Neutral (Cu-Li) complexes in GaP: The $(Cu\text{-}Li)_V$ bound exciton at 2.172 eV

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A detailed study of a complex defect in GaP created by low-temperature Li diffusion into previously Cu-diffused GaP is presented. This $(Cu\text{-}Li)_V$ defect is electrically neutral and binds an exciton with the lowest electronic state at 2.172 eV. The electronic structure of this bound exciton (BE) has a triplet-singlet pair as a lowest-energy configuration, with an electron-hole exchange splitting of ≈ 2 meV, while higher excited BE states are observed around 2.26 eV. Such an electronic structure is common for complex defects in GaP. It can be understood in terms of a hole-attractive centered-cell potential combined with a local strain field of compressive sign and low symmetry. Thermal quenching data are consistent with a conventional Hopfield-Thomas-Lynch model where the hole is bound in a localized potential and the electron is bound by Coulomb forces from the hole by a typical donor binding energy of ≈ 80 meV. The simplest model for the identity of the defect, consistent with the body of experimental data presented, has the structure of three foreign atoms in a configuration $Cu_{Ga}\text{-}Cu_i\text{-}Li_i$. Optically detected magnetic resonance data suggest that the Li_i is located off the trigonal $Cu_{Ga}\text{-}Cu_i$ axis, so that the total configuration of the defect is bent in a (110) plane.

I. INTRODUCTION

For some time there has been considerable interest in the bound-exciton spectroscopy of neutral defect complexes in semiconductors. This class of defects is characterized by charge neutrality with respect to the surrounding lattice in the sense that the defect does not bind any electronic particles in its ground state. A typical excited state of such a defect can be described as an exciton bound to the neutral center, which then contains no other electronic particles than the electron-hole pair. Accordingly, the neutral centers are sometimes referred to as isoelectronic complexes, by analogy with the substitutional isoelectronic defects.[1] This notion is perhaps somewhat misleading and will therefore be avoided below.

The simplest cases of neutral complexes involve pairs of isoelectronic impurities on different sites, such as the N-N pairs[2] and perhaps Sb pairs[3] on P sites in GaP. Another type of complex consists of a donor-acceptor pair on nearest-neighbor sites, such as the $Cd_{Ga}\text{-}O_P$ center in GaP.[4,5] In this case the complex may be regarded as neutral since the local bonding requirements are fulfilled by the closely associated pair.

Group-I species are often found to be fast diffusers as ionized interstitials at elevated temperatures in compound semiconductors.[6] On interstitial sites they are expected to act as single donors, and as such they can form complexes with acceptorlike substituents. Whether such a complex is neutral or charged should depend on the number, valence, and the local arrangement of the acceptorlike and the donorlike parts of the complex. Examples of previously studied neutral complexes are the $Li_i\text{-}Li_{Ga}\text{-}O_P$ center[7] and the $Cu_{Ga}\text{-}Cu_i\text{-}Cu_i$ center in GaP.[8]

The electronic configuration of the bound-exciton states closely reflects the local symmetry of the defect binding the exciton as well as the overall sign of the short-range strain field created by the defect center. The $Li_i\text{-}Li_{Ga}\text{-}O_P$ associate in GaP, e.g., gives rise to a local tensional strain, as recognized by the symmetry of the bound hole states. This is also true for the Cd-O complex in GaP.[9] By contrast, several centers involving Cu in GaP (Refs. 8 and 10) and InP (Ref. 11), as well as Li in Si (Ref. 12) and Cu + Li in GaP (Ref. 13) have been found to create compressive strain locally at the defect. All of these centers seem to have the common character of a hole-attractive central cell, with a localized hole wave function confined to the vicinity of the defect. Consequently the holes experience a large overlap with the local crystal field created by the defect complex. For a compressive sign of the strain field it has been shown that the hole states are orbitally nondegenerate, since a noncubic strain field increases the binding energy of hole states derived from the spinlike p_0 states, but decreases that of the $p_\pm$ states.[3]

When an electron and a hole form bound-exciton (BE) states the electronic configuration of the BE states depends on the magnitude of the exchange interaction between the two particles. In materials where the electron-hole mass ratio is very small, for example, InP and ZnTe, the exchange splitting of the BE states is in general negligible. Already a small magnetic field then completely decouples the electron and hole states, which then split independently of each other at higher fields. This is the

case for the exciton bound to the neutral trap InP:Cu,[11] as well as for different neutral and acceptorlike complexes of Cu in ZnTe.[14] Other examples in ZnTe illustrate the occasionally observed tight binding of both electronic particles of the bound exciton. One example is found for ZnTe:Ag, where for the 2.349-eV BE state an appreciable exchange interaction is observed, despite the shallow donor electron binding in ZnTe. This behavior illustrates that the Hopfield-Thomas-Lynch (HTL) model[15] for excitons binding to isoelectronic traps often fails in the case of neutral defect complexes. For a complex formed by the association of acceptorlike and donorlike parts with an associated local strain field, both electronic particles may be bound more deeply than the simplified scheme of the HTL model predicts, even in the above materials.

In semiconductors with larger electron-hole mass ratio, such as Si and GaP, with indirect band gaps, the exchange interaction between the electron and hole bound to a neutral complex cannot be neglected. The exchange splitting of rather shallow bound-exciton states associated with neutral defects is observed to be on the order of 1 meV in these materials. In the above-mentioned case of spinlike hole states coupling to spin-only electron states the BE states produced have a total spin of $S=0$ or $S=1$. In a series of papers we have focused our attention towards neutral centers binding excitons of this configuration in GaP. Defect complexes of this type include the characteristic-orange-luminescence (COL) defect in GaP (Ref. 8) which was proposed to be a Cu_{Ga}-Cu_i-Cu_i associate, together with another but deeper Cu-related center in GaP, the 1.91-eV center binding an exciton at 1.91 eV and tentatively assigned to a $(Cu\text{-}Ga)_{Ga}Cu_i$ split interstitial complex.[10]

In addition to these Cu-related defects a number of neutral associates appear in GaP which is diffused with Li after a previous Cu doping. Not less than five such Cu-Li centers have been observed via their BE spectra in the near band-gap-energy region $h\nu > 2.1$ eV, identified in different types of GaP starting material. Of these the most prominent ones, labeled $(Cu\text{-}Li)_I$ and $(Cu\text{-}Li)_{III}$, are described in separate publications,[13,16] whereas the third significant center, the $(Cu\text{-}Li)_V$ center, is the subject of this publication. Additional (Cu-Li)-related bound-exciton spectra occur at lower photon energies $h\nu < 2$ eV, but will not be discussed in this paper.

The Cu-Li centers referred to above have widely different binding energies, ranging from 46 meV for the 2.306 eV $(Cu\text{-}Li)_I$ center, through 110 meV for the 2.242 eV $(Cu\text{-}Li)_{III}$ center, to 180 meV for the deepest one, the 2.172 eV $(Cu\text{-}Li)_V$ center. Despite the different binding energies, the electronic configuration of the BE states of these centers is similar. The lowest-energy component is an isotropic triplet accompanied by a singlet line, about 1–2 meV higher in energy for all three centers. Clearly, the angular momentum of the hole states is quenched for all these Cu-Li centers. In other words, the bound holes must, in all cases, experience a strain-induced splitting that exceeds the effect of the spin-orbit splitting of the valence-band hole states. The spin-orbit splitting of the valence band of GaP and its effects on the bound state is in general reduced through the localization at the defect center.

In this paper we shall concentrate on the properties of the $(Cu\text{-}Li)_V$ center, compare its electronic and vibrational properties with the more shallow Cu-Li centers, and discuss the identity of the defect binding the exciton. In Sec. II we describe the doping procedure which was employed to produce the $(Cu\text{-}Li)_V$ spectrum. An outline of the experimental techniques is also included in Sec. II. Section III contains a description of the experimental results from photoluminescence (PL), photoluminescence excitation (PLE), and optically detected magnetic resonance (ODMR). The isotropic splitting of the lowest-energy component gives no information about the defect symmetry in Zeeman measurements. The ODMR measurements, on the other hand, give strong signals which clearly reveal a complicated anisotropy pattern.

A detailed study of the local phonon modes in the $(Cu\text{-}Li)_V$ system illustrates that the similarities between the three Cu-Li spectra are not limited to the electronic structure alone. In agreement with our findings for the $(Cu\text{-}Li)_I$ and $(Cu\text{-}Li)_{III}$ centers, isotope doping with Li reveals only one Li atom in the $(Cu\text{-}Li)_V$ associate. The isotope doping experiments are discussed in connection with the PL measurements in Sec. III A.

In the discussion section (Sec. IV), we discuss the identification problem for neutral centers in compound semiconductors with reference to the Cu and Cu-Li complexes in GaP. A remarkable similarity between the $(Cu\text{-}Li)_V$ center, discussed here, and the characteristic-orange-luminescence (COL) center is pointed out. The corresponding excitons have binding energies which differ by only 5 meV, and the spectral shapes of the luminescence bands are much the same. From the differences we conclude, however, that the $(Cu\text{-}Li)_V$ center is a reconstruction of the COL center. A possible model would be the replacement of one of the interstitial Cu atoms of the suggested Cu_{Ga}-Cu_i-Cu_i associate by an interstitial Li atom. The accumulated evidence for this model comes from the shape of the PL spectrum and the phonon structure, together with the orientation of the defect as derived from the ODMR data.

II. EXPERIMENTAL

A. Sample preparation

In contrast to the other two Cu-Li centers which are most easily produced in epitaxial wafers and solution grown material, the $(Cu\text{-}Li)_V$ is strongest in liquid-encapsulation Czochralski-grown (LEC) bulk material. A necessary prestage for its formation is a previous Cu diffusion of the GaP starting material at high temperatures, typically 950 °C for 1 hour, producing the previously mentioned COL defect. After the Cu diffusion, the samples were rapidly cooled to room temperature by immersing them directly from the furnace into water. A subsequent Li diffusion was then made in the temperature range 350–800 °C. The diffusion time was usually 4 hours for the lower temperatures, decreasing to about 1 hour for the higher ones.

After the Cu diffusion the samples often show the

characteristic-orange-luminescence spectrum. This luminescence band disappears after the Li diffusion, for all Li diffusion temperatures higher than 350 °C. Instead, the $(Cu\text{-}Li)_{III}$ and the $(Cu\text{-}Li)_V$ spectra appear, with different relative strength depending on the Li-diffusion temperature. The presence of the COL spectrum after the Cu diffusion is a necessary prerequisite for the observation of the $(Cu\text{-}Li)_V$ spectrum after subsequent Li diffusion. Furthermore, the $(Cu\text{-}Li)_V$ spectrum was favored for lower Li-diffusion temperatures and longer diffusion time. So it was found that in bulk samples the $(Cu\text{-}Li)_V$ luminescence was strongest after Li diffusion at 400 °C for 4 hours. The shallower $(Cu\text{-}Li)_{III}$ spectrum was strongest in such samples under the Li-diffusion conditions 800 °C for 40 min. Other Cu-Li spectra are usually weak in bulk material.

The diffusions were performed in sealed evacuated quartz ampoules. For the Cu diffusion a thin layer of Cu was evaporated onto the samples as a Cu-diffusion source. In the Li-diffusion step, a pellet of natural Li metal was placed in the ampoule. Separately, samples were also doped with enriched ^{6}Li isotope in order to trace isotope effects in the spectra. The natural Li metal (92.6% ^{7}Li, 7.4% ^{6}Li) served as the ^{7}Li isotope.

B. Experimental techniques

Photoluminescence measurements were performed at liquid-helium temperatures using the 5145-Å Ar^+-laser line as an excitation source. A typical excitation intensity was 100 mW. The PL spectra were dispersed through a 0.75-m double-grating monochromator (Jarrell Ash) and detected with an S20 extended photomultiplier tube. The signal was recorded with a Nicolet model No. 1170 signal averager. The optically detected magnetic resonance measurements were partly made at the University of Hull in a superconducting magnet system[17] operating at a microwave frequency about 9 GHz. The spectral response of the ODMR signal was analyzed through a Spex model No. 1402 monochromator and an S20 photomultiplier. The luminescence was excited with the 5145-Å argon-laser line also in the ODMR measurements. Similar ODMR measurements were also made at Linköping University employing a modified 9-GHz Bruker ER 200D-SRC system combined with an Oxford ESR 10 cryostat.

Photoluminescence excitation measurements were performed with a tunable dye-laser excitation with narrow-band detection through a monochromator or using filters to select a broader part of the PL band. In both cases the signals were very weak.

III. EXPERIMENTAL RESULTS

A. Photoluminescence spectra

Figure 1 shows the photoluminescence spectrum of the $(Cu\text{-}Li)_V$ center for an LEC bulk sample, Cu and Li doped under the optimal conditions, as described above. The spectrum consists of a pair of electronic lines, a magnetic singlet line $L\,1^0$ at 2.1742 eV and a triplet line $L\,2^0$ at 2.1721 eV, accompanied by a rather strong sideband to-

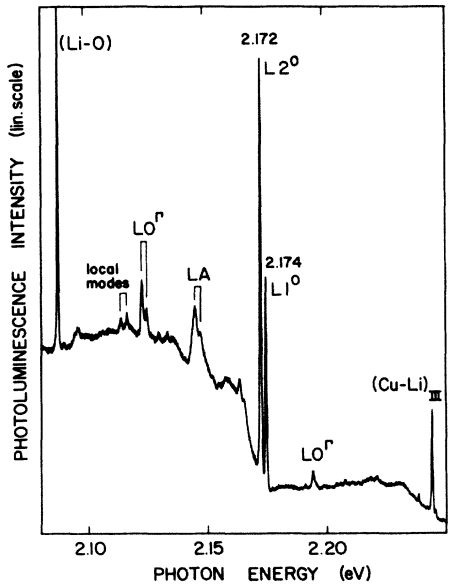

FIG. 1. Photoluminescence spectrum of the $(Cu\text{-}Li)_V$ bound exciton. Two no-phonon lines are seen: $L\,2^0$, a magnetic triplet and $L\,1^0$, a magnetic singlet. Also seen are quasilocalized modes as well as LO^Γ and LA bulk phonon replicas. Two other complex defects Li-O at 2.088 eV and $(Cu\text{-}Li)_{III}$ at 2.242 eV are also present. (The photoluminescence spectra shown in this paper are not corrected for the spectral response of the measuring equipment.)

wards lower photon energies. The shape of the phonon sideband is overall reminiscent of the Cu-related COL luminescence.[8] For the more shallow Cu-Li spectra the electron phonon interaction decreases with decreased localization,[13,16] to become characteristic for a dominant coupling to the one phonon density of states of the host in the case of the shallow $(Cu\text{-}Li)_I$ exciton.[13]

For the $(Cu\text{-}Li)_V$ center the shape of the phonon sideband is typical for the coupling to quasilocalized phonon modes, induced by the defect and enhanced by the localization of the exciton wave function in the vicinity of its central cell. Modes of this kind are responsible for the broad envelope of phonon replicas building up the phonon sideband, upon which a set of discrete phonon replicas of various origin is superimposed. An important group of low-energy phonon modes gives rise to a partly resolved peak on the high-energy edge of the TA density of states phonon wing. These quasilocalized modes, which are resonant with the TA branch, have phonon frequencies about 6—8 meV. These phonons seem to have closely related counterparts in the COL spectrum, where three well-resolved sharp low-energy modes occur at similar frequencies (5.3, 6.8, and 8.8 meV, respectively). In the COL spectrum these phonon modes were interpreted as the local vibrations of the two interstitial Cu atoms in the plane of the Cu_{Ga}-Cu_i-Cu_i associate. It was suggested that such vibrations were characteristic for heavy interstitial species.[8,18,19] We have not encountered low-energy modes of this kind in other Cu-Li spectra in GaP. In ZnTe, on the other hand, localized modes of even lower energy have been observed in the BE spectra of Ag-related neutral

complexes and attributed to interstitial Ag vibrations.[20] The common features of the COL and the $(Cu\text{-}Li)_V$ spectra will be discussed below in view of a possible relation between the defects causing the two spectra.

Another striking similarity between the COL and the $(Cu\text{-}Li)_V$ spectrum is the absence of the X-zone boundary phonon replicas TA^X, LA^X, and TO^X which dominate the coupling to the forbidden triplet transition in the other Cu-Li spectra.[16] The zone-center LO^Γ phonon is present; however, even this is in agreement with the COL spectrum. This is particularly obvious in Fig. 2, which shows the $(Cu\text{-}Li)_V$ spectrum at two different temperatures. At the lower one, thermalization favors the forbidden triplet, which dominates the spectrum together with its phonon replicas. At slightly higher temperature, the singlet state gets thermally populated and the triplet line disappears due to its forbidden nature. We note that there is no difference observable in the phonon coupling of the two components. The broad and strong 27.5-meV replica denoted by LA in Fig. 2 is still another common feature in both spectra. In the COL spectrum its counterpart at 27.1 meV was interpreted as a perturbed LA mode and believed to involve the motion of the Cu_{Ga} substituent.[8] In the COL spectrum this suggestion was supported by the substantial isotope shift of this mode when substituting ^{63}Cu for ^{65}Cu. No such shift could be observed in the $(Cu\text{-}Li)_V$ spectrum, however, presumably because of broader linewidths.

The appearance of true local-mode replicas in the $(Cu\text{-}Li)_V$ spectrum clearly distinguishes this spectrum from the COL spectrum, which shows no such modes. These replicas occur beyond the phonon cutoff frequency of the GaP host lattice and are shown in greater detail in Fig. 3. The figure illustrates the results of doping with the two Li isotopes ^6Li and ^7Li. In view of all the above dissimilarities between the $(Cu\text{-}Li)_V$ spectrum and the more shallow ones, it is interesting to note that as far as the isotope doping is concerned all Cu-Li spectra are largely identical.

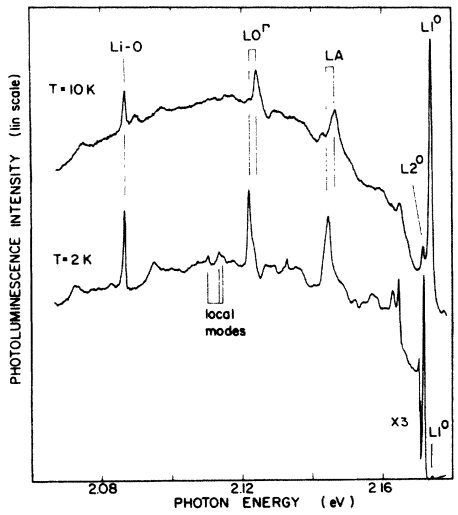

FIG. 2. The $(Cu\text{-}Li)_V$ bound-exciton emission at two different temperatures. The singlet $L\,1^0$ is seen to dominate at $T=10$ K. Higher temperatures also make the phonon sideband broader and more featureless.

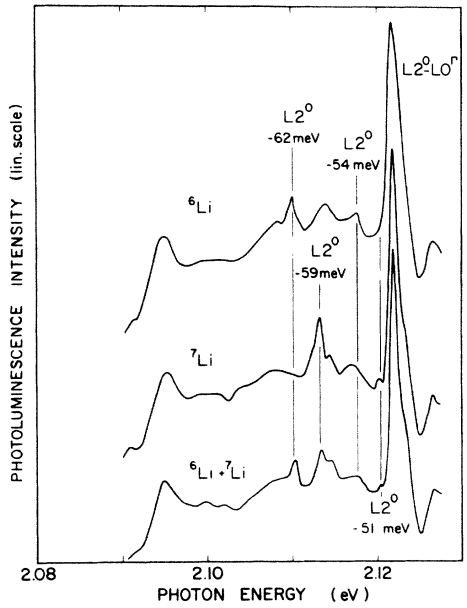

FIG. 3. A more detailed view of the local modes in the $(Cu\text{-}Li)_V$ spectrum. The two modes with energies 51 and 59 meV are ^7Li related. When ^6Li is diffused they move to 54 and 62 meV, respectively. With approximately equal amounts of ^7Li and ^6Li employed, no new local modes appear. Other features present correspond in energy to sums of vibrational modes other than the true local modes.

Thus the $(Cu\text{-}Li)_V$ spectrum has two Li-related local modes at 51.4 and 58.5 meV, respectively, for ^7Li, and 54.2 and 61.9 meV for ^6Li. As is obvious from Fig. 3, there are other features present in the spectrum in this energy range, but they have been carefully investigated and found to be unrelated to the local modes associated with $(Cu\text{-}Li)_V$. In agreement with the results for other Cu-Li spectra in our investigation,[13,16] mixed isotope doping with approximately equal amounts of both isotopes in the ampoule during diffusion reveals no new phonon modes.

The results from the isotope doping are most easily interpreted in terms of only one Li atom in the defect complex. Certainly the case of two or more Li atoms in a coupled motion can be excluded. The latter configuration inevitably leads to vibrational modes involving motion of mixed Li isotopes when both isotopes are present in the material. If not detectable from the natural abundancies, equal amounts of both isotopes would then clearly reveal such mixed modes. Instead, only the ^7Li and the ^6Li modes appear in the spectrum, with similar strength upon mixed isotope doping. The same was found for the $(Cu\text{-}Li)_I$ and the $(Cu\text{-}Li)_{III}$ centers. In the former case even the presence of 7.4% ^6Li in natural Li could be resolved in the local-mode spectra, with approximately corresponding intensity.

B. Temperature quenching of the PL emission

The influence of a rise in temperature on a PL spectrum such as the one in Fig. 1 is twofold; thermal broadening and quenching of the total emission intensity above a certain temperature. The first effect is most

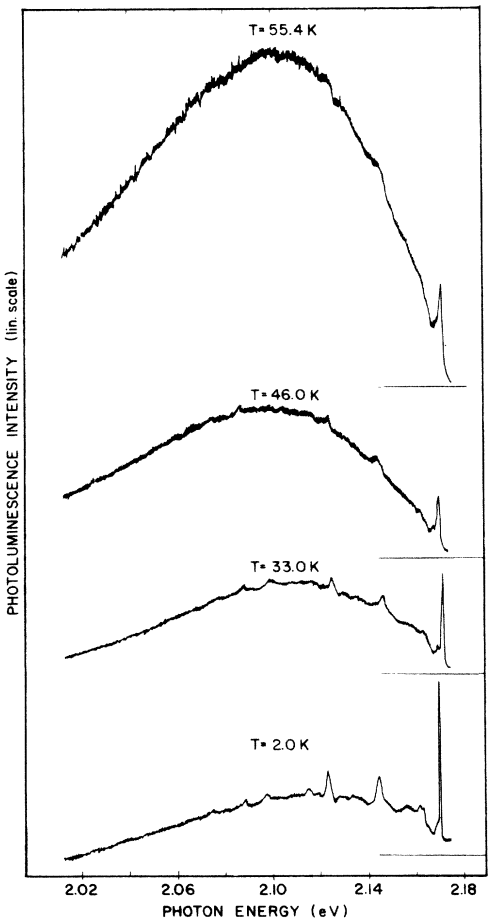

FIG. 4. Photoluminescence spectra of the $(Cu\text{-}Li)_V$ bound exciton at different temperatures. The intensities are arbitrarily normalized, see Fig. 5.

dramatically seen as a broadening of the electronic lines (and consequently any sharp phonon replicas of these lines), due to a rather strong linear coupling to low-energy phonons. A detailed analysis of such effects was presented for the COL emission in GaP,[19] and a similar thermal broadening and quenching of the electronic lines was observed for the $(Cu\text{-}Li)_V$ spectrum as shown in Fig. 4 for a few temperatures. We shall not analyze these phenomena in detail here, however. We note that the quenching of the no-phonon line by phonon broadening does not affect the total intensity of the entire emission phonon envelope. Therefore the discussion based on total thermal quenching of the emission, which is an electronic effect, is not affected by the details of phonon coupling active in quenching the electronic (no-phonon) lines.

Figure 5 shows the temperature dependence of the total emission intensity for temperatures up to 75 K. At low temperatures the emission intensity is constant, but starts to decrease drastically around 60 K to be at an undetectable level above about 75 K in our samples. It is possible to analyze the thermal quenching behavior in terms of a single activation energy E_1 for the nonradiative competing process to the $(Cu\text{-}Li)_V$ emission, according to

$$\frac{I(0)}{I(T)}-1=I_0 e^{-E_1/kT},$$

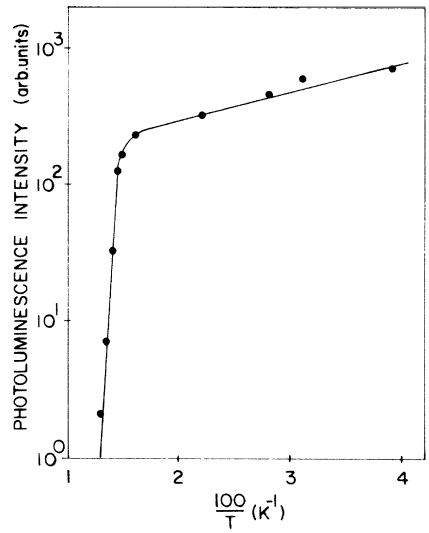

FIG. 5. Photoluminescence intensity of the $(Cu\text{-}Li)_V$ BE emission plotted against $1/T$.

where $I(0)$ and $I(T)$ are the PL intensity at very low temperature (2 K) and at the actual temperature of measurements, respectively.[21] From Fig. 5 an activation energy of 80 ± 10 meV is deduced from such a procedure. The most plausible interpretation of an activation energy for a nonradiative competing process in this case would be the thermal liberation of one charge carrier from the defect in the BE state.

For the $(Cu\text{-}Li)_V$ BE the total binding energy of the BE is $2.352-2.172=0.180$ eV at low temperature. This is considerably higher than the observed activation energy of 80 meV, which suggests that we probably do not observe the liberation of the BE as a whole. Rather, one of the particles would be assumed to be thermally excited, leaving the other at the defect, which is of course still sufficient to quench the BE emission.

If we assume that the $(Cu\text{-}Li)_V$ center is dominantly hole attractive, due to a Cu_{Ga} central-cell component, one would expect the electron to be thermally excited first. Electron (shallow donor) binding energies on Ga sites in GaP are typically found to be of the here observed order of magnitude (e.g., 82 meV for Si_{Ga}). We shall further relate these observations from thermal quenching to the electronic structure of the 2.172-eV BE below, in the discussion section (Sec. IV A).

C. Excitation spectra

Excitation spectra with tunable dye-laser excitation have given crucial information about the electronic structure of neutral defects in GaP, since also the excited electronic states of a BE can be revealed. A good example is the COL 2.1774-eV center in GaP, where only one electronic state is seen in PL emission, but several are seen in PLE spectra.[8] For the $(Cu\text{-}Li)_V$ BE emission, the observation similar PLE spectra was attempted. The intensities in PLE were extremely weak, mainly due to the very low oscillator strength of the BE states for $(Cu\text{-}Li)_V$ [similar to the cases of $(Cu\text{-}Li)_I$ (Ref. 13) and $(Cu\text{-}Li)_{III}$ (Ref. 16)]. Actually, the lowest-energy triplet-singlet pair at

2.172—2.174 eV could not be detected above the noise level in our experiment (partly due to an unfavorably low dye efficiency in that region). At higher photon energy, however, stronger electronic transitions are seen in Fig. 6, with resolved peaks at 2.254, 2.260, and 2.266 eV, respectively. These features are broadened, probably due to a short lifetime when they efficiently transfer excitation down to the lowest singlet-triplet ($S-T$) pair of the defect. Such stronger excited states are also seen with the Cu-related COL defect[8] and the 1.911-eV defect.[10] They are believed to originate from electronic excited states of the BE, connected to the $p_{\pm}$ hole states of the BE in all cases.[8,10]

D. ODMR spectra

The ODMR results for the $(Cu\text{-}Li)_V$ complex will be reported in some detail separately,[22] and therefore we only present a brief account of the most important experimental results in this section. ODMR data have been obtained in photoluminescence, i.e., the excited state of the defect, the bound-exciton state, is being probed. It is known from Zeeman data that the lowest-energy BE state is a triplet state, approximately isotropic in Zeeman spectra. Thus, one expects that the interpretation of ODMR data will be in terms of resonances within the ($S=1$) triplet state.

A typical ODMR spectrum taken with a microwave frequency of 9.25 GHz is shown in Fig. 7. The spectrum is of unusually strong intensity, typically 5% of the luminescence intensity is modulated by the microwave field in a total intensity detection mode (no polarizers employed). The spectrum contains a strong low-field resonance at ≈ 0.13 T, and in addition a large number of components centered around $g \approx 2$. The low-field nearly isotropic resonance is assumed to be the $\Delta M=2$ contribution to the spectrum, unusually strong in this case, while the angular-dependent part centered around $g \approx 2$ is referred to the $\Delta M=\pm 1$ triplet resonance contribution. This part of the spectrum is complicated by the fact that another defect spectrum with resonances around $g \approx 2$ is superimposed. This second spectrum is due to a separate trigonal defect, very efficiently excited via the $(Cu\text{-}Li)_V$ defect.[22,23] By taking ODMR spectra at different microwave modulation frequencies, it has been possible to see which components are related to the $(Cu\text{-}Li)_V$ ODMR spectrum. A complete angular dependence has been taken, and from rotation in a (011) plane it seems clear that the defect has monoclinic (C_{1h}) symmetry with spin Hamiltonian

$$H=\mu_B \mathbf{B}\cdot\vec{\vec{g}}\cdot\mathbf{S}+\mathbf{S}\cdot\vec{\vec{D}}\cdot\mathbf{S}\ ,$$

where the parameters for one of the 12 equivalent defect orientations are

$$g_1=2.05,\ g_2=2.00,\ g_3=2.08\ ,$$

$$D_1=0.0879\ \text{cm}^{-1},\ D_2=0.0936\ \text{cm}^{-1}\ ,$$

$$D_3=0.0057\ \text{cm}^{-1}\ .$$

In general, eight components, i.e., four inequivalent triplet resonances can be observed in most directions. The $\Delta M=\pm 1$ spectrum is rather close to collapsing when the magnetic field is in a $\langle 100\rangle$ direction, and the largest splitting is observed close to $\langle 110\rangle$. The overall orientation of the defect should therefore be close to $\langle 111\rangle$, but it is probably distorted off a linear configuration, since a $\langle 111\rangle$-oriented defect would give a simpler ODMR pattern than that observed for the $(Cu\text{-}Li)_V$ center. Since the defect is argued to consist of three atoms, a bent configuration is easily contemplated. A further discussion on the identity of the defects is given below. A full analysis of the ODMR spectrum is given separately.[22]

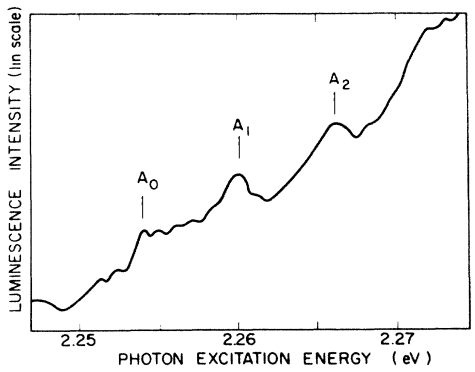

FIG. 6. Photoluminescence excitation spectrum for the $(Cu\text{-}Li)_V$ emission shown in Fig. 1. The peaks labeled A_0, A_1 and A_2 are the only ones consistently obtained. No detailed information is revealed due to the weakness and lifetime broadening of the peaks.

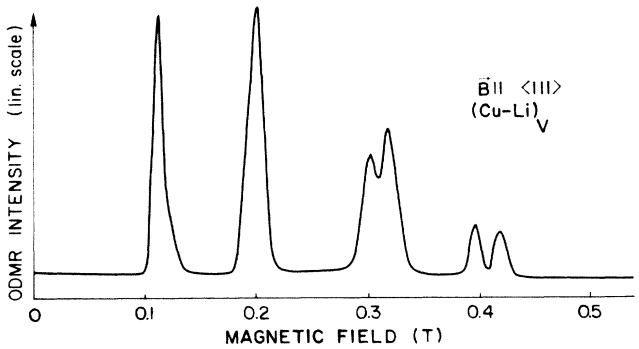

FIG. 7. A typical example of the well structured and strong ODMR spectra obtained from the $(Cu\text{-}Li)_V$ PL emission at 2 K, employing a 9-GHz microwave system.

IV. DISCUSSION

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

As demonstrated above, the BE state for $(Cu\text{-}Li)_V$ has a magnetic triplet as a lowest-energy state at 2.1721 eV, closely followed by a singlet state at 2.1742 eV. No other electronic states are found until around 2.26 eV, i.e., about 70 meV higher up in energy. This situation resembles the picture found for the previously studied COL defect BE in GaP,[8] although the splitting between the triplet and singlet was much larger in that case (21 meV compared to 2.1 meV here). Otherwise, as pointed out earlier, the PL

spectra for the COL center and the $(Cu\text{-}Li)_V$ center are very similar; they are close in photon energy and exhibit a very similar phonon coupling (see below).

The model for the formation of a triplet-singlet pair as the lowest-energy configuration of a bound exciton has been previously discussed.[8] In a simple effective-mass-like model it is understood in terms of a strong local stress field of compressive sign at the defect. If the effect on bound-hole states for this stress field dominates over the spin-orbit splitting, the lowest-hole state is an orbital singlet p_0 state, which means that the corresponding BE states created upon binding also an electron, are made up from a combination of a spinlike hole and a spinlike electron. The splitting observed between the triplet and singlet state is due to the electron-hole exchange interaction, directly related to the overlap of the corresponding bound-particle wave functions at the defect. The triplet state then becomes the lowest-energy state in the case of interacting particles of opposite charge.

The electronic structure for the $(Cu\text{-}Li)_V$ BE is schematically shown in Fig. 8. The excited strong electronic states in Fig. 6 probably correspond to the doublet configurations derived from the higher $p_\pm$ hole states, also appearing strong in the PLE of the COL center.[8] The low value of the S-T splitting for $(Cu\text{-}Li)_V$ should be interpreted as evidence for a small overlap between the electron and hole wave functions, i.e., they are not both strongly localized as in the case of COL (Ref. 8) or the 1.911-eV Cu-related defect BE (Ref. 10). In fact, the observation of a thermal activation energy of ≈ 80 meV in Fig. 5 is naturally explained as due to the release of a shallow electron from the hole already present at the defect, i.e., we should refer the $(Cu\text{-}Li)_V$ BE to the so-called HTL category,[15] where one of the charge carriers of a BE (in this case the electron) bound to an "isoelectronic" defect is "hydrogenic" and loosely bound by Coulomb forces. The situation is different for the COL defect, which shows a thermal activation energy for PL quenching of 153 meV, close to the Be localization energy. This is in turn consistent with the picture of a defect BE with both carriers rather well localized, as also evidenced by the large value of the S-T exchange splitting of 21 meV in that case.[8]

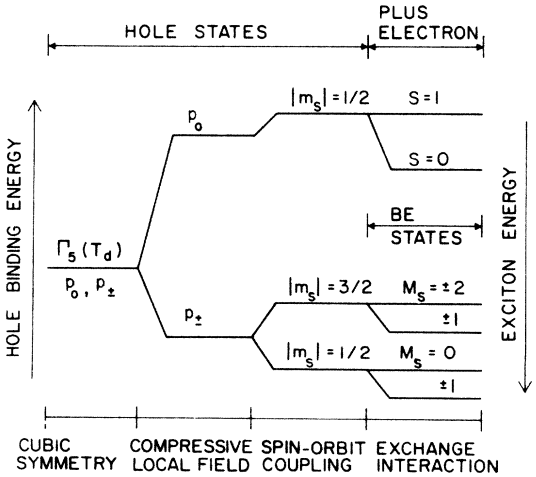

FIG. 8. A level scheme of the representations of the hole, electron, and bound-exciton states for the $(Cu\text{-}Li)_V$ center. The local stress field is larger than the spin-orbit coupling, giving a spin-only hole state (Γ_6). This couples with a Γ_6 electron giving a singlet (Γ_1) and a triplet (Γ_2, Γ_3) bound exciton.

From a previous study it is known that interstitial Li gives rise to two shallow donors in GaP, due to occupation of two inequivalent approximately tetrahedral interstitial sites.[24] This is consistent with the shallow binding of the electron in the $(Cu\text{-}Li)_V$ BE, although the symmetry of the electron state should be primarily dominated by the electron-repulsive Cu_{Ga} site, believed to dominate the localized potential of the defect. This is also under the assumption that Li enters an interstitial site at the defect, replacing a Cu_i in the analog COL defect (see below).

The above description of the origin of the electronic structure observed for the $(Cu\text{-}Li)_V$ defect in GaP is an oversimplification in one sense, that will be briefly discussed here. For a hole-attractive local potential, believed to be due mainly to the Cu_{Ga} potential in this case, the lowest hole state is rather localized, even though its binding energy as measured from the valence-band edge happens to be just ≈ 80 meV. A hole bound in a very localized potential cannot, in general, be described in an effective-mass-like picture, where only the hole states from the top of the valence band are used to build up the bound-hole wave function for the complex defect. Although the above description, in terms of a renormalization of hole states close to the valence-band top in a compressive local stress field, does indeed produce the correct electronic structure, a more general model leading to the same BE states is desirable. Such a localized hole state may, in principle, be built up from a large number of bands, including even the conduction band.[25]

The quenching of the angular momentum component of holes bound in a localized potential may also occur under more general conditions than the strong compressive axial strain field discussed above.

A difference for the separately studied $(Cu\text{-}Li)_{III}$ defect BE is that the lowest-energy electronic configuration of $(Cu\text{-}Li)_{III}$ is actually two S-T pairs closely intermixed in energy.[16] This is interpreted as evidence for a symmetry very close to trigonal for $(Cu\text{-}Li)_{III}$,[16] in contrast to the case of $(Cu\text{-}Li)_V$ discussed here, where a quite large distortion from trigonal symmetry is derived from the ODMR data.

B. Vibrational properties from BE spectra

As was noted previously the phonon coupling of the $(Cu\text{-}Li)_V$ defect resembles very much the structure observed for the COL defect.[19] The two spectra are shown in Fig. 9 for easy comparison. The most important difference is the occurrence of two distinct local phonon modes above the LO^Γ phonon energy in the sideband of the $(Cu\text{-}Li)_V$ BE, which are absent for the COL.[19] The broadened low-energy modes observed in the COL spectrum[8,19] were found to be related to the motion of Cu interstitials. We believe that the quite similar low-energy sideband found for the $(Cu\text{-}Li)_V$ BE is also primarily due to mixed modes

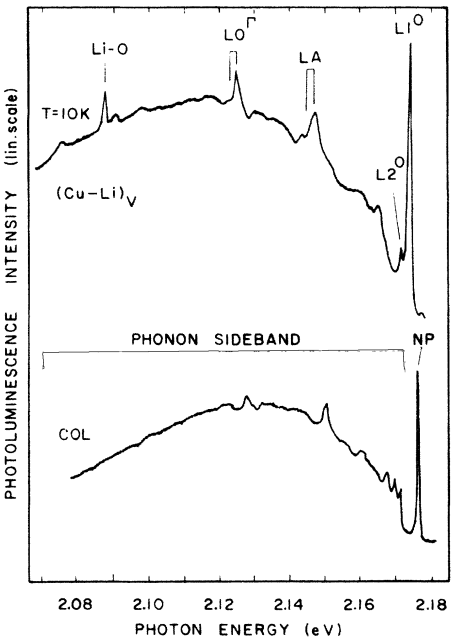

FIG. 9. A comparison of the $(Cu\text{-}Li)_V$ and COL PL spectra. The spectra are very similar, differing mainly in the better resolution in the phonon coupling to low-energy (6—8 meV) phonon modes for the COL case. The COL bound exciton has a large exchange splitting, so only the triplet is seen.

involving the rather heavy interstitial Cu atom believed to remain at the defect from the original COL identity, when the $(Cu\text{-}Li)_V$ center is created (see below). No Cu isotope shifts of these low-energy modes could be detected for the $(Cu\text{-}Li)_V$ BE, which is explained by the much broader shape of these replicas for $(Cu\text{-}Li)_V$ compared to COL.

The true local modes observed in Fig. 3 constitute the direct evidence for the attachment of a Li atom to the complex. The two modes are independent and couple strongly to both singlet and triplet electronic BE states, which means that they are probably both of A_1 symmetry. The simplest model for the defect, emerging from the analysis of these local modes upon isotope doping, is that only one Cu atom is substituted by Li in the original COL defect, to create the $(Cu\text{-}Li)_V$ defect. Why two different local modes are seen, both with A_1 symmetry, is not clear, but the bent configuration of the defect discussed below would certainly allow more than one possible such vibration of the defect, involving the Li interstitial. Only one such mode would be expected, if the defect were of the simpler Cu_{Ga}-Li_i type, in analog with previous results for the vibrational modes of a defect composed of an interstitial Li and a substitutional acceptor in Si.[26] The total shape of the sideband of the $(Cu\text{-}Li)_V$ defect is quite similar in strength to the COL emission, and involves strong contributions from a broad range of lattice phonons in GaP (Fig. 9). The strength of this phonon coupling is understood as derived from the localization of the primary particle of the BE, in this case supposed to be the hole bound to the Cu_{Ga} central cell of the defect. In fact, the similarity of this broad phonon sideband for the COL BE and the $(Cu\text{-}Li)_V$ BE is strong evidence that Cu_{Ga} is involved in both defects.

C. The possible identity of the $(Cu\text{-}Li)_V$ defect

The problem of identification of complex defects in semiconductors is still one of the major unsolved problems in this area, and is a bottleneck against stronger interaction between theory and experiment. No unique method is practical to identify complex defects, usually a combination of evidence from different experiments is used to arrive at a plausible conclusion on the identity of the defect. With this background in mind we shall discuss the collection of experimental data displayed in the previous sections for the $(Cu\text{-}Li)_V$ defect, and attempt to put forward a plausible model for the identity of the center. It seems natural to divide the discussion into two different parts, on the one hand the chemical identity of the impurity atoms involved in the defect, and on the other hand, their geometrical positions in the lattice to form a defect of observed properties.

A starting point in the discussion of chemical identity is that the COL defect is a necessary prestage in the formation of the $(Cu\text{-}Li)_V$ defect. The COL defect has recently been studied in considerable detail, and it has been concluded that it is related to Cu only.[8] This means that it is identified as a neutral complex of the nature Cu_{Ga}-Cu_i-Cu_i, i.e., two interstitial Cu atoms are needed to compensate for the double Cu_{Ga} acceptor site to make a neutral complex. More recent investigations with uniaxial stress show that the COL defect has a major axis close to a trigonal direction,[27] which might infer that both interstitials preferably will reside on the same side of the Cu_{Ga}. The fact that the COL defect can transform into the $(Cu\text{-}Li)_V$ defect at quite low Li-diffusion temperatures is consistent with a high mobility of interstitial Li (and Cu) already at very moderate diffusion temperatures. Since the local-mode behavior upon Li isotope doping in this case points towards the participation of one Li atom in the complex, the most natural assumption is that one of the Cu_i interstitials is replaced by a Li_i. This of course does not preclude the reorientation of the defect at the same time, so the Li_i need not occupy a similar interstitial site as does the replaced Cu_i in the COL defect.

Alternative models involving more than one Li atom tend to be more difficult to reconcile with all experimental data. If two interstitial Li atoms occur in the defect together with Cu_{Ga}, these interstitials must be perfectly isolated vibrationally not to cause any mixed local modes in the mixed isotope doping experiment. This requires that one Li_i atom be placed on a bond on the opposite side of the Cu_{Ga}.[13,16] Similar difficulties occur for the possible substitution of Cu_{Ga} by Li_{Ga}. The Li_{Ga} acceptor has not been firmly identified in GaP, but is believed to be deep, associated with broad ir PL bands around 1.2 μm. We believe that it is much more difficult to replace a bonded lattice site atom with another species in a low-temperature defect reaction, than it is to replace a simple interstitial, which is not bonded. In addition, a Li_{Ga}-Li_i pair as part of the complex should definitely give rise to mixed isotope modes, as shown in the case of the Li_{Ga}-Li_i-O_P defect in GaP.[7]

A problem not explained by the previous discussion is the fact that the creation of the $(Cu\text{-}Li)_V$ defect was much

easier in the bulk material than in liquid-phase epitaxy (LPE) epitaxial layers. It is difficult to suggest a simple explanation for this behavior, without having characterized in detail the residual defects present in both kinds of starting material. Certainly there is no evidence for the participation of atomic species other than Cu and Li in the defect. It seems that the most plausible reason for the dependence on the type of starting material would be that the Li-diffusion process is influenced by the different background of the residual defects in bulk and LPE GaP, respectively. It could be that other defects attract the Li interstitials more efficiently in LPE material, thereby quenching the formation of the $(Cu\text{-}Li)_V$ defect. More detailed work is needed to clarify this question.

Supposing that the $(Cu\text{-}Li)_V$ defect most likely consists of a Cu_{Ga} together with one Cu_i and one Li_i, the geometrical arrangement of these atoms needs to be specified to arrive at a complete identification. From the ODMR data it seems likely that the defect is considerably distorted from a ⟨111⟩ orientation. This is also consistent with the observation of just one set of triplet-singlet pair for the lowest-energy BE states, in contrast to the nearly trigonal $(Cu\text{-}Li)_{III}$ defect where two such sets are seen. A possible configuration of the $(Cu\text{-}Li)_V$ defect is shown in Fig. 10. If we assume that the original COL defect, which is a prestage of the formation of the $(Cu\text{-}Li)_V$ defect, is a (nearly) trigonal Cu_{Ga}-Cu_i-Cu_i configuration (where both the Cu_{Ga} and the two Cu_i atoms may be substantially relaxed along the ⟨111⟩ axis compared to the corresponding ideal high-symmetry positions in the GaP lattice), one can imagine that when one Cu_i leaves the defect it may be replaced by another approaching Li_i atom at some secondary axis away from ⟨111⟩. Such a low-symmetry arrangement might give rise to the complicated low-symmetry ODMR spectrum observed from the triplet resonances of the BE for $(Cu\text{-}Li)_V$.

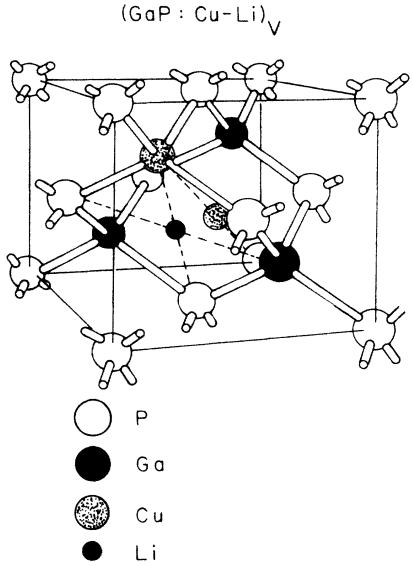

FIG. 10. An illustration of the proposed geometrical configuration of the $(Cu\text{-}Li)_V$ center. The Li_i is distorted away from the ⟨111⟩ direction.

V. SUMMARY AND CONCLUSIONS

A detailed study of a Cu- and Li-related neutral defect in GaP, created by a sequential diffusion of Cu and Li (in this order) is presented. A strong photoluminescence emission with the lowest electronic line at 2.172 eV is found to be related to this defect; in fact, this spectrum is very similar in general shape to the previously studied COL spectrum. It is found that the PL spectrum is associated with a bound-exciton recombination at the defect, and the electronic structure has as the lowest configuration a pair of lines, of which the lowest one is an isotropic magnetic triplet and the higher one is a singlet, separated from the triplet by a splitting of 2 meV, caused by electron-hole exchange interaction in the BE state. Further excited BE states are found around 2.26 eV in dye-laser-excited excitation spectra for this $(Cu\text{-}Li)_V$ defect BE.

This electronic structure with a lowest triplet-singlet pair is rather common for complex defects in GaP (and Si), where interstitials are involved, causing an overall compressive strain field locally at a defect with a predominantly hole-attractive central-cell potential. It is understood in a simple effective-mass-like model in terms of an effect of the local strain field on the bound-hole states that is larger than the corresponding effect of the spin-orbit splitting. The bound hole is then a p_0 spinlike state, which combines with a similarly spinlike electron state to give a triplet-singlet configuration for the lowest BE states. Probably, such a p_0 hole state is a general feature for strongly hole-attractive potentials in GaP, disregarding the above effective-mass-like arguments. Thermal quenching data for the PL emission further support the model of a hole-attractive central cell, while the electron is bound by about 80 meV in a typical shallow-donor-like state by Coulomb attraction in the conventional HTL model.[15]

Several clues to the identity of the defect are given by details in the phonon coupling to the BE, in addition to chemical evidence from the preparation procedure. Low-energy quasilocalized phonon modes in the PL spectrum are taken as evidence for the participation of Cu_i in the center, as also observed for the COL spectrum. Two distinct A_1 symmetry local modes, which are not intermixed upon mixed isotope doping with ^6Li and ^7Li, provide good evidence that one Li_i interstitial is involved in the defect. The complicated symmetry revealed by ODMR spectra for the defect is evidence for a bent configuration, where a Cu_{Ga}-Cu_i pair in an approximate ⟨111⟩ direction is supplemented by a Li_i at an interstitial position along a different direction.

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