(\text{Cu-Li})_{\text{I}}$ center are necessary. Since the concentration of the defect binding the exciton under study appears to be rather low, and the oscillator strengths are also weak, the only feasible way of achieving such information is from PLE measurements, employing a cw dye laser. To avoid detection of excitation light, it is in practice necessary to detect a part of the characteristic emission for a particular center, displaced some suitable distance away from the excitation region to be covered. For that reason the $(\text{Cu-Li})_{\text{I}}$ is rather unsuitable for direct PLE measurements, since the phonon-assisted part of the spectrum is too weak (at least in the epilayers). However, in these samples it was possible to obtain indirectly a (nonselective) PLE spectrum by detecting the intensity of the deeper $(\text{Cu-Li})_{\text{III}}$ spectrum, excited via excitation transfer from $(\text{Cu-Li})_{\text{I}}$ (Fig. 4). The no-phonon transition to the 2.3062-eV triplet ground state is just barely seen below the 2.3072-eV transition. The measured difference in oscillator strength is about a factor of 10—15 in favor of the 2.3072 singlet state. In the solution-grown samples the intensity of the $(\text{Cu-Li})_{\text{I}}$ luminescence was totally dominating over both $(\text{Cu-Li})_{\text{III}}$ and the *N* exciton lines. In this case a direct selective PLE spectrum was obtainable, although never with strong signal. This spectrum is identical to the nonselective spectrum of Fig. 4 with respect to the $(\text{Cu-Li})_{\text{I}}$ components.

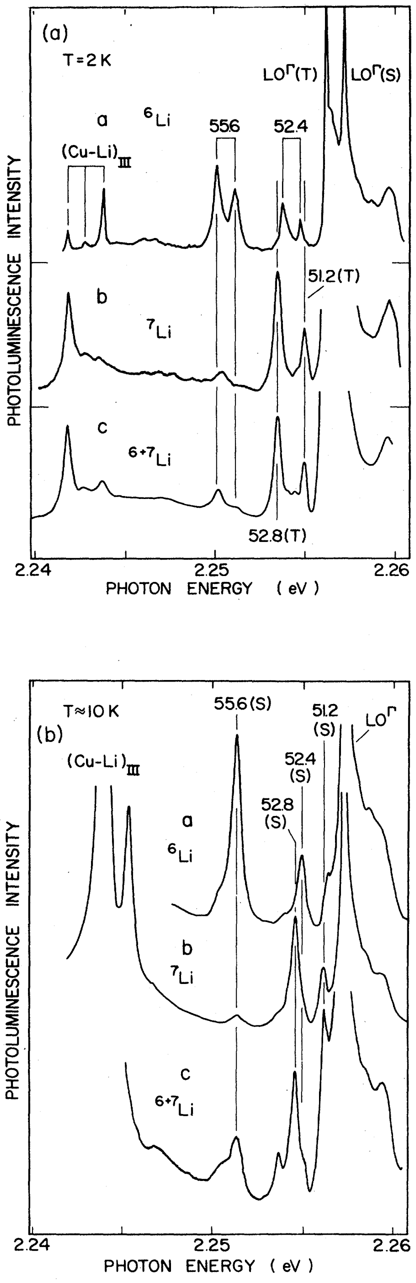

FIG. 3. (a) Portion of the low-temperature PL spectrum of $(\text{Cu-Li})_{\text{I}}$ showing the true local modes for samples doped with the ^{6}Li isotope (curve *a*) natural Li with 92.6% ^{7}Li abundance (curve *b*) and approximately equal amounts of both Li isotopes (curve *c*). ^{7}Li gives rise to two discrete local modes at 51.2 and 52.8 meV, respectively. Note that a weak peak corresponding to the natural abundance of ^{6}Li (7.4%) appears in the spectrum for natural Li (curve *b*). The mixed isotope doping (curve *c*) shows no new modes but only confirms the result from the natural Li with different relative isotope ratios. (b) Same portion of the $(\text{Cu-Li})_{\text{I}}$ PL spectrum at higher temperature than in (a). Here the singlet transition L_{I}^{1} dominates and consequently its replicas are strong. Owing to the closely spaced local-mode replicas of $(\text{Cu-Li})_{\text{I}}$ it is necessary to register intensity variations of the replicas with temperature in order to sort out the modes correctly.

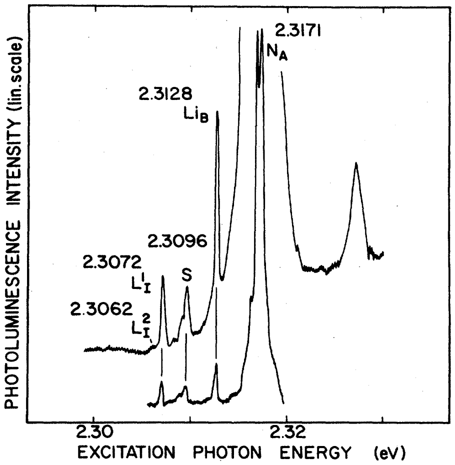

FIG. 4. Low-temperature PLE spectrum of the $(\text{Cu-Li})_{\text{I}}$ BE monitoring the $(\text{Cu-Li})_{\text{III}}$ PL. The spectrum was measured with a tunable dye-laser excitation using the same epitaxial wafer as in Fig. 1. In this kind of sample selective detection of the $(\text{Cu-Li})_{\text{I}}$ luminescence was not possible owing to weak phonon sidebands. Detection was instead made possible through excitation transfer to the $(\text{Cu-Li})_{\text{III}}$ spectrum. The spin-forbidden triplet L_{I}^{2} is very weak while the singlet L_{I}^{1} is stronger. Other well-known BE's in GaP are observed through a similar excitation transfer to $(\text{Cu-Li})_{\text{III}}$. Observe that Li$_{B}$ is strong whereas no sign of Li$_{\text{A}}$ is seen in PLE or PL spectra. The peak at 2.328 eV is related to the pronounced *N* bound exciton.

C. ODMR results

ODMR experiments have been described many times before and details can be found in Ref. 15. The present measurements were performed at 2 K with the sample mounted in either a rectangular microwave cavity operating at 9 GHz or a cylindrical cavity operating at 16 GHz. The luminescence was excited either with a 5145- or 4880-Å argon ion laser and detected via a monochromator and an *S*20 photomultiplier. Angular dependence studies of the ODMR resonances at both microwave frequencies showed that these resonances belong to triplet excitons bound at centers with orthorhombic symmetry with principal axes, $x\,||\langle 211\rangle$, $y\,||\langle 011\rangle$, and $z\,||\langle 111\rangle$. The Hamiltonian describing these exciton states in a magnetic field B is

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

where

$$S=1,\ \ g_x=1.98,\ \ g_y=1.93,\ \ g_z=2.00\ ,$$

$$D=3.5\times 10^{-3}\ \text{meV},\ \ E=5.8\times 10^{-4}\ \text{meV}\ .$$

Full details are planned to be published elsewhere.[16]

IV. DISCUSSION

A. Electronic structure

The (Cu-Li)$_\mathrm{I}$ center has a pair of electronic lines, the one at lowest energy being a magnetic triplet separated from a higher-energy singlet by 1.0 meV. The triplet component has a relatively pure spin character, as can be judged in a magnetic field up to 3.5 T. The splitting is nearly isotropic in the resolution of the Zeeman measurements, with a g value which is close to the electron-spin value. The triplet-singlet configuration of the (Cu-Li)$_\mathrm{I}$ center therefore corresponds to the BE systems which have been studied for Cu complexes in GaP (Refs. 10 and 11) as well as other (Cu-Li) centers in GaP.[12,13] In agreement with these BE systems the ODMR measurements confirm the near isotropic behavior of the triplet states [there are exceptions, however, such as the COL center which fails to show any ODMR signal (Ref. 10)]. The higher resolution of the ODMR as compared with Zeeman measurements nevertheless reveals the symmetry of the (Cu-Li)$_\mathrm{I}$ center.

The L_I^2 recombination of the (Cu-Li)$_\mathrm{I}$ center occurs from a spinlike triplet to a singlet state of a neutral associate, which is isoelectronic with the GaP lattice. According to our observations such a transition is forbidden and therefore strong in PL only when thermally favored at the lowest temperatures. In a magnetic field thermalization is observed between the magnetic subcomponents of this line (Fig. 1). This proves that the splitting takes place in the initial excited state of the exciton, implying that the final state in fact is spin-free. Further evidence for the forbidden nature of this triplet line is the coupling to X zone-boundary phonon modes which is stronger than for the singlet (Fig. 2). Also it vanishes at temperatures when the highest state becomes thermally populated. Because of the allowed character of the singlet its lifetime is much shorter and therefore it dominates the radiative recombination. The lifetime of the triplet line is long, on the order of a millisecond. Final evidence is the fact that the triplet component of the BE is very weakly seen in PLE. In contrast to this, the singlet transition occurs between a $S=0$ magnetic singlet and the spin-free final state of the center. This transition is allowed by the spin selection rule $\Delta S=0$, but the observed lifetime of the transition is 20 μs which is unusually long compared with similar previously studied transitions.

Forbidden transitions from $S=1$ BE triplets have been observed in several other cases as mentioned above.[10–12] A common feature for previously studied singlet-triplet pairs in GaP seems to be the combination of a hole-attractive central cell and a compressive noncubic strain field by the local arrangement of defect atoms. In case of a strong crystal field dominating the relatively small spin-orbit splitting of the valence band of GaP (80 MeV), the p-like hole states are split in such a way that an orbital singlet state has the lowest hole energy.[10,11] Consequently the BE states are formed through the combination of two spin particles. The sum of two $S=\frac{1}{2}$ particles results in two BE states with total spin $S=0$ and 1. The

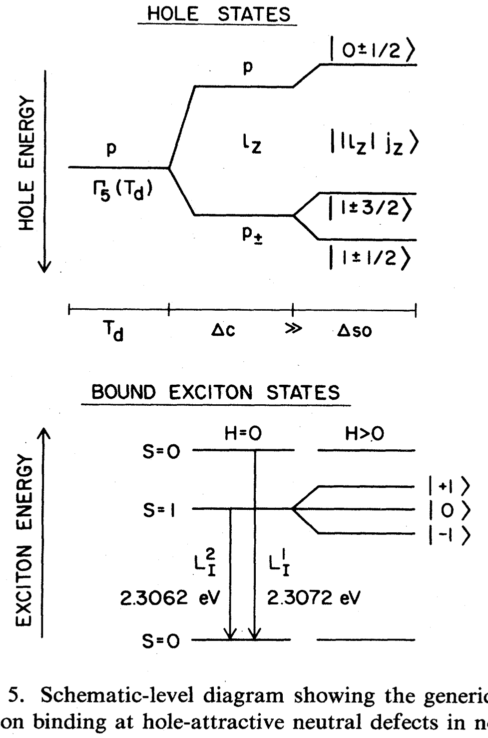

FIG. 5. Schematic-level diagram showing the generic model of exciton binding at hole-attractive neutral defects in noncubic symmetry. The orbitally threefold-degenerate hole states split in a compressive strain field that exceeds the spin-orbit interaction of the host lattice. The ground state of the holes is the orbitally nondegenerate $|0,\pm\frac{1}{2}\rangle$ state in the $||1_z|,j_z\rangle$ notation after spin-orbit coupling. When this hole state couples to a similarly nondegenerate electron-spin state, the bound exciton states have the spin-only-like singlet-triplet configuration $S=0$; $S=1$. Thermalization within the magnetic subcomponents in a magnetic field reveals whether the splitting occurs in the initial or final state of the transition. The former case is observed here in agreement with this scheme.

schematic electronic configuration of such a bound exciton is shown in Fig. 5.

In the $(\text{Cu-Li})_{\text{I}}$ spectrum the triplet BE state has the lowest energy. Assuming that no other correlation terms exist the spacing between the two components is the exchange splitting of the electron and hole of the bound exciton. The energy $\Delta_{\text{exc}} = 1.0$ meV is about the order of magnitude usually found for BE systems in GaP.[3] The electronic configuration of the BE states indicates that the dominating central cell of the $(\text{Cu-Li})_{\text{I}}$ defect is hole-attractive. This is in a general agreement with the tentative assumption that the central cell involves the acceptor-like substitute Cu_{Ga} as will be discussed in more detail below under Sec. IV. B.

B. Model discussion of the $(\text{Cu-Li})_{\text{I}}$ center

We recall from the experimental section (Sec. II) that the doping experiments give no evidence of impurities other than Cu and Li being present in the (Cu-Li) complex. Also the presence of Li is explicitly proved by the isotope shifts of both the significant local modes in the spectrum. The participation of Cu cannot be unequivocally proved by means of isotope doping with Cu, owing to lack of suitable phonon replicas predominantly caused by the motion of Cu alone.

The main reason for assigning the luminescence spectrum described above to a complex involving Cu besides Li is from the doping experiments. We find that the doping procedure always requires a Cu diffusion at high temperatures (900—1100 °C) and a subsequent Li diffusion at lower temperatures, typically 400—650 °C. The $(\text{Cu-Li})_{\text{I}}$ center has never been observed in GaP material which is not deliberately Li doped. Further, in Li-doped material which is not previously Cu doped this center is always absent.

The dominant BE spectra in GaP after the Cu diffusion at high temperature have electronic lines at 2.177 eV (Ref. 10) and 1.911 eV.[11] The centers responsible for the Cu luminescence spectra therefore bind the excitons more deeply than is the case for the $(\text{Cu-Li})_{\text{I}}$ center. Both centers have been attributed to complexes containing inequivalent Cu atoms, Cu_i and Cu_{Ga}, respectively. The latter is established to have a $\langle 100 \rangle$-oriented symmetry axis ascribed to a linear defect of Cu and possibly a native defect such as Ga_i. The 2.177-eV luminescence band shows a complicated phonon coupling to the lattice vibrations suggesting a complex of three Cu atoms. These two Cu-related luminescence bands always vanish as a consequence of the Li diffusion for all diffusion temperatures higher than 350 °C. This is partly a result of the heat treatment caused by the Li-diffusion procedure (Ref. 17). In the temperature interval around 250 °C, Li diffusion produces the $(\text{Cu-Li})_{\text{I}}$ luminescence in coexistence with the COL luminescence. It must be noted that since the $(\text{Cu-Li})_{\text{I}}$ center has a smaller binding energy than either of the Cu-related excitons, the appearance of the former at the same time as the latter ones disappear necessarily implies a reconstruction of the Cu complexes and not a fast excitation transfer to the $(\text{Cu-Li})_{\text{I}}$ center. In agreement with that, no signs of the Cu-related excitons can be seen in the PLE spectra of the Cu-Li co-doped samples. [This is also true for the $(\text{Cu-Li})_{\text{III}}$ center (Ref. 12)].

Both the interstitial Cu and Li are highly mobile in the GaP lattice by an interstitial diffusion mechanism. Evidently they are likely to form complexes with substitutional Cu (assumed to exist on Ga sites, ionized at the diffusion temperatures). We argue that the Cu_{Ga} of the $(\text{Cu-Li})_{\text{I}}$ center is most likely to have a d^{10} configuration and consequently forms a complex with two interstitial species to ensure charge neutrality and spin-free ground state of the center. Strong Auger processes may be expected to compete with the luminescence and shorten its lifetime, in the case of open-shell configurations.[18] This is in contrast with observations for the $(\text{Cu-Li})_{\text{I}}$ luminescence. Further, there are strong arguments against an unfilled d shell for Cu_{Ga} in GaP, in view of theoretical calculations which place the Cu_{Ga} d^9 state about 5 eV below the valence-band top for the related GaAs.[19]

Hence, we suggest that a neutral isoelectronic center, involving a substitutional Cu in the d^{10} configuration, is responsible for binding the $(\text{Cu-Li})_{\text{I}}$. From the isotope doping experiments the associate is known to involve a Li atom. As will be discussed below in Sec. IV C, the most straightforward interpretation of the isotope doping is that the $(\text{Cu-Li})_{\text{I}}$ center involves just one Li atom. However, we cannot be definite of this point, and in fact we suggest a defect involving two vibrationally isolated Li_i atoms as one possible identity of the center below.

C. Analysis of local modes

An analysis of local-mode energies is a complicated task even in cases where the microscopic identity of the defect is known. In the case of $\text{Li}_i\text{-Li}_{\text{Ga}}\text{-O}_{\text{P}}$ the mixed isotope doping provided evidence for the model of the complex.[9] However, a detailed calculation was not possible even in this case. It is obvious that a model for the local-mode vibration must include the adjustment of force constants that is necessary to reduce the expected local-mode energy of Li_{Ga} (110 MeV) (Ref. 9) to the observed energies close to 50 meV. Such an analysis is certainly warranted but will not be attempted at this stage.

Instead, we discuss the most striking features of the local-mode structure in relation to possible defect models. There are three unusually strong localized modes present in the spectrum. The two local modes show substantial shifts when replacing ^7Li with ^6Li as shown in Table I. The gap mode at 37.7 meV shows no detectable isotope shift, and therefore probably involves a mixed motion of the defect atoms or even pure Cu motion. It is expected that the relative changes in energy with isotope substitution are smaller for gap modes than for local modes, however.[9]

In a simple model of the local vibrations the complex is regarded as coupled linear harmonic oscillators centered on each atom in the complex. The atomic masses and the force constants between the atoms are responsible for the energy levels of the harmonic oscillators. In the case of a light atom such as Li one expects high energies of the vibrational quanta and thus localized phonon modes. The energy change $\Delta\hbar\omega$ of a phonon with energy $\hbar\omega$ upon substitution of ^{7}Li with ^{6}Li can be expressed as a change in the ion mass ΔM, given that the force constants are independent of the ion mass M:

$$\Delta\hbar\omega = \frac{1}{2}\hbar\omega(\Delta M/M) f_{\mathrm{KE}} \ .$$

Here f_{KE} is the fractional kinetic energy. The vibration of one atom is generally not an eigenfunction of the system. The vibrational symmetries can be found from group theory given the microscopic structure of the defect. The system eigenfunctions are linear combinations of the linear harmonic-oscillator eigenfunctions of the atoms which depend on the symmetry. The fractional kinetic energy f_{KE} measures how much a given atom takes part in a vibrational eigenfunction of the system. At the same time it gives information on the applicability of this simple model.

The isotope shift of the 52.8-meV mode is $55.6-52.8=2.8$ meV. Hence, we arrive at the value for the fractional kinetic energy $f_{\mathrm{KE}}=0.74$. This is rather low for a local mode, since the value $f_{\mathrm{KE}}=1$, corresponding to a vibration of the Li atom alone, is perhaps expected. For the 51.2-meV mode the isotope shift is $52.4-51.2=1.2$ meV. Here a fractional kinetic energy $f_{\mathrm{KE}}=0.27$ is deduced, which is a very low value. These values indicate that the local modes do not involve the motion of Li atoms alone.

Two important results from the isotope experiments are crucial for any model of the defect. Firstly, we can detect the local modes corresponding to the natural abundance of Li (92.6% ^{7}Li) in our best spectra. Here we observe about 7% intensity of the 55.6-meV mode relative to the total intensity of the 55.6- and 52.8-meV modes together. This excludes the possibility of two connected Li atoms in the defect since the pure modes should then appear with the relative intensities 0.93^2 and 0.07^2. The ^{6}Li mode would indeed be undetectable in this case.

Secondly, we observe no additional local modes for approximately equal amounts of ^{6}Li and ^{7}Li in the diffusion source. We only obtain pure ^{7}Li and ^{6}Li modes simultaneously strong as shown in Fig. 3. This highly inhibits the probability of two or more coupled Li atoms moving either in equivalent or inequivalent sites. In the former case a mixed mode involving ^{7}Li and ^{6}Li would appear at an intermediate energy between the extreme energies for the pure modes. This mode would be equally strong as both the pure modes together for 50% abundance of each isotope. In case of two inequivalent Li atoms causing the local modes four equally strong modes are expected for equal abundances of each Li isotope. We clearly see nothing of the kind.

To conclude, we state that there is only one Li atom responsible for both local modes of the (Cu-Li)$_{\mathrm{I}}$ spectrum. Any coupled motion of Li atoms in the defect would give rise to modes of mixed isotope motion when both Li isotopes are present in detectable concentrations. The possibility of two vibrationally isolated Li atoms cannot be completely excluded by these arguments. Whether they are on equivalent sites and hence have identical vibronic properties, or completely inequivalent would not be deducible from the data. In the latter case only one of the Li atoms would give rise to both modes, however. A hypothetical configuration for such isolated Li motion would be a pair of interstitial Li atoms, one on each side of the heavier substitutional Cu$_{\mathrm{Ga}}$ atom.

The almost identical Li-related local-mode structure found for the (Cu-Li)$_{\mathrm{III}}$ center[12] was assigned to an interstitial Li atom being bond centered between a Cu$_{\mathrm{Ga}}$ substituent and a neighboring P atom along the $\langle 111 \rangle$ direction. It was suggested that such a configuration would explain the two sharp Li-related local modes as a mixed motion of Li and P atoms, thus accounting for the different isotope shifts observed.[12] In view of the similarity between the (Cu-Li)$_{\mathrm{I}}$ and the (Cu-Li)$_{\mathrm{III}}$ spectra as far as the local-mode structure is concerned it seems natural to assume that both defects involve a Li atom in a similar configuration. Below we arrive at the conclusion that the local-mode structure of the (Cu-Li)$_{\mathrm{I}}$ center is caused by a bond-centered Li$_i$ atom in agreement with the (Cu-Li)$_{\mathrm{III}}$ center[12] (Sec. IV D).

D. Identity of the (Cu-Li)$_{\mathrm{I}}$ center

To summarize the discussion so far we have deduced that the (Cu-Li)$_{\mathrm{I}}$ center is a neutral isoelectronic associate binding an exciton in a magnetic singlet-triplet configuration. The electronic configuration is consistent with an axial hole-attractive defect binding the hole from orbitally nondegenerate valence-band states, as a consequence of the compressional sign of the local strain field. The symmetry of the defect is orthorhombic with axes $x \| \langle 211 \rangle$, $y \| \langle 011 \rangle$, and $z \| \langle 111 \rangle$ as revealed by the ODMR measurements. Further, we have shown that the defect contains a Li atom. The isotope doping excludes the possibility of two or more Li atoms in a coupled motion, but if the complex contains more than one Li atom they have to be vibrationally independent of each other.

This accumulated evidence does not lead to an unequivocal model for the identity of the (Cu-Li)$_{\mathrm{I}}$ center. In fact, similar arguments are used to arrive at the proposed model for the (Cu-Li)$_{\mathrm{III}}$ center as a $\langle 111 \rangle$-oriented Li$_i$-Cu$_{\mathrm{Ga}}$-Cu$_i$ complex. The Li$_i$ atom was suggested to be bond centered between the substitutional Cu$_{\mathrm{Ga}}$ and a neighboring P host atom, along the $\langle 111 \rangle$ direction.[13] This configuration ensures charge neutrality of the (Cu-Li)$_{\mathrm{III}}$ center, since Cu$_{\mathrm{Ga}}$ is a double acceptor and the interstitial atoms are expected to act as single donors in view of their group-I character. It was found difficult to fit other neutral configurations along the $\langle 111 \rangle$ axis of the zinc-blende structure under the above conditions.

Returning to the (Cu-Li)$_{\mathrm{I}}$ center we obviously must suggest an identification which is consistent with the different symmetries of the two complexes and which also accounts for both common features in the two spectra and the differences. Apart from the energy position and the consequences of the shallower binding of the (Cu-Li)$_{\mathrm{I}}$ center (such as the generally weaker phonon interaction), the main spectral differences seem to be related to the electronic configuration. There is only one singlet-triplet pair present for the (Cu-Li)$_{\mathrm{I}}$ center, whereas two pairs were observed for the (Cu-Li)$_{\mathrm{III}}$ center. Further, the singlet state of (Cu-Li)$_{\mathrm{I}}$ was found to couple more strongly to the X zone-boundary phonons than does its counterpart of

$(\text{Cu-Li})_{\text{III}}$. This suggests differences in the local symmetry of the two defects, as resolved in the ODMR measurements.

The striking similarity between the Li-related local modes of the $(\text{Cu-Li})_{\text{I}}$ and $(\text{Cu-Li})_{\text{III}}$ center suggests that both involve Li atoms in similar lattice positions. Consequently, we assign the Li-related local modes in the $(\text{Cu-Li})_{\text{I}}$ spectrum to a bond-centered interstitial Li atom. The light Li_i atom could distort off the bond-centered position giving the orthorhombic symmetry observed in the ODMR measurements. The choice of a Li_i atom excludes a Li atom on a Ga site, since two nearby Li atoms would give rise to a coupled vibrational motion. We therefore suggest that the hole-attractive Ga-site substitute of the $(\text{Cu-Li})_{\text{I}}$ center is Cu as in two other most thoroughly studied Cu-Li centers.[12,13] As a natural consequence of the above discussion we suggest that the $(\text{Cu-Li})_{\text{I}}$ center is a $\langle 111 \rangle$-oriented complex composed of $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-}D$, where D is a single donor. We have tentatively assumed that the $(\text{Cu-Li})_{\text{I}}$ center involves only Cu and Li, because of the lack of correlation with any other dopant in different GaP material. Hence, an interstitial Cu atom or a second interstitial Li atom may be the second donorlike species of the $(\text{Cu-Li})_{\text{I}}$ center. The two Li atoms in the latter model are inequivalent, since one is bond centered (giving rise to the local modes) and the other occupies an interstitial position of the GaP lattice. Thus the proposed model does not contradict the conclusions from the isotope doping.

If the $(\text{Cu-Li})_{\text{I}}$ center contains two Li atoms behaving as one with respect to the isotope doping, parallels can be drawn with the 969-meV center in Si.[20] Consisting of two substitutional C atoms and a Si atom in a nearby interstitial site between the nearest-neighboring C substitutes, the C-related local modes have an isotope dependence which is characteristic for only one C atom moving in the vibration.[20] If, on the other hand, the second interstitial atom is Cu, the only difference between the $(\text{Cu-Li})_{\text{I}}$ and the $(\text{Cu-Li})_{\text{III}}$ centers would be the defect symmetry. It is not possible to say whether a lower symmetry would lead to a decreased binding energy for the $(\text{Cu-Li})_{\text{I}}$ center as compared with the $(\text{Cu-Li})_{\text{III}}$ center. This is required, however, if the chemical identities of both centers are identical.

To summarize, we propose that the $(\text{Cu-Li})_{\text{I}}$ center is an orthorhombic $\langle 111 \rangle$-oriented associate, presumably $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Li}_i$ or $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Cu}_i$. At the present stage it is impossible to distinguish between the two proposed models, however. Although the microscopic models are tentative, it must be noted that both are consistent with all the generic aspects of defects of the class discussed in this paper. They also account for the experimental observations characterizing the $(\text{Cu-Li})_{\text{I}}$ center which were listed at the beginning of this section.

V. CONCLUSIONS

The $(\text{Cu-Li})_{\text{I}}$ center appearing in GaP co-doped with Cu (900—1100 °C for 1 h) and Li (typically 400—600 °C for 40 min) has been studied by photoluminescence techniques via the bound-exciton spectrum associated with the center. A model for the identity of the center is deduced from the doping procedure employed, the electronic structure of the exciton bound by the center and details in its vibrational sidebands.

The electronic configuration of the $(\text{Cu-Li})_{\text{I}}$ bound exciton is a magnetic triplet at 2.3062 eV and a singlet at 2.2072 eV, separated from the triplet by an electron-hole exchange splitting of 1.0 eV. The center binding this exciton is a neutral associate of isoelectronic molecular type. This identification is based on the requirement of a neutral and spin-free final state of the BE recombination for a singlet-triplet pair of BE states to occur. Moreover, a thermalization between the magnetic subcomponents of the triplet in a magnetic field in PL measurements shows that the splitting occurs in the initial state of the BE recombination. An additional requirement for the observed electronic configuration is that the orbital angular momentum of the involved hole states is quenched in the local strain field. The strain field must necessarily have a compressional sign. The magnetic triplet state of an exciton formed under such conditions should split almost isotropically in magnetic field. This is indeed observed for the $(\text{Cu-Li})_{\text{I}}$ bound exciton. The slight anisotropy present in the triplet splitting has been resolved by the ODMR technique, which reveals an orthorhombic symmetry with a $\langle 111 \rangle$ z axis for the $(\text{Cu-Li})_{\text{I}}$ center. This information was obtained from the angular dependence of typical triplet resonances in the ODMR signal.[16]

The chemical identification of the $(\text{Cu-Li})_{\text{I}}$ center is based on the doping procedure, which always requires Cu doping prior to the Li doping for the BE spectrum to appear. The presence of Li in the defect associate is also explicitly proved by the Li-isotope doping. Well-resolved shifts of the local-mode energies are caused by the substitution of ^{7}Li by ^{6}Li. We also find that the 55.6-meV local mode appears with an intensity ratio corresponding to the natural abundance of ^{6}Li when doping with natural Li metal (92.6% ^{7}Li, 7.4% ^{6}Li). Further, we find that doping with approximately equal amounts of both Li isotopes introduces no modes of mixed-isotope vibrations. The Li-isotope doping excludes the possibility that the local modes are caused by a coupled motion of two or more Li atoms. If the defect complex contains more than one Li atom these must be vibrationally independent of each other. From the compiled information on the $(\text{Cu-Li})_{\text{I}}$ center we propose a model for its identity as an associate consisting of $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Li}_i$ or $\text{Li}_i\text{-Cu}_{\text{Ga}}\text{-Cu}_i$ along the $\langle 111 \rangle$ direction. The two Li atoms of the former configuration are inequivalent, since the first one is suggested to be bond centered between a Cu_{Ga} substitute and a nearest-neighbor P host atom, whereas the second one occupies an interstitial lattice position.

Either the bond-centered Li atom or the second interstitial atom is proposed to be distorted off the $\langle 111 \rangle$ direction, thus giving the orthorhombic symmetry. Both Li-related local modes in the $(\text{Cu-Li})_{\text{I}}$ spectrum are ascribed to the bond-centered Li_i atom.

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