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Optical properties of the Cu-related characteristic-orange-luminescence center in GaP

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A detailed investigation on optical properties of the characteristic-orange-luminescence (COL) center in GaP is reported, combining photoluminescence data with dye-laser-excited excitation spectra. Evidence from the doping conditions required to produce this defect suggests an identification of the COL center with a defect containing Cu only. The novel optical data support this view, since the COL spectrum is identified as originating from an exciton bound to a nonlinear isoelectronic Cu_I-Cu_{Ga}-Cu_I associate. The complicated local mode coupling and the rather strong coupling to the lattice continuum modes is expected for such a defect structure, where the Cu_{Ga} can be considerably relaxed. The strong compressive axial strain field created by this defect causes a splitting of the hole states at the defect and decouples the spin and orbital angular momentum of these states. For a complete decoupling the bound exciton is formed by combining a pure spin hole state and an electron. This results in the observed $J=1$ spin triplet as the lowest bound exciton state and a higher $J=0$ singlet state. From the rich structure observed in excitation spectra a large exchange splitting of 23.2 meV is obtained between the $J=1$ ground state and the $J=0$ state. No orbitally excited states of one particle in the Coulomb field of the other are observed for this bound exciton, probably a consequence of the fact that both electronic particles are relatively deeply bound. A typical feature for this class of defects seems to be that transitions involving the singlet $J=0$ state have a much stronger total oscillator strength than those involving the $J=1$ ground state. This is a consequence of a spin selection rule $\Delta S=0$, also manifested by the long decay time of the $J=1$ bound exciton emission ($\tau \approx 100\ \mu s$).

I. INTRODUCTION

Cu is known to be easily incorporated into GaP as a contaminant during growth or heat treatment. Several investigations on bound electronic states associated with Cu in GaP have been published during the last two decades,[1-12] and a large number of different Cu-related defects seems to be present in material prepared by different methods. The origin of these Cu-related defect levels has not been identified in any case from the data presently available,[1-12] although vague indications for the presence of complex centers have been presented in some cases.[5,6,10,11] This problem of defect identification is of course not restricted to Cu in GaP, but rather it is common to most deep-level defects in semiconductors. Obviously, for the case of Cu in GaP, considerably more detailed experimental data are necessary to assist in such defect identification.

The electronic behavior of Cu in GaP is not easily predictable at this stage. A simple substitutional Cu_{Ga} acceptor state may not exist, at least not on an undistorted lattice site. Recent electron-paramagnetic-resonance (EPR) data do not reveal any sign of such an undistorted Cu_{Ga} state.[13] On the other hand, Raman-scattering data for Cu acceptors in GaP have recently been interpreted as an indication of the prominence of just such a simple substitutional acceptor state.[14]

Several of the Cu-related centers in GaP are found to give radiative recombination, which allows detailed information to be obtained from pho-

toluminescence (PL) measurements. In particular, bound exciton spectra which give sharp electronic lines in emission and absorption have proved to be very useful in characterizing defect centers in III-V and II-VI compounds.[15] If one looks at the situation in other III-V compounds, such as GaAs, bound exciton spectra believed to be related to Cu acceptors with binding energies of 0.15 and 0.47 eV, respectively, have indeed been found, and the Cu-related defects involved were found to have a symmetry lower than cubic in both cases.[16] Sharp line structure has actually been observed previously for some deep Cu-related centers in GaP,[5,6,11] and tentatively interpreted as due to bound exciton recombinations.

In the present investigation we focus our attention to the prominent 2.1774-eV characteristic-orange-luminescence (COL) emission in Cu-diffused GaP. As already mentioned, preliminary PL investigations of this emission were published several years ago.[17–19] Unfortunately, the early literature was misleading in one important aspect: ascribing the spectrum to a V_{Ga}-O_P complex.[17–19] This was later shown to be in error, and the emission was linked to Cu via isotope-shift analysis in PL data.[5,6] At that time only emission spectra could be observed, since with conventional light sources, the absorption for this COL transition was too weak to be detected due to a low oscillator strength.[17] With the availability of cw dye lasers this problem can now be overcome. In this paper is included complementary absorption data, taken as photoluminescence excitation (PLE) spectra of the low-temperature COL emission. A rich structure of higher electronic states is found in these low-temperature PLE data, unrevealed in PL data. The interpretation of these spectra is simplified by studies of Zeeman splitting in magnetic fields up to 3.5 T.

In Sec. II, information is given on the preparation of the Cu-doped samples used in this investigation, together with details of the experimental procedure. Experimental data for PL spectra of this COL emission are discussed briefly in Sec. III, and serve as a comparison with absorption data. Section IV contains the absorption data from PLE measurements, which show a rich structure due to excited electronic states and a complicated phonon coupling to the bound exciton (BE) transitions. In Sec. V, the detailed observations from both emission and absorption spectra are discussed in relation to a suggested model of a Cu_I-Cu_{Ga}-Cu_I defect, to which the exciton is bound.

II. SAMPLES AND EXPERIMENTAL PROCEDURE

Several different types of GaP samples were used in these investigations, Cu-doped as well as undoped for reference. Most experiments were carried out on nominally undoped layers grown by liquid phase epitaxy (LPE), which were Cu-diffused in the temperature range 900—1100 °C. Such crystals showed rather strong COL luminescence, with minimal interference with other emissions, since the shallow donor-acceptor- (*D-A*) pair spectra peaking at about 2.2 eV were of very low intensity. To be able to exclude possible effects from the substrate material, experiments were also carried out on bulk crystals. Some of those were liquid-encapsulated Czochralski- (LEC) grown material, others were needles grown by the wet H_2 transport technique, Cu-contaminated accidentally during growth. These samples showed similar results for the COL emission, but the needles suffered from a much reduced PL intensity. Other bulk samples were solution grown in a temperature cycle 1000 °C→800 °C, with Cu and sometimes Te (to produce *n*-type material) in the solution. It has not been possible to correlate the occurrence of the COL spectrum with any shallow donor dopants (in addition to Cu), in agreement with earlier studies.[5] On the other hand, it was established that the COL emission can easily be produced by Cu-diffusion at 900—1100 °C in both *n*-type and *p*-type GaP.

Steady-state photoluminescence spectra were obtained, either with Ar^+ or Kr^+ laser excitation, or with selective excitation from cw dye lasers, employing suitable dye solutions. For excitation spectra the dye-laser wavelength was continuously scanned with a controlled drive unit. To further reduce the stray-light level from the dye laser, in the case of weak emission intensity, it was combined with a synchronously scanned grating filter. The spectral linewidth of the dye laser was about 0.3 Å, and a similar linewidth could be maintained on the detection side. There we used a Jarrel Ash 0.75-m double-grating monochromator for the recording of PL spectra, and for the selection of a suitable wavelength in recording PLE spectra. For studies of PL and PLE spectra in a magnetic field, a 3.5-T Varian electromagnet was employed together with a 2-m Bausch and Lomb spectrograph equipped with a scanning exit slit and photomultiplier detector. The 2.1774-eV photoluminescence band is sufficiently broad that PLE spectra were readily obtained from the most strongly lumines-

cent samples using a low-energy pass filter to reduce the intensity of scattered light in the single monochromator, even when the PLE spectrum was recorded from the region of the 2.1774-eV no-phonon line.

III. PHOTOLUMINESCENCE SPECTRA

PL spectra were recorded for a large number of Cu-doped GaP samples between 1.8 and 140 K. A typical low-temperature spectrum of a Cu-diffused sample with a fairly strong orange COL emission is shown in Fig. 1. From measurements on different types of samples it seems that this emission is strong in all samples diffused with Cu at high temperatures (900—1100 °C) and rapidly quenched, as was previously reported.[5,18] As already mentioned, the COL emission is most easily studied in samples with a low shallow level doping, since in this case the background from shallow donor-acceptor pair emissions is much reduced.

The spectrum shown in Fig. 1 is similar to the one earlier published,[5,6,17,19] and consists of a zero-phonon line at 2.1774 eV at 1.8 K (which in high resolution actually shows a ~0.15-meV splitting[6]), together with a dominating and complicated photon-assisted wing extending down to about 1.9 eV. The zero-phonon line appears very sharp at the lowest temperatures (usually the linewidth was resolution limited to 0.15 meV at 1.8 K). The zero-phonon line is followed on the low-energy side by a broad continuum background, due to coupling with low-energy phonons in the acoustic band. Starting at 5.3 meV below the zero-phonon line, a discrete-phonon spectrum is superimposed on the continuum background, with several discrete quasi-localized phonon modes, as listed in Table I. The total emission envelope has a considerable width, and the dominating background must be regarded as a convolution of a continuum one-phonon spectrum, displacing the peak of the envelope some 65 meV below the zero-phonon line in emission (Fig. 1).

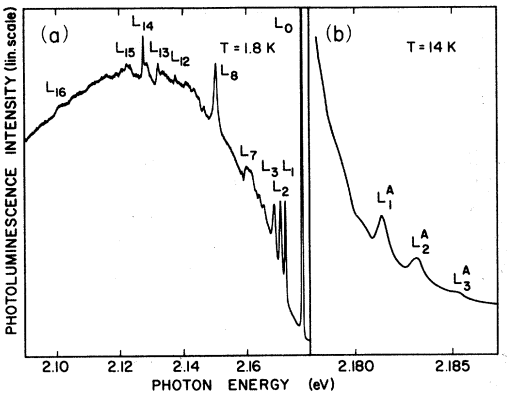

FIG. 1. (a) Photoluminescence spectrum for the COL bound exciton at 1.8 K for a Cu-doped GaP epitaxial layer, excited with a 5145-Å Ar^+ laser line. The $J=1$ electronic transition L_0 occurs at 2.1774 eV. Energies of phonon replicas labeled L_1-L_{16} are listed in Table I. (b) High-energy part of the COL photoluminescence spectrum at 14 K for the same crystal as in (a). At this temperature, anti-Stokes phonon replicas $L_1^A-L_3^A$ are clearly observed. The phonon energies in the excited vibronic state are somewhat reduced compared with the corresponding phonon replicas, L_1-L_3 in the ground state (see Table I).

In the temperature range 5—20 K we observe anti-Stokes replicas for the discrete-phonon replicas L_1-L_3 (Table I), as also shown in detail in Fig. 1. These observations directly confirm that the features L_1-L_3 are phonon replicas, and not electronic transitions. Apparently these discrete phonons are of somewhat smaller energy in the upper electronic state of the optical transition (Table I). This is in agreement with the data from PLE spectra to be presented. The temperature dependence of the discrete line spectrum and the total envelope of the COL emission has been investigated in detail, and is included in a separate publication.[20]

IV. EXCITATION SPECTRA

The optical transition responsible for the COL emission has a low oscillator strength, which means that excitation spectra cannot be obtained in the conventional way.[17] A tunable dye laser provides both adequate intensity and spectral resolution for detection of narrow absorption lines. The intensities of both the no-phonon line and the total emission are linear functions of the excitation intensity for this emission. Therefore, the excitation spectrum is directly proportional to the absorption coefficient, after a linear correction for the variation of excitation intensity.

A typical PLE spectrum for the COL emission at 2 K is shown in Fig. 2. An experimental difficulty in the measurements was the presence of a strong continuum background in the PLE spectrum. This background appears to be caused by excitation of the COL center through capture of photoexcited free carriers, which are in turn pro-

TABLE I. (a) Energy positions of the observed phonon replicas in the COL emission spectrum in Fig. 1. Phonon energies and interpretations are included. (b) Energy positions and interpretations of the structure observed in the photoluminescence excitation spectrum of the COL bound exciton shown in Fig. 2.

(a) Emission

Notation	Phonon energy (eV)	Energy difference (meV)	Interpretation
L_0	2.1774	0	$J=1$ triplet
L_1	2.1721	5.3±0.1	L_1^A 4.7±0.1
L_2	2.1706	6.8±0.1	L_2^A 6.4±0.1
L_3	2.1686	8.8±0.1	L_3^A 8.1±0.2
L_4	2.1654	12.0±0.2	
L_5	2.1639	13.5±0.2	
L_6	2.1631	14.3±0.3	
L_7	2.1593	18.1±0.5	
L_8	2.1503	27.1±0.2	LA perturbed
L_9	2.1449	32.5±0.3	
L_{10}	2.1437	33.7±0.3	
L_{11}	2.1418	35.6±0.3	
L_{12}	2.1377	39.7±0.3	
L_{13}	2.1320	45.4±0.3	TO_Γ
L_{14}	2.1273	50.1±0.3	LO_Γ
L_{15}	2.1224	55.0±0.7	2LA
L_{16}	2.1004	77.0±1.0	

(b) Absorption

Notation	Photon energy (eV)	Energy difference from B_0 (meV)	Interpretation
B_0	2.1774	0	$J=1$ triplet
B_1	2.1819	4.5	
B_2	2.1834	6.0	
B_3	2.1861	8.7	
A_0	2.2006	23.2	$J=0$ singlet
A_δ	2.2034	26.0	$A_0+2.8$ meV
A_1	2.2056	28.2	$A_0+5.0$ meV
A_2	2.2068	29.4	$A_0+6.2$ meV
A_3	2.2084	31.0	$A_0+7.8$ meV
A_4	2.2100	32.6	
A_5	2.2134	36.0	$A_0+\mathrm{TA}(X)$
A_6	2.2199	42.5	$A_2+\mathrm{TA}(X)$
A_7	2.2267	49.3	$A_0+26.1$ meV
A_8	2.2327	55.3	$A_2+25.9$ meV
A_9	2.2413	63.9	$A_0+40.7$ meV
A_{10}	2.2450	67.6	
A_{11}	2.2456	68.2	
A_{12}	2.2493	71.9	
C_0	2.2864	109.0	
C_2	2.2932	115.8	$C_0+6.8$ meV
C_5	2.3004	123.0	C_0+14 meV

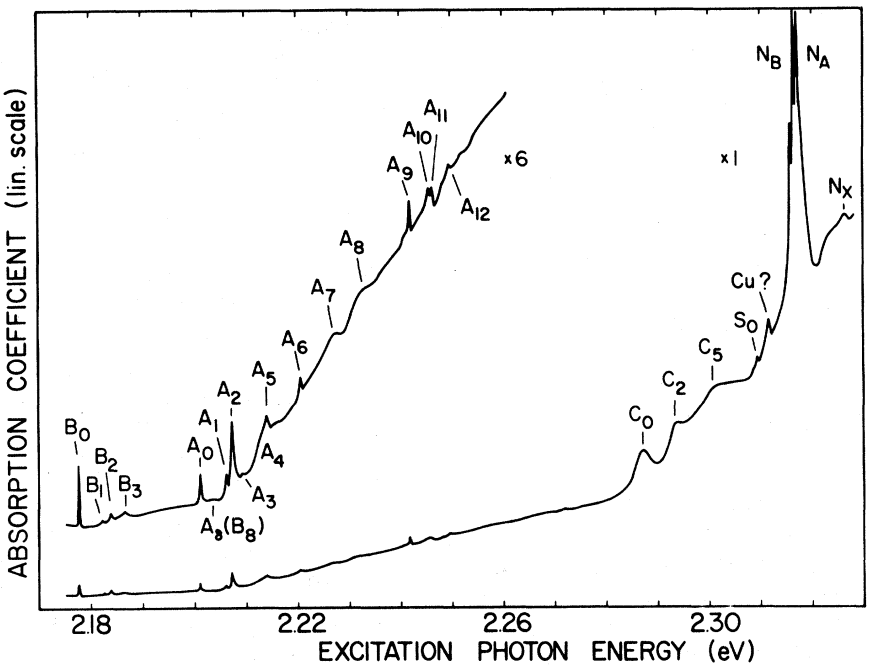

FIG. 2. Excitation spectrum of the COL emission at 2 K obtained with tunable dye-laser excitation with the detection wavelengths set to 5870 Å. The spectrum shows the $J=1$ electronic transition B_0 at 2.1774 eV and three discrete low-energy phonon replicas B_1-B_3 corresponding to the L_1-L_3 replicas in emission. The three peaks A_1-A_3 above the $J=0$ electronic transition A_0 at 2.2006 eV are the same phonon modes with different relative strength. For interpretation see Table I.

duced by two-step excitations via deep levels within the band gap. Such two-step excitations have been shown to be rather efficient for common deep levels such as O in GaP.[21,22] The general impression from the spectrum in Fig. 2 is the presence of strong narrow spectral features from the lowest bound exciton line at 2.1774 eV up to the band-gap energy. Clearly, most of this structure cannot be related to the lowest BE state. Rather it is a manifestation of excited-state configurations for the bound exciton under study. This behavior is remarkable since excited BE states in previously studied absorption spectra for GaP are usually due to exchange and crystal-field splitting of the order of a few meV from the lowest BE state,[15,23–26] or to a simple hydrogenic series for the excitation of the loosely bound particle in the isoelectronic case.[15,27]

The possibility that these sharp features could be related to other centers than the COL center has been thoroughly investigated. The PLE spectrum of Fig. 2 was only observed when the detection wavelength was chosen within the range of the COL-emission spectrum. In addition, it was found that if the dye-laser excitation was set to any one of the sharp lines (Fig. 2), only the usual COL emission was recorded, i.e., no emission specific for some other center was superimposed. Another important observation is that the sharp lines in excitation disappear with approximately the same thermal-quenching behavior as in the emission.[20] Further, we do not see any coincidence in photon energy between any of the lines and other known centers in GaP, except the well-known cases S and N indicated in Fig. 2. The possibility of the observed lines being due to an excitation transfer from such centers can therefore be excluded. This is also supported by the observation that for crystals prepared by quite different techniques (solution growth, LEC growth, and wet H_2 transport, respectively); these features in Fig. 2 occur with the same relative strength. This observation also excludes the possibility of interference with centers in the substrate material for the LPE layers.

The COL PLE spectrum with the electronic line B_0 at 2.1774 eV (Fig. 2), and up to $\sim$2.20 eV it looks very much like a mirror image of the PL spectrum at the same temperature (Fig. 1). A detailed comparison of the strength of the continuum part of the phonon envelope is difficult, however, due to the presence of a strong background in the PLE data. As shown in more detail in Fig. 3, the

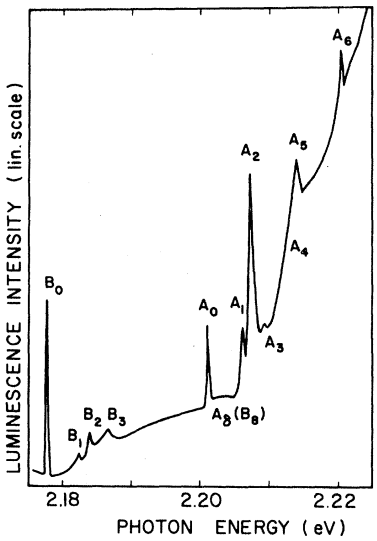

FIG. 3. Low-energy part of the excitation spectrum in Fig. 2. Here the electronic transitions B_0 ($J=1$) and A_0 ($J=0$) are shown in more detail together with their low-energy phonon replicas B_1-B_3 and A_1-A_3, respectively. Most of the slowly varying background is subtracted.

three discrete-phonon modes L_1, L_2, and L_3 seen in emission are observed in absorption as B_1, B_2, and B_3, but displaced towards lower phonon energies by about 10–15% (Table I). These observations compare favorably with our findings in the anti-Stokes wing of PL spectra, as reported above, and again confirm that the peaks L_1-L_3 in Fig. 1 are indeed phonon replicas of quasilocalized modes. This conclusion is additionally supported by the magneto-optical data presented below. The relative strengths of these low-energy absorption lines B_1-B_3 appear to be significantly different from what is observed in emission (for L_1-L_3) at the same temperature (Fig. 1 and Fig. 3). The line B_1 seems to be only about half as strong as B_2 at 2 K, while L_1 and L_2 are of comparable strength in emission at 2 K. The ratio in absorption corresponds to what is observed in emission at somewhat elevated temperatures.[20]

Starting with a sharp line A_0 displaced 23.2 meV above the lowest bound-exciton line B_0, new features are superimposed on the broad phonon-assisted wing expected from a mirror image of the ground-state emission alone. The energies of these features are tabulated in Table I. The sharp line A_0, 23.2 meV above the 2.1774-eV line, does not correspond to the 27.1-meV L_8 phonon mode in emission (Fig. 1), as obvious from the magneto-optical data presented below. We therefore conclude that this A_0 line is of electronic origin. Also, the broad feature A_8, about 26 meV above B_0 in Fig. 3, has approximately the proper strength and width expected for the L_8 mode in the excited vibronic state of the center. In that case it is more correctly labeled B_8.

A much stronger COL-related absorption starts with a group of lines displaced about 30 meV from B_0, and from there on we believe that phonon replicas related to the B_0 ground state will not be seen. Rather the state A_0 appears to possess a remarkably strong phonon coupling compared with the BE ground state B_0. The simplest interpretation of the group of three lines A_1-A_3 is that they are phonon replicas of A_0, and thus generically correspond to the weaker replicas B_1-B_3 of the BE ground state B_0. This view is in agreement with magneto-optical data (see below). In analogy with B_1-B_3, A_1 is the lowest line and also the narrowest one, A_2 is the strongest transition, as is B_2 in absorption, while A_3 like B_3 is broad. The phonon energies of the two series do not agree exactly, indicating a stronger nonlinearity of phonon coupling connected with the A_0 state, consistent with the increased strength of phonon coupling. A_1 lies 28.2 meV above B_0, i.e., 5.0 meV above A_0, while A_2 (29.4 meV above B_0) involves a phonon energy of 6.2 meV and A_3 (31 meV above B_0) a phonon energy about 7.8 meV. These phonon energies are to be compared with the corresponding values for B_1-B_3 in Table I. Second-order replicas with phonon energies corresponding to A_1-A_3 are expected to build up the broad background around A_5, while the rather sharp peak, A_5, might also contain a contribution from a zone-boundary TA(X) replica of A_0. Similarly, the rather sharp line A_6 must contain an additional discrete contribution such as a TA(X) replica of A_2. The broad peaks A_7 and A_8 may be replicas of A_0 and A_2, respectively, involving the absorption version of the very strong L_8 mode in emission (Fig. 1). This mode would have an energy of about 26 meV, similar to B_8, which is 26 meV above B_0.

Line A_9, 40.7 meV above A_0, is very sharp, actually only about 30% broader than A_0, which in principle makes it a good candidate for electronic transition. Such an interpretation is not readily consistent with the magneto-optical data, however (see below). A sharp local "gap-mode" replica of A_0 is the only obvious alternative. A sharp mode, L_{12}, connected with the BE ground state is observed at similar energy, 39.7 meV, in emission (Fig. 1 and Table I). Such gap modes are often ob-

served to be quite sharp.[26] Similarly, the broader peaks $A_{10}-A_{12}$ could correspond to phonon replicas of A_0 in the optical-phonon region between 45 and 50 meV. The most plausible assignments of all lines in Figs. 2 and 3 are summarized in Table I.

In the region above 2.25 eV only weak structure occurs until a very strong and broad line C_0 appears at 2.2864 eV, i.e., 109 meV above the ground state B_0. Two quite strong and broad replicas of this line occur, C_2 and C_5, possibly corresponding to the A_2 and A_5 replicas of the A_0 transition. C_0 must obviously be a new electronic transition, and its relation to the other COL-related electronic states is further discussed below. Of the other lines at higher energies only the one at 2.311 eV cannot be identified with previously observed bound excitons related to centers other than Cu (such as S and N). This line could therefore correspond to an independent Cu-related center, possibly the Cu_I donor, binding an exciton in a rather shallow state.

When a temperature is raised above 2 K, the behavior of the COL excitation spectrum is very similar to the case of emission.[20] Accordingly, thermal quenching of the 2.1774-eV line is also evident in PLE in the same temperature range, i.e., below 45 K.[20] Similarly, all other sharp lines in Fig. 2 below 2.31 eV disappear in the same temperature range ($\sim$45 K), as expected, if they correspond to excited BE configurations. As in emission, the broad phonon background above 2.18 eV remains essentially unchanged around 45 K, but even the strong rise above 2.21 eV is observed at these temperatures. The behavior with rising temperature strongly suggests that the A_0 state couples in a qualitatively similar manner to the low-energy phonon modes which promote the temperature quenching of the sharp line structure.[20] This is also consistent with the finding in PL spectra that strong electronic quenching effects only occur at significantly higher temperature.

In an attempt to determine the nature of the observed structure in the PLE spectrum (Fig. 2), magneto-optical experiments were performed in magnetic fields up to 3.5 T. In agreement with earlier data, the BE ground state at 2.1774 eV shows a splitting into a very slightly unsymmetric triplet, and the splitting is almost isotropic for different crystallographic orientations of the magnetic field direction. Therefore, a definite determination of the symmetry axis for the COL defect from the orientational dependence of Zeeman splitting has not been obtained. A similar splitting into three components was observed for the lines B_1-B_3, consistent with the identification of these lines as low-energy phonon replicas of the 2.1774-eV electronic transition [Fig. 4(a)]. All higher-energy lines of reasonably low spectral width in the PLE spectrum were also investigated in a magnetic field. It was found that no splitting was detectable for any of these, as can be seen in Fig. 4(b). The finite width of these lines at zero field does not rule out a small splitting in most cases, but any

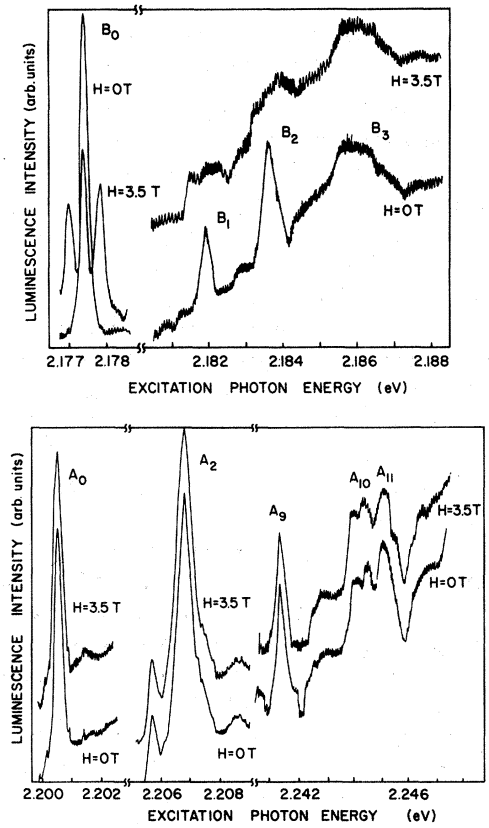

FIG. 4. (a) Excitation spectrum of the $J=1$ electronic transition B_0 and its low-energy phonon replicas, measured in magnetic field $H=3.5$ T in the Voigt configuration, with $\vec{H}\|[110]$. As a comparison the zero-magnetic-field spectrum is shown. The B_0 line is observed to split into a slightly anisotropic triplet. The similar splitting of the three components B_1-B_3 is consistent with the identification of these as phonon modes of B_0. (b) Excitation spectrum of the $J=0$ electronic line A_0 and its dominating phonon replica A_2 in magnetic field $H=3.5$ T as above. No splitting is observed when compared with the zero-field spectrum which is also shown. The peaks A_9-A_{11} are also unsplit in the magnetic field, consistent with a classification of these peaks as phonon replicas of A_0.

such splitting seems to be about an order of magnitude smaller for the rather narrow lines A_0-A_2 and A_9-A_{11} [Fig. 4(b)] than the splitting observed for the 2.1774-eV line and its phonon replicas B_1-B_3. The simplest rationalization of these data is that these lines in fact are all of singlet character. This is consistent with the above classification of the sharp features A_0-A_{12} as corresponding to the singlet $J=0$ state, A_0, and phonon replicas of transitions to this state.

V. DISCUSSION

A. The identity of the COL center in relation to optical data

In early work on the COL center the interpretation of data was focused around the assumption that the center was a V_{Ga}-O_P complex.[17–19] Later it became clear that neither V_{Ga} nor O_P were necessarily involved in the center.[8,9] Instead it was shown to involve Cu, since isotope shifts were observed in some phonon replicas of the COL emission upon comparing spectra from samples doped with ^{63}Cu and ^{65}Cu, respectively.[5] The L_1 replica was observed to shift downwards in energy about 0.15 meV when ^{63}Cu was replaced by ^{65}Cu. The corresponding shift for the modes L_2 and L_3 was 0.3 meV and for L_8, 0.5 meV. Doping experiments involving different shallow dopants (S, Si, Te, N, and Zn) have failed to establish any relationship between the observation of the COL emission and the abundance of such shallow dopants. An associate involving Cu and shallow donors or acceptors is therefore less probable for the identity of this center. Consequently the basic conclusion from doping studies is that Cu is involved, and also that it seems natural to suggest an identity of the COL defect based on Cu atoms alone.

The identification of the lowest BE transition at 2.1774 eV as a nearly isotropic spin triplet[19] necessarily limits the choice of possible defect configurations to a center where no unpaired spin is present in the final state of the transition. This fact immediately sorts out all possible cases of neutral acceptor configurations, where at least one extra particle would be present in the absence of the exciton.[28] In addition such a configuration would lead to strong Auger effects upon recombination of the exciton, while the long decay time of the emission (~ 100 μs) proves that Auger effects are not important for the COL recombination. Another possibility is an ionized acceptorlike center, where no spin would be present in the final state. The strong appearance of the COL emission in both n-type and p-type GaP is a strong argument against the ionized-center model, since the same charge state would hardly dominate in both cases. In addition, excitons bound to ionized centers are not expected and have not been observed in GaP. We are therefore left with the neutral isoelectronic center as the only reasonable identity for this Cu-related defect. In the case of an isoelectronic center there should be no extra particle in the final state of the transition, which can take part in Auger processes. Bound-exciton states of a triplet-singlet character are also possible, e.g., in a strong axial field produced by the local strain between the atoms of a complex.[15,29]

The previous discussion has ruled out all possible models of the defect based on an isolated substitutional Cu_{Ga} acceptor, since in that case two holes are present on the defect if neutral. We note that for tightly bound excitons we also have to rule out the presence of a d hole in the final state of the COL transition, since such a hole might experience a strong overlap with the hole involved in the exciton, and thus be sensitive to Auger processes under recombination. The presence of the COL emission in both n-type and p-type GaP is also a strong argument against the involvement of a $3d$ hole, with the corresponding acceptor state within the band gap. Therefore, even a two-atomic Cu complex such as Cu_{Ga}-Cu_I with Cu_{Ga} in a $3d^9$ configuration is insufficient as a candidate for the COL center. This model would simply create a single axial acceptor, which would not be isoelectronic. It is necessary to involve two interstitial Cu atoms, each acting as a singly charged donor with the $4s$ electron as the donor electron, to compensate the double Cu_{Ga} acceptor and create a neutral isoelectronic associate in the same sense as, e.g., the Zn-O complex in GaP.[6]

In the zinc-blende structure there are two types of interstitial sites that impurity atoms can occupy without forming bonded configurations. The rather large tetrahedral site is surrounded by four atoms of the same type, either Ga atoms or P atoms in GaP. Between two tetrahedral sites of different sublattice type, there is a hexagonal site in the center of a six-membered ring, with three atoms of each kind.[30] The most probable arrangement for the COL center seems to be a central Cu_{Ga} and two interstitial Cu atoms on each side. Then the Cu_I atoms can either occupy tetrahedral sites or hexagonal ones. The former arrangement

is linear in the ⟨100⟩ direction, whereas the latter would lead to a slightly nonlinear configuration, with an overall symmetry approximately ⟨110⟩. No optically detected magnetic resonance (ODMR) signal has been detectable for the COL emission, indicating a strong thermalization in the initial triplet state of the transition. Since the isotropic nature of the transition does not provide any reliable information on the defect symmetry from Zeeman measurements either, we cannot exclude any of the two arrangements of Cu atoms at the present stage. In diamond and Si the hexagonal site has been calculated to have lower energy than the tetrahedral one for self-interstitials, but no such information for the zinc-blende structure is known to the authors.[30]

The complicated phonon coupling to the COL transitions provides information on the defect structure, which seems to support the suggested model of three Cu atoms given above. The strong L_8 mode of 27.1 meV (Fig. 1) is assigned to a perturbed LA mode involving the motion of Cu_{Ga} alone.[31] This is supported by the large isotope shift of this mode when replacing ^{63}Cu by ^{65}Cu, and the fact that only the LA(X) mode involves selective motion of the Ga sublattice. Vibrations of Cu_{Ga} along the ⟨100⟩ direction could then produce this strongly localized resonance mode. The three complex low-energy modes L_1-L_3 also show large isotope shifts, characteristic of pure Cu motion. In view of the low energy of these modes and the additional degrees of freedom of interstitial atoms compared with substitutional ones, the modes L_1-L_3 are understood in terms of vibrations of the Cu_I atoms. The vibrational modes involving the motions of Cu_I can be classified according to parity under reflections which interchange the two Cu_I atoms. The even parity modes then yield the observed replicas L_1-L_3.[20,31]

At the rather high temperatures where the COL centers are formed (900–1100 °C), we may assume that a sufficient amount of Ga vacancies (V_{Ga}) is present to provide the prestage of Cu_{Ga} substitutes. It is assumed that Cu diffuses quite rapidly at these temperatures by an interstitial mechanism,[3] which should provide a large amount of Cu_I donors. The pairing of the charged species $(Cu_{Ga})^{2-}$ and $(Cu_I)^{+}$ at the diffusion temperature into a neutral isoelectronic complex would then be expected. On rapid quenching down to room temperature these complexes will be frozen in, and they are expected to dominate the impurity-related PL spectra from such Cu-diffused undoped GaP, as observed. The failure to associate with shallow donors can be explained by the much lower mobility of these species.

B. Electronic structure of the COL center

The excitation spectra of the COL center, which were measured for the first time in this work, provide important information on excited bound-exciton states, relevant for the identification of the center. Previous data[32] on excited states for relatively deep bound excitons are scarce, however, and essentially limited to simpler cases of isoelectronic traps, such as nitrogen pairs (NN)[27] or Bi (Ref. 33) in GaP, where only one of the particles is deeply bound. For the molecular isoelectronic traps such as Cd-O (Refs. 23–25) or Li-Li-O (Ref. 26), low-lying electronic states within a few meV of the BE ground state have also been observed. In the case of the NN pairs a well-defined hydrogenic series of s-like excited states for the holes in the Coulomb field of the electron was observed,[27] as expected from the Hopfield-Thomas-Lynch model.[34] In addition some evidence was found for the observation of excited states of the electrons in the case of nearest-neighbor nitrogen pairs.[27]

In the case of the COL center, a comparison with the simple model of one particle loosely bound in the Coulomb field of the other (tightly bound) particle might be of limited value, since we believe that both the electron and hole are rather tightly bound to the COL center. The higher BE states observed for the COL center are, instead, analogous to the cases of molecular traps such as Cd-O or Li-Li-O,[23–26] with the important difference being that the axial field has the opposite sign and the exchange splitting is about an order of magnitude larger for the COL case.

The suggested identity of the COL center has the natural consequence that the Cu atoms are in a strong compressive strain field, since two interstitial Cu atoms are accommodated locally. This is in contrast to, e.g., the substitutional Cd-O complex in GaP, where the small size of the O_P atom creates a local tensional strain field.[23–25] The observed spin triplet for the BE ground state implies strongly quenched spin-orbit effects for the hole states involved, which can be understood as a direct consequence of the strong axial crystal field.[15] In the absence of axial field the p-like Γ_{15} valence-band states of the GaP host are split into a $j=\frac{3}{2}$ Γ_8 band and $j=\frac{1}{2}$ Γ_7 split-off band, due to the spin-orbit interaction in cubic symmetry.[35] This splitting amounts to 82 meV in GaP at the Γ

point. An axial strain field lowers the symmetry and splits the fourfold-degenerate Γ_8 hole state into a $|\frac{3}{2},\frac{3}{2}\rangle$ state and a $|\frac{3}{2},\frac{1}{2}\rangle$ state with the usual $|j,m_j\rangle$ notation of total angular momentum (j) and magnetic quantum number (m_j). Bound exciton states derived from these hole states split in a similar way.

Strain-induced mixing between the basic hole states $|\frac{3}{2},\frac{1}{2}\rangle$ and the split-off state $|\frac{1}{2},\frac{1}{2}\rangle$ occurs as symmetry allows coupling of states with the same $|m_j|$ value. These states can be written as

$$|\tfrac{1}{2},\tfrac{1}{2}\rangle=\frac{1}{\sqrt{3}}(p_0\uparrow-p_+\downarrow),$$

$$|\tfrac{3}{2},\tfrac{1}{2}\rangle=\frac{1}{\sqrt{6}}(2p_0\uparrow+p_+\downarrow),$$

where p_0 and p_+ are the orbital angular momentum components relative to the symmetry axis of the defect, and $\uparrow$ indicates the spin direction. A compressive axial strain field increases the binding energy of the $|m_j|=\frac{1}{2}$ holes. A very strong axial field of this sign eventually decouples the spin and orbital angular momentum of the $|m_j|=\frac{1}{2}$ hole states, leaving the hole as a pure spin particle ($s=\frac{1}{2}$) in the ground state of the bound holes. Figure 5 shows a level diagram illustrating this situation. The axial field is shown much stronger than the spin-orbit interaction, which is expected to be reduced below the Δ_{so} of the GaP lattice, or even show a negative sign compared to the host. This may occur through hybridization of the hole wave function with the d orbitals of Cu, which shows an inverted sign of the spin-orbit splitting.[36] In any case the axial strain field is shown to split the threefold, orbitally degenerate, valence-band states Γ_{15} into a p_0 state at highest hole binding energy and a twofold-degenerate $p_\pm$ state. This latter state splits in two states when including the smaller spin-orbit interaction. The lowest bound exciton states are formed by coupling an electron with the pure spin hole, giving a $J=1$ spin triplet and a $J=0$ singlet state, with the triplet lowest. Transition to these states correspond to the B_0 line ($J=1$) and the A_0 line ($J=0$) in Fig. 2. The electron-hole exchange interaction will split off the $J=0$ state with the antiparallel spin configuration, since the involved particles have opposite charge. The $p_\pm$ hole states split-off by the axial field give rise to higher excited BE states, of which one could probably be identified with the strong C_0 line, 109 meV higher than the lowest BE state B_0 (Figs. 2 and 5).

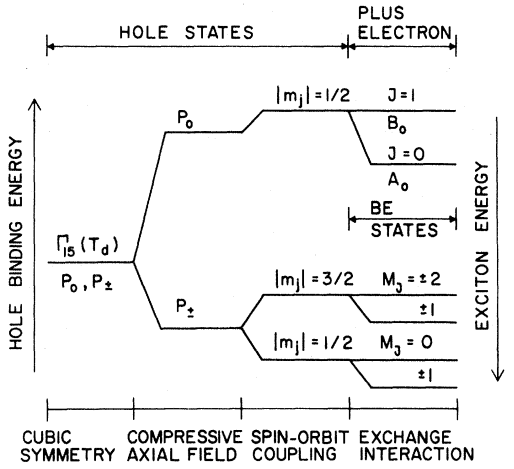

FIG. 5. Schematic model of energy levels for the COL bound exciton states, showing the relative influence of the different coupling mechanisms. As shown to the left, the axial field is assumed to be very strong and to have the sign of a local compression, due to the large ionic radii of the Cu_I atoms involved. This sign of the crystal field creates a splitting of the p-like hole state Γ_{15} into the hole states p_0 at highest hole binding energy and the split-off state $p_\pm$. The coupling of a hole in the pure spin state p_0 to an electron leads to the observed singlet-triplet pair for the bound exciton. The pure spin triplet $J=1$ is the BE ground state at 2.1774 eV (B_0), while the $J=0$ singlet (A_0) is split-off 23.2 meV by the exchange interaction. Bound exciton states from the weakly bound $p_\pm$ hole states are considered responsible for the high energy transition C_0 in Fig. 2. Exchange and spin-orbit splittings involving these relatively weakly bound $p_\pm$ holes are probably less than shown schematically here.

This picture of the electronic configuration for the COL bound exciton is supported by the experimental data. Zeeman data show essentially isotropic magnetic splittings in agreement with a quenching of the hole angular momentum in a strong axial field. Further, there is a rather large strain-induced splitting, $D=0.15$ meV, of the B_0 line in a zero magnetic field. This is evidence for the effect of a strong strain field on a spin triplet, which should be nearly unaffected by the crystal field. The long decay time of the COL emission is expected for a spin-forbidden transition from the $J=1$ triplet to the $J=0$ ground state, which violates the spin selection rule $\Delta S=0$ (i.e., $\Delta J=0$ with our notations). The much larger total oscillator strength of the $J=0$ transition, A_0 (including

the phonon wing), is also understood in terms of this spin selection rule.

The binding energy of the COL bound exciton can be understood as a consequence of a strong hole-attractive central cell at the Ga site, combined with an enhanced electron binding energy, induced by the compressional strain field.[37] As pointed out previously, the absence of Coulomb excited states also indicates a strong binding for both particles in the bound exciton states. The strong electron-hole overlap in the vicinity of the central cell of the COL defect will then produce the unusually large J-J splitting energy Δ_{JJ} of 23.2 meV. This is not the case for previously studied molecular isoelectronic traps, where one particle is loosely bound, as, e.g., the Cd-O BE in GaP, with hole binding energy of about 35 meV. Consequently, these BE only show small exchange splittings. As a comparison, a similar order of the lowest BE states as well as an even larger J-J splitting between the $J=0$ and $J=1$ states is found in another deeper isoelectronic Cu complex, with lowest BE line at 1.911 eV.[37]

VI. CONCLUSIONS

The electronic properties of the COL center in GaP described in this paper, are of basic interest since they establish a new class of isoelectronic defects with properties dramatically different from previously studied isoelectronic traps of the single substitutional type or the molecular pair type.[15] The identification of the COL center as a defect containing only Cu is supported by evidence from variation in doping conditions, since the COL spectrum was not found to be influenced by any additional dopants besides Cu. Further, the COL spectrum seems to be strong in both n-type and p-type GaP, provided that proper Cu-diffusion temperatures and rapid quenching is employed. No evidence in addition to these circumstances and the optical spectra themselves could be obtained to support this identification, since no EPR signal was observed for Cu in GaP,[13] and no ODMR signal related to the COL spectrum could be observed either. From the evidence presented, a Cu_I-Cu_{Ga}-Cu_I molecular defect complex appears to be the natural identification of the COL center, which was misinterpreted in the early literature as a V_{Ga}-O_P defect.[23–25] Three Cu atoms are necessary in this case to create the neutral isoelectronic associate required to explain the spectroscopic data. The natural positions for the Cu_I atoms are either the nearby tetrahedral interstitial sites on each side of Cu_{Ga}, giving a linear ⟨100⟩-oriented defect, or the hexagonal interstitial sites resulting in a nonlinear orientation with approximately ⟨110⟩ symmetry.

The presence of a strong axial strain field at the defect is expected in this case, since two extra interstitial Cu atoms are accommodated locally in the lattice. This has profound effects on the electronic bound exciton states. The strain field decouples the angular momentum components of the basic hole states, leaving pure spin states, from which the lower $J=1$ and $J=0$ components of the BE are formed. Hybridization of the hole wave function with the Cu $3d$ orbitals is believed to promote a reduction of the hole spin-orbit splitting Δ_{so} well below the value of 82 meV, appropriate for GaP, so that the main factor determining the electronic level structure of the BE is the local strain field.

Another unique feature expected for the Cu_I-Cu_{Ga}-Cu_I defects is a rather strong binding for *both* electronic particles in the complex. This is unlike the case of substitutional isoelectronic defects and also previously studied substitutional molecular traps in GaP, where one of the particles is always found to be quite loosely bound, even for the deep centers.[15] In agreement with this idea we do not observe any orbitally excited states of one of the particles in the Coulomb field of the other, as was seen, e.g., with the NN pairs in GaP.[27] The large J-J splitting of 23.2 meV between the ground-state triplet B_0 at 2.1774 eV and the singlet A_0 at 2.2006 eV is explained by a strong overlap of the electron-hole pair, where the particles have comparable binding energies. This is also an extraordinary feature, since J-J splittings are found to be typically of the order 2 meV for excitons bound to isoelectronic centers in GaP, and only slightly larger values have been found in alloys.[38]

A typical feature for this isoelectronic defect seems to be that the higher $J=0$ BE state has a stronger total oscillator strength than the $J=1$ ground state, mainly due to a much stronger phonon coupling in the $J=0$ state. This is understood in terms of the spin selection rule $\Delta S=0$, according to which transitions between a spin triplet and a $J=0$ ground state are forbidden. The larger oscillator strength associated with the $J=0$ excited BE state is even more pronounced in another deeper Cu-related bound exciton with ground state at 1.911 eV.[37] The peculiarities in phonon coupling

to the COL center will be described separately,[20] but the observation of several low-energy quasilocalized modes is one piece of evidence for the presence of interstitial Cu_I atoms in this center. Studies on the properties of a large number of additional Cu-related defects are continued in order to clarify the intriguing role of Cu in connection with defect-related properties of GaP.

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