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Optical Properties of Excitons Bound to Copper-Complex Centers in Gallium Arsenide

F. Willmann, D. Bimberg,* and M. Blätte
Max-Planck-Institut für Festkörperforschung, 7 Stuttgart, Germany
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The photoluminescence of copper-doped high-purity epitaxial GaAs in the near-gap region is investigated as a function of excitation intensity, temperature, and an external magnetic field up to 5.7 T. Sharp emission lines are identified as originating from the recombination of excitons bound to neutral-copper-complex centers of C_{3v} and C_{2v} symmetry with ionization energies of 156 and about 450 meV, respectively. The spectrum exhibits replicas of these lines, which are due to the simultaneous excitation of resonant modes of 3.6- and 6.1-meV energy. The relative intensities obey a Poisson distribution law. The dissociation of the bound excitons takes place in a two-step process: First a free single particle is liberated, whereas at higher temperatures free-electron–hole pairs are created. The linear dependence of the luminescence on the excitation intensity leads to the conclusion that photocreated coupled electron-hole pairs are trapped directly by the binding center. A group-theoretical analysis of the Zeeman pattern attributes the different lines to the appropriate electronic transitions between states of the double groups C_{3v} and C_{2v}. The crystal field is sufficiently strong to completely decouple the $|m_j|=1/2$ and 3/2 levels of the acceptor ground state. The $|m_j|=3/2$ state is degenerate with the valence-band continuum.

I. INTRODUCTION

Photoluminescence, absorption, and reflection measurements of copper-doped GaAs crystals have first been performed in the near-gap energy range by Gross *et al.*[1] The luminescence of this relatively impure bulk material was dominated by an unresolved recombination band labeled B. In high-purity epitaxial GaAs this band was later identified as arising from conduction-band–acceptor (e,A^0) and donor-acceptor (D^0,A^0) recombination.[2] The luminescence spectra of Gross showed two additional lines at the high-energy tail (C_0 and C_1) and two lines at the low-energy tail (F_0 and F_1) of the B band with a half-width of about 1 meV at 4.2 K. These lines C_0 and F_0 were interpreted to be caused by the recombination of excitons bound to copper centers. Piezospectroscopic and reaction-kinetic studies led to the assumption that the copper centers are anisotropic and have trigonal (C_0 line) and orthorhombic symmetry (F_0 line). A comparison of the luminescence and absorption spectra showed that the C_1 and F_1 lines are electronic transitions accompanied by the simultaneous excitation of a vibrational quantum.

In this paper, we present the results of a systematic study of the luminescence of the copper-induced bound-exciton lines and of the multivibrational-mode emission processes. The investigations were performed with an epitaxial material of much lower impurity content than that used in the earlier mentioned work. The improved technique leads especially to a reduction in the half-widths of the lines by an order of magnitude. The luminescence was measured as a function of (a) the excitation intensity, (b) the sample temperature, and (c) an external magnetic field. The variation of these different parameters leads to an identification of the binding complex centers and to new results on the spectral positions of the lines, the binding energies of the excitons to the complex copper centers, the dissociation processes of the bound excitons arising by an increase of the temperature, and to the electronic structure of the binding center and the bound exciton.

II. EXPERIMENTAL

The samples were mounted in an immersion Dewar for most of the photoluminescence measurements and excited by an Ar^+ laser (514 nm) at normal incidence. Variation of the excitation intensity was achieved by a set of calibrated neutral density filters. The detecting system consisted of a $\frac{3}{4}$-m Spex grating monochromator and a photomultiplier (RCA C31000E) cooled by dry nitrogen gas. We used a photon-counting technique, with a storage of spectra which is similar to the multiscaling setup, published recently by Bachrach.[3] A multichannel analyzer system (Nuclear Data 4410) for data acquisition was used. It easily provides data manipulation such as background subtraction and integration operations in a given spectral range. Typical dark-count rates were less than 25 pulses/sec.

The temperature-dependent data were measured

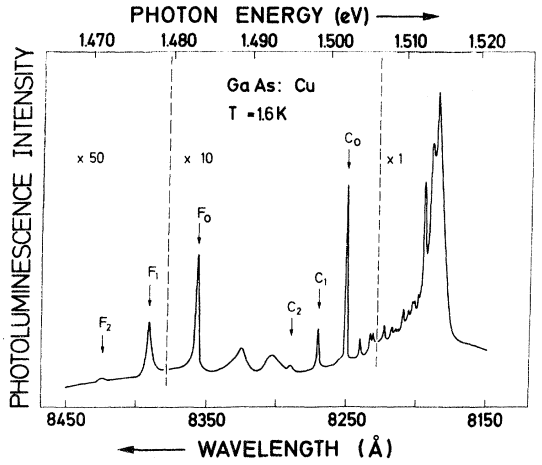

FIG. 1. Photoluminescence spectrum of a copper-doped GaAs crystal diffused for 7 min at 700 °C. In the magnified parts of the spectrum the background has been subtracted. $C_{0,1,2}$ and $F_{0,1,2}$ are recombination lines of excitons bound at two different complex copper acceptors and their resonant phonon replicas.

with a vaporization Dewar at very low excitation intensities to avoid any heating effects. The temperature was measured with a carbon resistor in the range 1.5–30 K and with a Pt resistor from 15 K to higher temperatures. For the magnetic-field-dependent measurements the samples were mounted in a split-coil NbTi superconducting magnet (maximum magnetic flux density of 5.73 T) in a Voigt configuration (field perpendicular to the direction of the emitted radiation).

High-purity GaAs crystals were grown by liquid-phase epitaxy with electrical properties comparable to those of undoped crystals investigated earlier.[4,5] We evaporated a thin layer of about 100-Å copper (99.999% purity) at a pressure of 10^{-6} Torr. The diffusion of the metal was performed in quartz ampoules for a few minutes at about 700 °C. Residual copper was removed from the epitaxial layers by etching in a KCN solution. After the diffusion process the samples showed p-type conductivity.

III. RESULTS

Figure 1 shows the luminescence spectrum of a copper-doped GaAs crystal. The spectrum is dominated by the near-gap radiation, which is typical for high-purity GaAs.[4–8] In addition, the spectrum reveals the copper-induced C_0 and F_0 lines. These lines are, in our case, well separated from the weak transitions (e,A^0) at 1.493 eV and (D^0,A^0) at 1.489 eV and their half-width is about 0.1 meV. The spectral positions of these lines and the associated replicas are listed in Table I. The absolute intensities of the C and F lines are very different in different crystals depending on diffusion and etching conditions. However, the ratios of the intensities of the C_0, C_1, C_2, and F_0, F_1, F_2 lines and their spectral positions remain constant.

Figure 2 shows the integrated intensities of the C_0 line [curve(a)] and the F_0 line [curve(b)] as functions of excitation intensity in a double-logarithmic plot. The starting excitation intensity I_0 corresponds to a power density of about 10 W cm^{-2} of the 514-nm Ar-laser line. The oscillator strengths of the C and F lines are shown to be linear functions of the excitation intensity in the investigated range. The spectral positions of the lines are independent of the excitation intensity.

Figure 3 is a plot of the integrated intensities

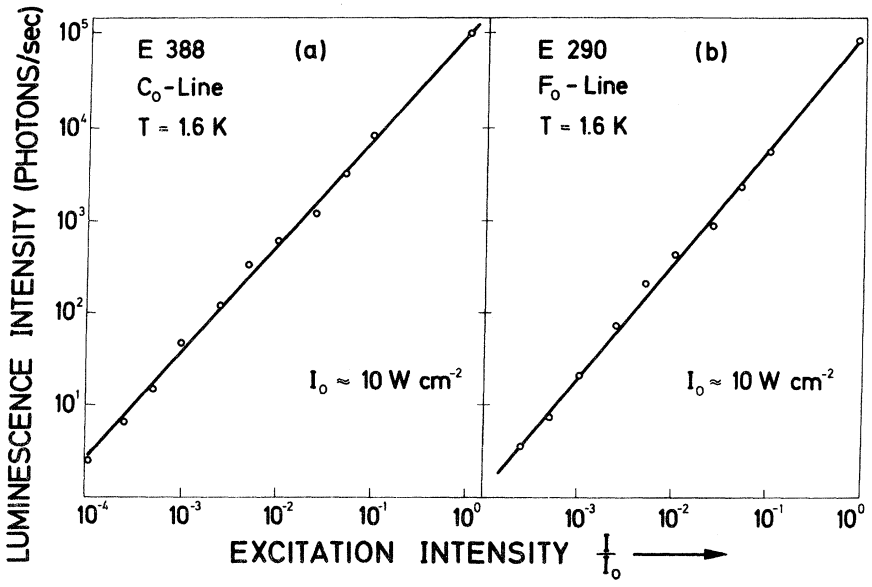

FIG. 2. Integrated luminescence intensity of (a) C_0 line and (b) F_0 line as a function of excitation intensity. The sample temperature is 1.6 K.

TABLE I. Spectral positions of the copper-induced bound-exciton lines in GaAs. The converting factor from wavelength to energy is 1.23952 eV/μm at 8200 Å and 20 °C.

	C_0	C_1	C_2	F_0	F_1	F_2
λ (Å)	8249.3	8269.0	8288.9	8357.1	8391.3	8425.7
$h\nu$ (eV)	1.5026	1.4990	1.4954	1.4832	1.4771	1.4711

of the C_0 line [curve(a)] and the F_0 line [curve(b)] as a function of reciprocal temperature on a semilogarithmic scale. The intensity of the recombination radiation saturates below 8 K. By increasing the temperature, the intensity decreases, showing in different temperature ranges two different activation energies. The lines also show a shift towards lower energies. This shift could be followed up to 55 K in the case of the F_0 line, where the line vanishes.[9] Besides the experimental points, the figure includes theoretical fits discussed later, using one and two different dissociation processes with different activation energies kT_1 and kT_2, which are listed in the inset of Fig. 3.

In Figure 4, the C_0 and F_0 lines are shown at zero magnetic field and with the maximum available field of 5.73 T. The lines shift in the field towards higher energies and split into four compo-

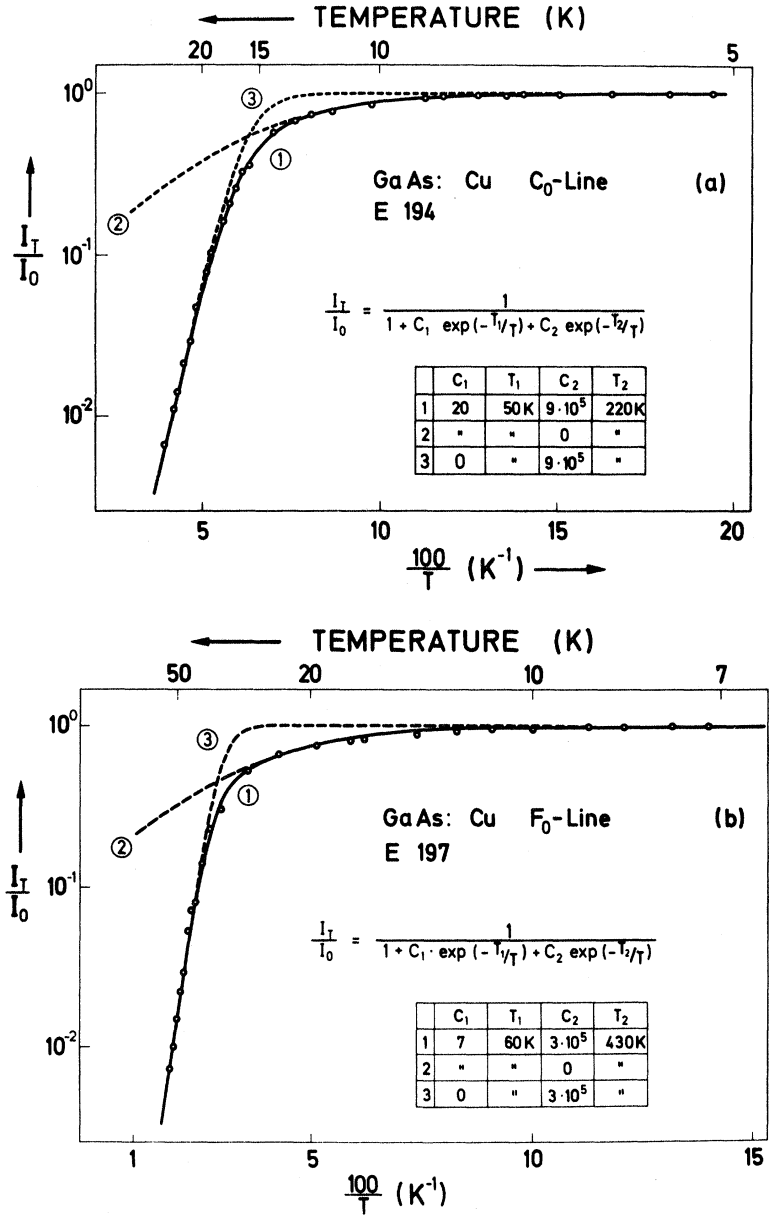

FIG. 3. Temperature dependence of (a) C_0 line and (b) F_0 line. The open circles are experimental points. The dashed and full lines are theoretical fits according to the formula in the figure assuming one or two activation energies, respectively.

nents. In the case of the F_0 line, the magnitude of the splitting, the number of components, and the intensity ratio of different components was found to be independent from polarization of the emitted radiation. No angular dependence on the direction of the magnetic field could be observed. However, the magnetic splitting of the C_0 line contains a small anisotropy. The separation of the outer components is about 0.3 Å smaller for the polarization of the luminescence light $\vec{E} \parallel \vec{H}$ than for

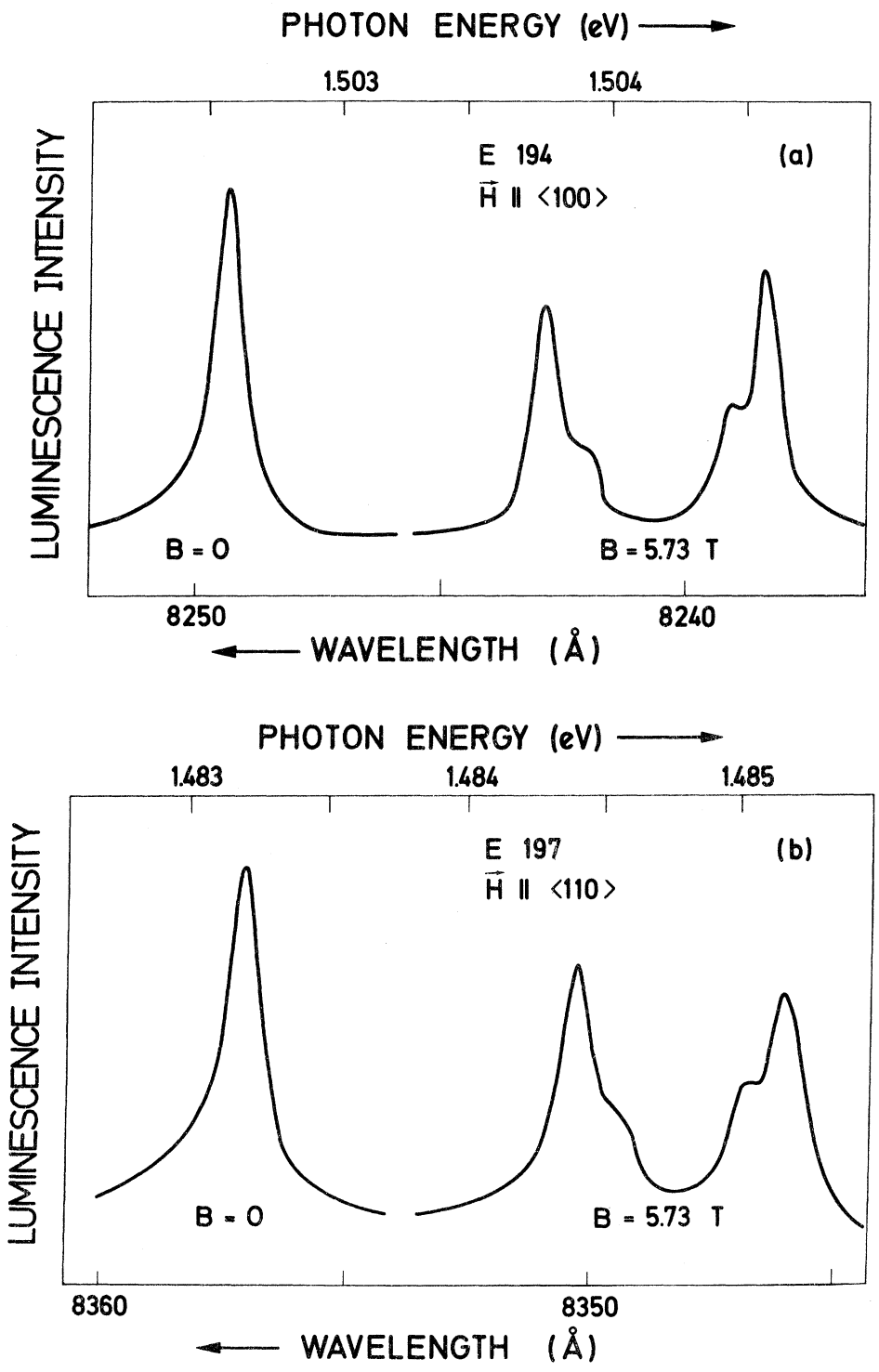

FIG. 4. Luminescence spectra of (a) C_0 line and (b) F_0 line at zero field and at maximum available magnetic field, taken at 2 K and with $\vec{E} \parallel \vec{H}$ and $\vec{E} \perp \vec{H}$. The lines are obviously not polarized. Note the asymmetrical line shape at zero field (Ref. 12).

$\vec{E} \perp \vec{H}$ for $\vec{H} \parallel \langle 110 \rangle$ and $\langle 111 \rangle$ at maximum field strength.[10] The vibrational-mode replicas split in the same way as the zero-phonon lines.

IV. DISCUSSION

A. Spectral Positions and Binding Centers

Bound excitons in GaAs are known to exhibit narrow lines with a half-width less than kT at low temperatures.[4,11] The half-widths of the C and F lines as observed by Gross *et al.*[1] were about five times larger than kT. Therefore, their assignment of the lines was based only on the resonant appearance of these lines in both luminescence and absorption spectra and the dependence on copper doping. As is shown in Figs. 1 and 4, the recombination lines have half-widths of about 0.1 meV at 1.6 K which are only slightly broadened even at 10 K. In addition, an asymmetrical line shape was observed which extends to lower photon energies.[12] It should be remarked that the spectral positions of all our lines deviate about 0.5 meV from the earlier published positions.[1] The reason for this is not clear.

Taking the values of Table I and the free-exciton energy gap $E_{\text{gap}}^{\text{ex}} = 1.5151$ eV,[5] one gets for the binding energies of the excitons to the impurities the values of $E_B^C = 12.6$ meV and $E_B^F = 31.9$ meV. The binding of these excitons is much tighter than that of the exciton bound to the effective-mass acceptor.[4] From the binding energy E_B it is possible to estimate roughly the depth of the binding center E_A according to Haynes's rule.[13] It was shown[11] that in the case of GaAs:Sn, the ratio E_B/E_A is only half that of the value predicted by Haynes. Taking these two values as limits for an estimate of the binding energies E_A^C and E_A^F of the corresponding impurities, one arrives at $0.13 < E_A^C < 0.25$ eV and $0.32 < E_A^F < 0.64$ eV.

It is well known that copper introduces nonhydrogenic acceptor states into GaAs.[14,15] Evidence has been found that the 0.156-eV acceptor state belongs to a complex with trigonal symmetry.[16] Stress experiments[1] showed that the C line is caused by an exciton bound to a center of such a symmetry. This is confirmed by the results of our Zeeman investigations as shown in Sec. IV D. According to the above estimate, we therefore conclude that the impurity responsible for the C line is the trigonal copper center with $E_A^C = 0.156$ eV.

Still deeper copper-induced acceptor levels (about 0.45 eV above the valence band) have been found by several investigators.[17,18] The symmetry of these centers has not been investigated so far. We state, however, that our estimate of the binding energy E_A^F would agree with this 0.45-eV value.

Variation of excitation intensity has been successfully used to identify different kinds of recombination centers.[5,11,19] It also exhibits information about the capture processes which lead to the formation of bound excitons. In our case, neutral acceptors exist in thermal equilibrium. Figure 2 shows that the luminescence intensity J_l varies linearly with the excitation intensity J_{ex}. However, $J_l \propto [X]\,[A^0]$, where $[X]$ is the concentration of electron-hole pairs and $[A^0]$ is the concentration of neutral acceptors. The observation of $J_l \propto J_{ex}$ leads consequently to a proportionality $[X] \propto J_{ex}$, if $[A^0]$ is independent of J_{ex}. Thus, photocreated electron-hole pairs are captured directly or after the formation of free excitons by neutral acceptors. A nonlinear dependence should be expected if the excited electrons and holes relax independently.

The C and F emission lines did not shift by varying the excitation intensity. A shift was observed in the case of the free exciton,[5,20] and attributed to screening effects by free charge carriers. It was predicted[20] that such effects should not be observed in the case of tight-bound excitons at the same free-carrier density as in the case of the free exciton because of the much lower radii of the orbits of the tight-bound electrons and holes in the nonhydrogenic binding potential of a deep center. This is proved by our experiments.

B. Phonon Replicas

The spectrum depicted in Fig. 1 shows new emission lines C_2 and F_2 which have not been observed in the earlier work.[1] They are attributed to the excitation of two vibrational quanta for transitions in the C and F centers, respectively, because (i) the energy differences

$$h\nu(C_0) - h\nu(C_1) = h\nu(C_1) - h\nu(C_2) = 3.6 \text{ meV},$$

and

$$h\nu(F_0) - h\nu(F_1) = h\nu(F_1) - h\nu(F_2) = 6.1 \text{ meV}$$

and (ii) the intensities follow a Poisson distribution[21]

$$W_n \sim \bar{N}^n/n! \,, \tag{1}$$

where n is the number of the replica and $\bar{N}$ is the average phonon-coupling parameter, which is determined experimentally from the ratio I_1/I_0 of the intensity of the first replica I_1 and the intensity of the zero-phonon line I_0. Formula (1) gives $W_2(C) = 0.031$ and $W_2(F) = 0.0038$ with $\bar{N}(C) = 0.25$ and $\bar{N}(F) = 0.085$, which is in excellent agreement with the experimental values $I_2(C)/I_0(C) = 0.03$ and $I_2(F)/I_0(F) = 0.004$.

While the energy and the average phonon-coupling parameter of the vibrational modes in the C center are identical with the values found in bulk material, the energy of the vibrational quantum in the F centers is 1 meV larger and the coupling parameter is a factor of 2 smaller in our epitaxial material.

C. Thermal Activation of the Excitons

In a recent paper, Bimberg *et al.*[4] have proposed a detailed study of the thermal dissociation of excitons bound to neutral acceptors in GaAs. A formula has been derived applying Boltzmann statistics assuming two dissociation energies to describe these processes. The temperature dependence of the C and F lines (Fig. 3) includes all characteristic features observed in Ref. 4. At low temperatures ($T < 8$ K), the integrated intensity of the recombination radiation is constant (I_0). At higher temperatures, the thermal quenching of the lines is fitted with the assumption of two activation energies kT_1 and kT_2 according to the formula given in Fig. 3. The dashed lines fit either the low (2) or the high (3) temperature quenching with only one dissociation energy, which are listed in the inset of Fig. 3. Assuming that the C_0 and F_0 lines originate from the recombination of excitons bound to neutral acceptors, the thermal dissociation is interpreted as follows: The first intensity drop is caused by the dissociation of a single particle from the bound-exciton complex with an activation energy of 4.3 meV (5.2 meV) for the C_0 (F_0) line. This energy does not increase linearly with the binding energy E_B of the exciton in accordance with the observation in Ref. 4. A second dissociation process begins to dominate at about 15K (30 K) for the C_0 (F_0) line with an activation energy $kT_2 = 19$ meV (37 meV). The energies kT_2 are in close agreement with the values of $E_B + E_x$ giving a further confirmation to the model proposed in Ref. 4: The activation process dominating at higher temperatures is caused by the liberation of free-electron-hole pairs. We notice that the low-temperature quenching of the bound-exciton luminescence due to dissociation of free excitons would result in an activation energy which is equal for all bound excitons. A comparison of the energies kT_1 of Ref. 4 and of this work excludes this model, because a monotonic increase of kT_1 with the depth of the binding center is found. It should be mentioned that our interpretation leads to the consequence that the trapping time of the exciton is shorter than the thermal lifetime.

D. Zeeman Effect

Acceptor–ground-state wave functions in GaAs form a basis for the irreducible representation Γ_8 of the double group T_d.[22] Possible states of an exciton bound to a neutral acceptor are characterized by the representations Γ_6, Γ_7, and $\Gamma_7 + \Gamma_8$ belonging to the total angular momenta $J = \frac{1}{2}$, $\frac{3}{2}$, and $\frac{5}{2}$ resulting from j-j coupling of two identical $j_h = \frac{3}{2}$ holes and one $j_e = \frac{1}{2}$ electron excluding the states which are forbidden by the Pauli principle.[11,22,23] The term scheme of exciton states bound to neutral acceptors in GaAs has been discussed in detail, but still alternative interpretations are possible.[11,23]

Figure 5 shows the term scheme of the two complex (A^0, X) centers and the corresponding acceptors, including crystal field splitting and some of the dipole-allowed transitions in a crystal field with symmetry C_{3v} and C_{2v}. Furthermore, Fig. 5 shows the Zeeman splitting of the acceptor ground states and of the $J = \frac{1}{2}$ exciton states. Reducing the symmetry of GaAs to the acceptor-site symmetry C_{3v},[1,16] the fourfold degenerate acceptor state splits into two twofold degenerate states Γ_4 and $\Gamma_5 + \Gamma_6$. The Γ_5 and Γ_6 of C_{3v} are degenerate to retain the twofold spin degeneracy as is required by Kramer's theorem.[24] It is known[25,26] that under stress the binding energy of a hole in the $|m_j| = \frac{1}{2}$ state becomes larger relative to the hole in the $|m_j| = \frac{3}{2}$ state. In

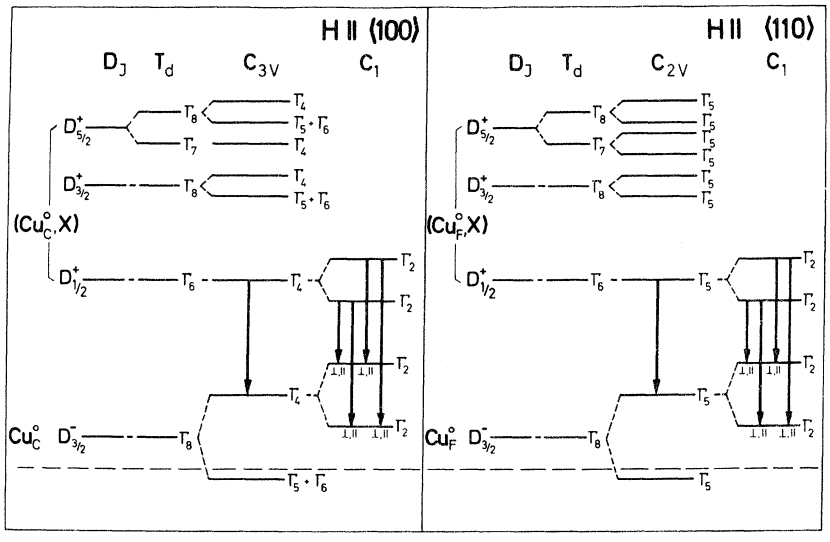

FIG. 5. Schematic energy levels for an exciton trapped at α neutral acceptor with point symmetry C_{3v} and C_{2v}. An external magnetic field splits the levels as shown. The arrows denote dipole-allowed transitions with the electric vector of the emitted radiation $\vec{E} \perp \vec{H}$ and $\vec{E} \parallel \vec{H}$. The broken line indicates the valence-band continuum.

a crystal field of symmetry C_{2v}, the acceptor ground state splits into two Γ_5 sublevels.

The magnitude of the splitting of the acceptor ground state caused by the crystal field of the anisotropic centers is not known. Since we observe only one zero-phonon line belonging to the point group C_{3v} or C_{2v}, two cases are possible: (a) The magnitude of the crystal field splitting is smaller than the half-width of the exciton lines or (b) the $|m_j| = \frac{3}{2}$ acceptor state is split off into the valence-band continuum. Assumption (a) implies that the local symmetry of the acceptor wave function remains cubic and can therefore be described by Γ_8 of T_d. However, we expect case (b) because of the following arguments:

(i) The holes are tightly bound by the copper acceptors which results in a strong localization of the wave functions in real space.

(ii) The influence of the crystal field has been observed even in the excited states of the acceptor,[16] which have larger radii of the wave functions than the ground state treated here.

(iii) An anisotropic splitting of the bound exciton lines has been observed under uniaxial stress which does not reflect the properties of the band structure of GaAs.[1]

(iv) For $\vec{H} \parallel \langle 100 \rangle$ only four unpolarized Zeeman lines could be detected. A $\Gamma_6 \rightarrow \Gamma_8$ transition, however, results in six different polarized lines.[11,23] Thus, we conclude that the $|m_j| = \frac{1}{2}$ and $|m_j| = \frac{3}{2}$ acceptor states are completely decoupled. The lower-energy component disappears in the continuum of the valence band.

In the case of the center with C_{3v} symmetry it is concluded that the zero-phonon line is consequently described by a $\Gamma_4 \rightarrow \Gamma_4$ transition of the double group. For $\vec{H} \parallel \langle 111 \rangle$ crystal axis, the splitting of the C_0 line is polarized. The separation of the outer components is 0.3 Å smaller for $\vec{E} \parallel \vec{H}$ than for $\vec{E} \perp \vec{H}$ at maximum field strength. Since the axial centers are statistically distributed along the four equivalent $\langle 111 \rangle$ axes, the anisotropy is explained by a different splitting of the centers oriented parallel to the magnetic field and of the centers which form an angle of $\cos\alpha = \frac{1}{3}$ with the magnetic field. We observe a lifting of the orientation degeneracy by the magnetic field. The same arguments hold for the observed anisotropy in the splitting of the C_0 line with $\vec{H} \parallel \langle 110 \rangle$. The fact that for $\vec{H} \parallel \langle 100 \rangle$ all lines are unpolarized (Fig. 5) is another proof for the local symmetry to be C_{3v}. In this case all centers include an angle of $\cos\alpha = \frac{1}{3}$ with the magnetic field and the orientation degeneracy is not lifted.

In a field with symmetry C_{2v} the acceptor ground state splits into two Γ_5 levels (Fig. 5). As in the case of the C_{3v} center, one of the Γ_5 states is split off into the valence band. The strong symmetry reduction causes a quenching of the hole angular momentum to $j = \frac{1}{2}$,[22] and thus the acceptor does not reflect the valence-band structure. This means that the anisotropy in the g value is reduced and isotropic Zeeman spectra result. Since C_{2v} complexes are statistically distributed along six equivalent orientations, Fig. 5 shows only the Zeeman splitting of four equivalent centers having an angle $\cos\alpha = \frac{1}{2}$ between an axis of C_{2v} and the direction of the magnetic field. In addition the direction of the magnetic field is perpendicular to the C_2 axis of one kind of centers and parallel to another kind.

V. SUMMARY

Extensive studies of the C and F lines in the photoluminescence spectrum of high-purity epitaxial GaAs:Cu have been made, including variation of excitation intensity and temperature dependence and their behavior in an external magnetic field. The results prove that both the C_0 and F_0 lines originate from the recombination of excitons bound to neutral acceptors. The binding center in the case of the C line is shown to be the 0.156-eV copper-complex acceptor of C_{3v} symmetry, and in the case of the F line it is assumed to be a complex acceptor of C_{2v} symmetry and with a depth of about 0.45 eV. The bound excitons are formed by photocreated-coupled electron-hole pairs which are trapped either directly or after the relaxation to free excitons by neutral acceptors. The dissociation process of the bound excitons at raised temperatures consists of a two-step mechanism: First a single particle bound to the exciton complex is activated and at higher temperatures the quenching of the luminescence is caused by the liberation of free-electron-hole pairs. Evidence is drawn from a group-theoretical analysis of the Zeeman effect that the binding acceptors are neutral copper complexes with trigonal (in the case of the C line) and orthorhombic symmetry (in the case of the F line). This shows that the acceptor ground states are split by the crystal field interaction. The $|m_j| = \frac{3}{2}$ state is degenerate with the valence-band continuum. The purely electronic transitions are accompanied by replicas due to the simultaneous excitation of vibrational quanta. The intensities of multivibrational-mode emissions are described by a Poisson distribution law, and the equivalent parameters are derived.

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*Permanent address: Hochfeld-Magnetlabor Grenoble, B. P. 166 Centre de Tri, F 38 Grenoble, France.

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