PHYSICAL REVIEW B VOLUME 32, NUMBER 10 15 NOVEMBER 1985

Optically detected magnetic resonance investigation of a deep Li-related complex in GaP

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(Received 11 April 1985)

A broad photoluminescence (PL) band peaking at ≈ 1.70 eV in Li-doped GaP is investigated by optical spectroscopy. No electronic lines are observed for this PL spectrum, indicating a strong phonon coupling with a no-phonon energy of ≈ 1.80 eV. Optically detected magnetic resonance (ODMR) data reveal a triplet configuration for the lowest excited electronic state of the corresponding defect, which proves that it is a neutral complex defect, binding an exciton in a predominantly hole-attractive local potential with a compressive local strain field at the defect. The ODMR data can be fitted to a triplet spin Hamiltonian $H=\mu_B \mathbf{B}\cdot\mathbf{g}\cdot\mathbf{S}+D[S_z^2-\frac{1}{3}S(S+1)]+E(S_x^2-S_y^2)$ with evaluated parameters $g_x=2.0$, $g_y=1.9$, $g_z=2.05$, $D=1.2\times10^{-5}$ eV, and $E=8\times10^{-7}$ eV $x||[001]$, $y||[1\bar{1}0]$, $z||[110]$. The defect, therefore, has a bent symmetry, and the identity is suggested to involve Li_{Ga} together with two interstitials in a (110) plane, probably both Li atoms.

I. INTRODUCTION

Li is a rapid interstitial diffuser in GaP and is known to introduce two different interstitial shallow donors in GaP.[1] Li_{Ga} (Ref. 2) is believed to be a deep acceptor, since it has not been observed in optical spectra in the visible spectral region.[3] Neutral "isoelectronic" complexes involving both Li and Cu have been studied recently, and several bound-exciton spectra related to such defects have been found in the visible region.[3–6] These complex defects are believed to involve Cu_{Ga}, i.e., Li is incorporated at interstitial sites.[2–4] Li_{Ga} is tentatively believed to be involved in a complex defect causing a deeper bound-exciton emission in the infrared around 1.2 eV in GaP.[7] In addition Li_{Ga} has been shown to be part of the Li_i-Li_{Ga}-O_P complex defect in GaP, giving rise to bound-exciton emission at 2.09 eV in GaP.[8]

GaP intentionally doped with Li alone shows bound-exciton (BE) spectra and donor-acceptor-pair spectra associated with the shallow interstitial donors,[1] and in addition usually the red Li-Li-O BE spectrum with no-phonon lines close to 2.09 eV.[8] At lower photon energies a broad emission peaking at 1.70 eV is consistently observed with Li doping, as already noted in the earlier work by Dean.[8] In this work a more detailed study of this emission is presented. It is shown to be associated with a neutral Li-related complex of low symmetry.

The main body of new information presented in this paper is obtained from optical detection of magnetic resonance (ODMR), performed in the emission mode, i.e., the excited state of the defect is being probed in photoluminescence (PL).[9] ODMR spectra have previously been observed for (Cu-Li)—related complex defects in GaP, due to the fact that the bound excitons associated with these defects have a magnetic triplet as the lowest electronic state.[10,11] The Li-Li-O defect has two magnetic doublets as the lowest electronic configuration,[8] which means that ODMR's are not expected to be observed, in agreement with experiments in the present investigation. The deep red Li-related emission, however, does show an ODMR spectrum typical for a triplet resonance. Such a triplet configuration is possible if the defect experiences a local strain field of compressive sign.[3,12–14] Further, the angular dependence of the ODMR's suggests that the defect is bent in a (110) plane.

In Sec. II below, details about sample preparation and the experimental procedure are briefly summarized. Section III contains the photoluminescence spectral data in the absence of microwaves and magnetic fields. The broad 1.70-eV band shows no structure from electronic lines, unfortunately. Section IV gives a description of the ODMR data obtained for the 1.70-eV PL emission band, as summarized above. Finally, a discussion of the results on Li-related complex defects in GaP deduced from this work is provided in Sec. V. A structural model for the possible identity of the defect causing the 1.70-eV emission band is also suggested.

II. SAMPLES AND EXPERIMENTAL TECHNIQUES

The samples used for the specific work on Li-doped GaP reported here were small solution-grown platelets, which were selected to be single crystals. The samples were originally nominally undoped but contained residual impurities such as S, Si, N, and O. Li doping was performed by diffusion in evacuated quartz ampoules. Li-metal pellets were placed on an additional quartz support plate inside the ampoule to avoid serious chemical attack on the ampoule quartz wall during heat treatment. Typical Li diffusion conditions were 600—800 °C for one hour. The ampoules were rapidly quenched to room temperature in water after the diffusion.

Photoluminescence spectra were measured by above-band-gap excitation with an Ar^+ laser, and extrinsic excitation either with a Coherent 590 tunable-dye-laser system or with a Kr^+ laser. The spectral dependence was recorded with an S20 photomultiplier via a SPEX 0.85-m double monochromator. ODMR data were obtained with a 9-GHz cylindrical microwave cavity, mounted on an Ox-

ford SR10 He cryostat. The spectral dependence of the ODMR luminescence signal was monitored via a small Jobin Yvon 0.25-m single monochromator. Signal averaging and storage of optical spectra were performed with a Nicolet 1172 signal averager for both PL and ODMR spectra.

III. PHOTOLUMINESCENCE SPECTRA

In Fig. 1 is shown a photoluminescence spectrum at 2 K for a typical Li-doped solution-grown GaP crystal used in this study. The entire visible region is shown in Fig. 1, and it is obvious that in this case the 2.09-eV Li-Li-O BE emission completely dominates the spectrum, due to the presence of O in the starting material prior to Li diffusion. Li-related spectra are also seen closer to the band gap. In Fig. 1 these spectra are actually dominantly associated with various (Cu-Li)—related defects as reported in a separate study.[3,4] This is due to a slight Cu contamination of the crystal during the Li diffusion. In Fig. 2 the less prominent spectral regions in Fig. 1 are displayed in more detail. The $(Cu\text{-}Li)_I$ complex in Fig. 2(a) is responsible for the BE line at 2.306 eV.[3] The deep red broad band finally is shown more clearly in Fig. 2(b). It has a shape that varies slightly from sample to sample and with different excitation conditions, indicating that it overlaps somewhat with other similarly broad emission bands in the background.

The broad band peaking at 1.70 eV is to be interpreted as an envelope of an emission composed of a weak (not resolved) electronic line (or lines) with a strong phonon coupling. The half-width of the band is about 100 meV, indicating a Franck-Cordon shift $\sum_i \lambda_i \hbar\omega_i$ of a similar order.[15] (Here $\hbar\omega_i$ denotes the different phonon energies participating in the phonon coupling to the optical transition, and λ_i denotes the corresponding coupling strength.[16]) The electronic no-phonon line should be around 1.80 eV, judging from the spectral shape in Fig. 2(b).

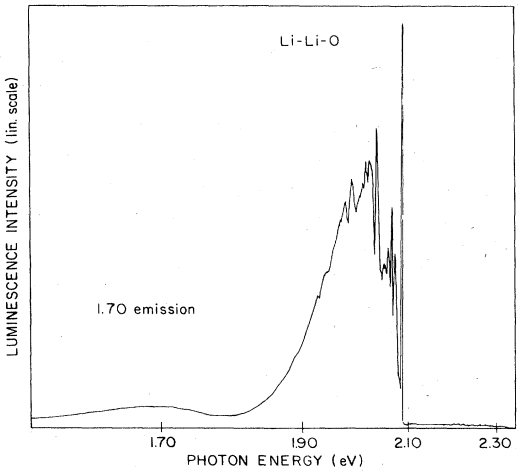

FIG. 1. A photoluminescence spectrum at 2 K for a Li-doped crystal showing a dominating Li-Li-O bound-exciton emission and a broad band peaking at about 1.70 eV. The luminescence close to the band gap is weak in comparison.

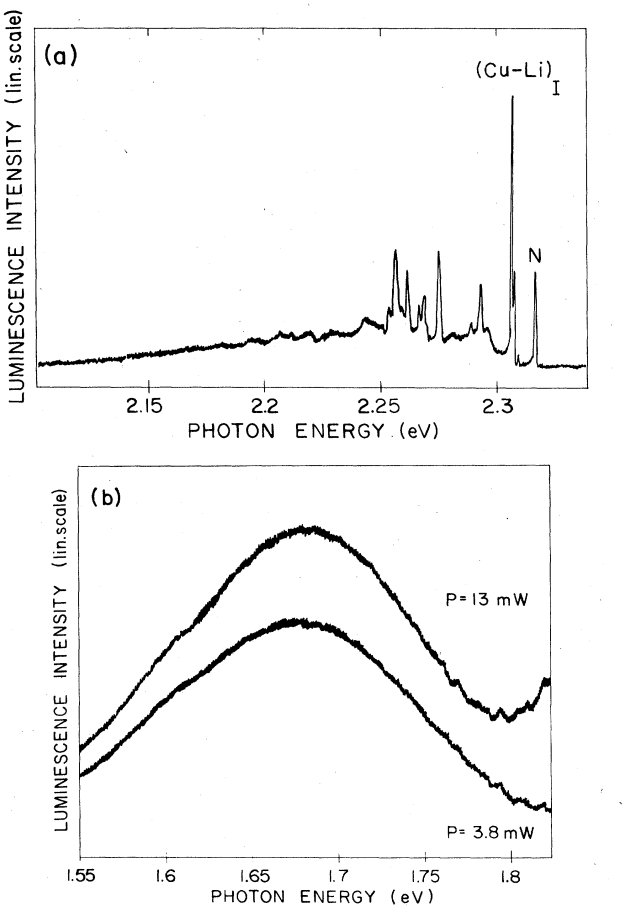

FIG. 2. (a) Photoluminescence spectrum at 2 K close to the band gap, for the same sample as in Fig. 2, is seen to be dominated by the $(Cu\text{-}Li)_I$ bound exciton Ref. (3), and the N bound exciton. (b) A comparison of the 1.70-eV emission at two different excitation power densities. A small shift in peak position is observed along with a change in the lineshape. This is believed to be caused by a saturation of an emission at slightly lower energy at high excitation density.

IV. ODMR SPECTRA

The recording of ODMR spectra for complex defects in GaP is not very straightforward, because transfer of excitation may easily occur between different defects. This gives rise to the possibility of registration of ODMR signals from a certain PL spectrum, while the resonance is actually taking place in another higher-energy excitation, subsequently transferred to the defect causing the detected emission.[17,18] In the present case severe Cu contamination had to be avoided, since several (Cu-Li)—related defect BE's give rather strong triplet ODMR signals,[10,11] which may be detected also at lower photon energies due to BE transfer.[17] This is particularly serious for the $(Cu\text{-}Li)_V$ BE at 2.172 eV, which gives an unusually strong ODMR signal.[4,10] The 2.09-eV Li-Li-O—related BE emission does not give rise to a detectable ODMR signal. This is understandable, since in this case the lowest electronic lines are magnetic doublets, $M_z = \pm 2$ and $M_z = \pm 1$,

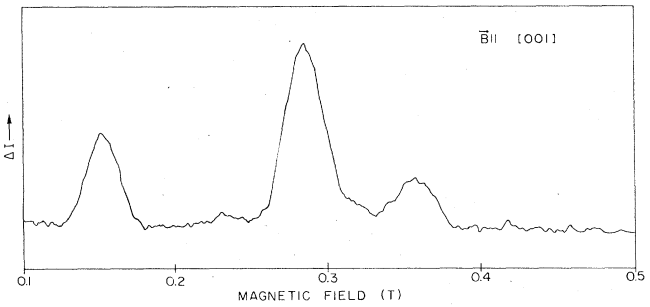

FIG. 3. The well-structured ODMR signal for the 1.70-eV band. At 0.15 T, a $\Delta M=2$ resonance occurs and for $\mathbf{B}//[001]$ resonances can be seen for $B\approx 0.3$–0.4 T.

respectively.[8] Microwave-induced transitions $\Delta M_z=\pm 4$ and $\Delta M_z=\pm 2$ are forbidden, and in addition there is no strong difference in oscillator strength between the transitions from $M_z=+2,1$ and $M_z=-2,-1$, respectively, down to the BE ground state. Therefore, no ODMR effect is expected, nor is it observed for the Li-Li-O PL spectrum.

The broad 1.70-eV band, however, does show a rather weak ODMR signal, as shown in Fig. 3. The spectrum is characteristic of a triplet resonance exhibiting pairs of $\Delta M=\pm 1$ lines centered around $g\approx 2$ (i.e., ≈ 3300 G). In addition, a strong low-energy line is observed at about 1500 G, interpreted as due to a $\Delta M=2$ resonance. The resonance lines are fairly broad, with a half-width of typically 300 G, possibly due to an unresolved hyperfine interaction for Li atoms with nuclear spins $I=\frac{3}{2}$. The angular dependence of the spectrum was also investigated, as shown in Fig. 4. The defect is found to be bent in a (110) plane from the clear symmetry pattern observed for the $\Delta M=\pm 1$ lines in Fig. 4. A fitting of the angular dependence of Fig. 4 was performed with the standard Hamiltonian[9]

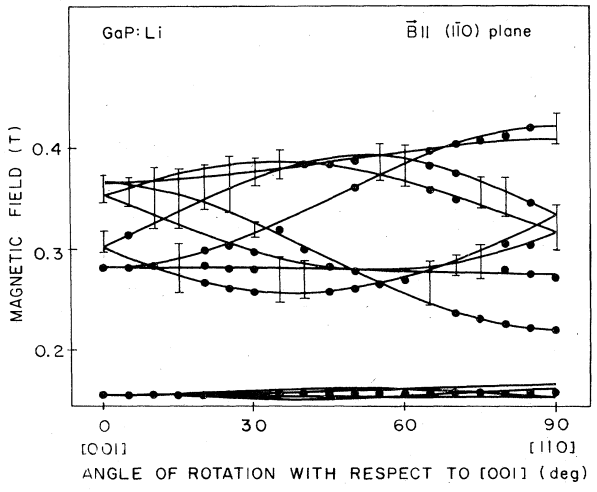

FIG. 4. Angular dependence of the ODMR signal showing a complicated anisotropy pattern, consistent with a defect which is bent in a (110) plane.

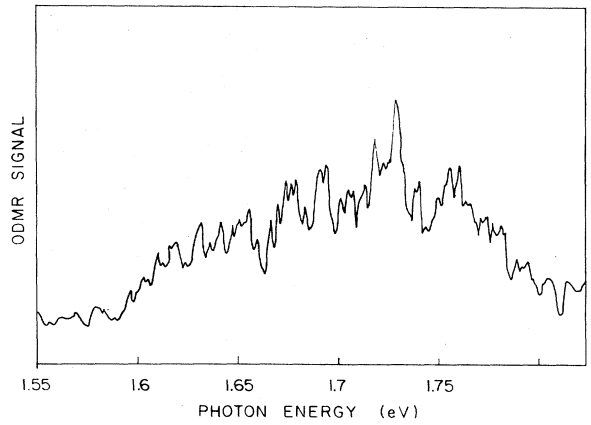

FIG. 5. Spectral dependence of the ODMR signal. As can be seen, the ODMR-PL shape corresponds to the ordinary photoluminescence shape, [Fig. 2(b)].

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

A best fit is obtained with the following parameters: $g_x=2.0$, $g_y=1.9$, $g_z=2.05$, $D=1.2\times 10^{-5}$ eV, $E=8\times 10^{-7}$ eV, where $x||[001]$, $y||[1\bar{1}0]$, and $z||[110]$.

To ascertain the origin of the ODMR signal the spectral dependence of PL was obtained at resonance with a magnetic field of 2900 G, as shown in Fig. 5. The spectrum is very similar to the one shown in Fig. 2(b), indicating that the 1.70-eV band does produce the ODMR resonance. The ODMR-PL band in Fig. 5 peaks at slightly higher photon energy than the band in Fig. 2(b), which can be explained if a lower-energy band is in fact overlapping in the PL spectrum of Fig. 2(b). The problem of excitation transfer from higher-energy bound-exciton states may be excluded in this case, since the (Cu-Li)–related spectra, being the only realistic candidates for such transfer, give ODMR spectra which are well known from previous work,[10,11] and which are easily distinguishable from the spectra found here (Figs. 3 and 4).

Consequently it is reasonable to assume, as a result of the ODMR data, that the 1.70-eV spectrum is connected with a defect which has a bent configuration in a (110) plane and with a lowest-electronic bound-exciton excitation of a triplet $S=1$ nature.

V. DISCUSSION

A. Electronic structure of excitons localized at neutral complex defects

The 1.70-eV broad PL band studied in this work is associated with a complex neutral defect, as is evident from

the triplet structure observed for the electronic bound-exciton state from ODMR data. This is a nice demonstration of the power of ODMR in a case where the electronic line is too weak to be observed and consequently unavailable for Zeeman spectroscopy. The conditions for observation of a triplet state at lowest energy for a bound exciton have been discussed in previous papers,[3–5,12–14] and will be briefly summarized here. A triplet BE state with an almost isotropic g factor occurs when a spinlike hole is combined with a spinlike electron state, to form an $S=1$ state for parallel spins. In addition an $S=0$ state is present for antiparallel spins higher in energy, split off from the lowest $S=1$ state by the electron-hole exchange interaction energy $\Delta_{JJ}^{e\text{-}h}$. This situation requires that only two particles (one electron and one hole) are present in the excited state (the bound-exciton state), i.e., the center is a neutral one (isoelectronic). A condition for obtaining a spinlike bound-hole state is a hole-attractive localized potential and, in addition, an overall strong compressive strain field at the defect of axial or lower symmetry, which will push the $p_{\pm}$ bound-hole states[12] down in the valence band by an amount larger than the effect of spin-orbit interaction on the bound-hole states. This situation is summarized in Fig. 6(a). In a tensional noncubic local strain field the $J=\frac{3}{2}$ bound-hole states have lowest energy and will dominate the magneto-optical behavior of the BE, so that the g factor becomes completely anisotropic. An example is shown in Fig. 6(b), where the expected electronic structure is shown for the case of a weak tensional axial strain field, such as for the Li-Li-O defect studied earlier.[8]

The observation of a triplet bound-exciton state thus provides the valuable information that the defect responsible for the 1.70 eV emission is a neutral complex defect with a hole-attractive potential in a strongly compressive local stress field. The low symmetry deduced from the detailed fitting of Fig. 4 deviates from a simple trigonal configuration, and is most conveniently described as orthorhombic. The observation of a strong "$\Delta M=2$" resonance in the ODMR spectrum is also an indication of a symmetry lower than trigonal. Earlier data on Cu-related[13] and (Cu-Li)—related defects[6,7,10,11] indicate that strong $\Delta M=2$ ODMR lines are seen when the symmetry is drastically different from trigonal, as, e.g., in Refs. 7 and 11. The three substates of the triplet in a magnetic field are to first order split into the $|0\rangle$ and $|\pm1\rangle$ states. However the terms $D[S_z^2-\frac{1}{3}S(S+1)]$ and $E(S_x^2-S_y^2)$ in the triplet spin Hamiltonian, arising mainly from the anisotropic part of the electron-hole exchange interaction, will drastically change the character of these substates. This is particularly true at low magnetic fields as appropriate for a 9-GHz ODMR experiment, where the character of the wave functions for these "$|0\rangle$" and "$|\pm1\rangle$" states may have been changed to an extent that M_z is no longer a good quantum number. In that case it is not surprising that the so-called $\Delta M=2$ transitions in the ODMR spectrum appear as allowed microwave transitions, particularly for defects with symmetry lower than trigonal, in which case the $E(S_x^2-S_y^2)$ term will have a strong influence on the character of the substates at low fields.

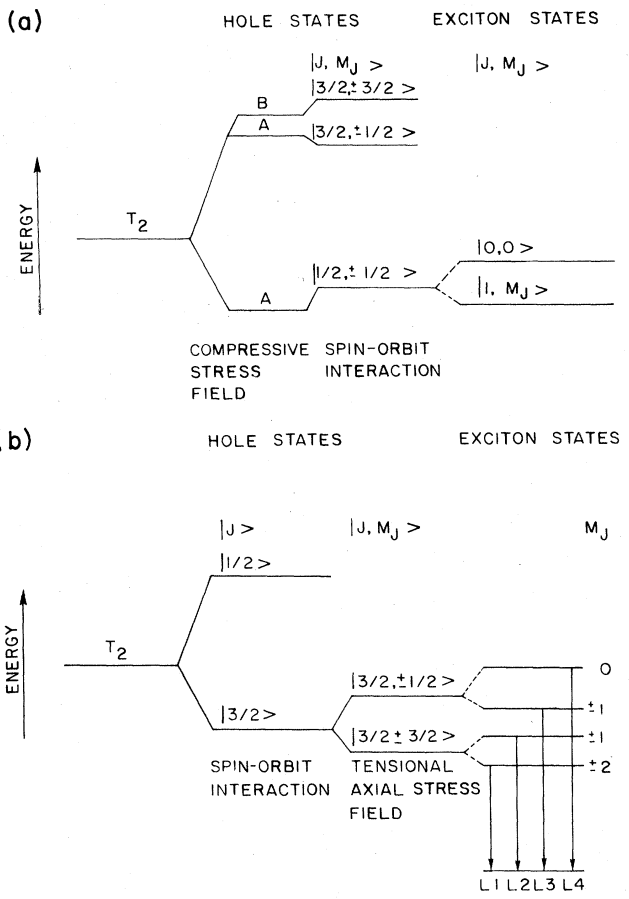

FIG. 6. (a) A schematic figure on the effect of a strong compressive stress field, exceeding that of the spin-orbit interaction, on the electronic states of a bound exciton. For low symmetry the T_2 hole state (in T_d) is split into three states, labeled A, A, B. These are shifted by the spin-orbit interaction. The $|\frac{1}{2},\pm\frac{1}{2}\rangle$ state is lowest in energy. Coupling with an $S=\frac{1}{2}$ electron gives two states, one singlet and one triplet. The use of J and M_J quantum numbers is not strictly correct but serves as a guide to compare with other defects of higher symmetry. (b) The effect of a weak tensional axial stress field applied to a bound exciton. The spin-orbit interaction will split the T_2 hole state into a $J=\frac{1}{2}$ and a $J=\frac{3}{2}$ state. The stress field will cause a splitting of the $J=\frac{3}{2}$ state according to M_J values indicated in the figure.

B. Possible identity of the defect responsible for the 1.70-eV PL emission

The 1.70-eV emission is only observed when GaP is doped with Li, which means that it can be safely stated that Li is part of the defect. The presence of Cu in the defect cannot be definitely excluded since Cu is very easily introduced as a contaminant in GaP during Li diffusion. We have not found any evidence for an enhanced intensity of the 1.70-eV emission with Cu doping, but this is no definite argument against Cu being part of the complex. We have observed that in GaP crystals deliberately doped with both Cu and Li, the 1.70-eV PL band does not ap-

pear strongly. Cu doping alone gives rise to a broad band at slightly lower photon energies, centered at about 1.65—1.7 eV.[19] This band is believed to be related to the 0.51-eV Cu-related acceptor in GaP,[19,20] and a separate study reveals that it does not give rise to any ODMR spectrum in the range of magnetic fields employed in this study. This Cu-related emission could form part of the low-energy background in the PL spectrum in Fig. 2(b), however. No correlation with another dopant is found, and the 1.70-eV emission can be found with comparable intensity for Li diffusion into both doped (n or p) and nominally undoped (doping level 10^{15}—10^{16}cm^{-3}) GaP.

The collected evidence from the photoluminescence spectra in relation to the doping and diffusion conditions mentioned above seems to favor a model where Li_{Ga} is the dominating hole-attractive central cell of the defect. Li_{Ga} is supposed to be a deep double acceptor in GaP; in fact it has not yet been positively identified. It has been argued that the deep (Cu-Li) complexes giving PL emissions around 1.1 eV in GaP are, in fact, deep due to Li_{Ga} being part of these defects.[11] On the other hand, the Li_i-Li_{Ga}-O_P defect is more shallow, with a hole-binding energy of only about 200 meV.[8] The partition between electron and hole-binding energies for the 1.70-eV bound exciton is not known (temperature-quenching data were unreliable, due to spectral overlap with other broad emission bands), but it may be assumed that the hole-binding energy is of the order 0.5 eV, and the electron-binding energy much smaller, say of the order 50 meV.[1] This is natural if the defect is dominantly hole attractive, in which case the electron is bound as a secondary particle with a binding energy possibly reduced even below the value for a shallow donor electron by the electron-repulsive defect potential dominated by Li_{Ga}.

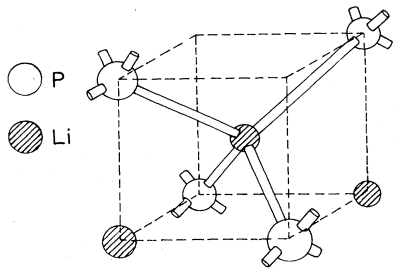

FIG. 7. A possible model of the Li-related defect studied in this work. Li on a Ga site is surrounded by two interstitial Li atoms. The defect is bent in a (110) plane as inferred from ODMR data. One Li_i atom might also be displaced off a trigonal axis.

Li_{Ga} is a double acceptor, which means that two donor electrons are necessary to make the center neutral and satisfy the local bonding in a tetrahedral configuration. If no P-site impurities are involved in the defect (which is natural from the above discussion), these donorlike species must be interstitials. Li_i interstitials on the two tetrahedral sites are shallow single donors,[1] and two such interstitials would suffice to make a neutral center together with Li_{Ga}. Such a model is illustrated in Fig. 7, where one interstitial is supposed to occupy a tetrahedral site on a trigonal axis, while the second interstitial is occupying another site off this trigonal direction, so that the total defect configuration is bent. Such a model seems to be in agreement with the symmetry derived above from the angular dependence of ODMR data. As mentioned above it cannot be definitely excluded that one of the interstitials could be a Cu atom. The most likely conclusion, however, is that both interstitial atoms are Li, which means that the defect should be denoted Li_i-Li_{Ga}-Li_i.

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