RAPID COMMUNICATIONS

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# Electronic properties of an electron-attractive complex neutral defect in GaAs

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This Rapid Communication reports the first detailed optical study of a complex neutral defect in GaAs (probably $Cu_{Ga}$-$As_{Ga}$), binding an exciton at 1.429 eV. Zeeman data at 10 T for the bound exciton are analyzed in detail, considering both the electron-hole exchange interaction and the local strain field. The defect has an electron-attractive local potential and a tensional local strain field. The $g$ value for the deeply bound electron $g_e=0.9$ is strongly modified from the value $g_e=-0.46$ for a shallow donor, while the bound hole remains effective-mass-like.

The properties of neutral "isoelectronic"[1] defects in GaAs have not been discussed previously, since such defects are usually not able to localize excitons in the band gap in this material.[2] This is in sharp contrast to most other III-V materials, where excitons bound to neutral defects have been observed and studied in detail.[3] The study of residual complex defects in GaAs is of considerable technological importance though. In this Rapid Communication we present the first detailed optical study of the electronic structure of a complex neutral defect in GaAs, which gives rise to a bound exciton (BE) at 1.429 eV at 2 K. From the magnetic properties of this BE it is concluded that the defect has $C_{1h}$ symmetry, and a dominantly electron-attractive local potential.

The defect studied in this work is created by long-term diffusion (20 h at $\sim 500\,^{\circ}\mathrm{C}$ in evacuated ampoules) of Cu into bulk horizontal Bridgman-grown GaAs, Zn doped during growth to a level of $\approx 1.3\times10^{16}$ $\mathrm{cm}^{-3}$. After the diffusion the ampoules were rapidly quenched in water. More details of the preparation procedure are given elsewhere.[4,5] The Cu-doping procedure does not drastically change the electrically active Zn doping, presumably because of a low concentration of the produced complex defects. The 1.429-eV defect described below has only been observed when Zn-doped $p$-type GaAs was used as starting material, and only after a rather long-term Cu diffusion. Consequently, both Zn and Cu are active in the creation of the defect.

Optical absorption associated with the 1.429-eV BE was too weak to be detected in the transmission spectra of a 3-mm-thick sample, and therefore the experimental data are restricted to emission spectra [photoluminescence (PL)]. Magneto-optical data for fields up to 10 T were obtained in the Voigt configuration with a superconducting magnet at the Max Planck Hochfeld Magnetlabor in Grenoble.

A PL spectrum of the 1.429-eV emission at 2 K is shown in Fig. 1. As is obvious from the inset in Fig. 1 three electronic zero-field lines are resolved in PL at somewhat elevated temperatures at 1.4285 eV ($L3$), 1.4299 eV ($L2$), and 1.4308 eV ($L1$). This manifold of PL electronic lines is induced by the electron-hole ($e$-$h$) exchange interaction and the local strain field at the defect (see below). The temperature dependence of the relative PL intensity for these lines is consistent with thermalization in the excited (BE) state only, as expected for a neutral defect with no electronic particle bound in the ground state.

The electronic structure of the 1.429-eV defect is revealed from a careful analysis of Zeeman data. In Fig. 2(a) we show the development of the electronic lines with magnetic field along the [110] direction up to 10 T. Obviously, the $L3$ and $L2$ lines are each composed of two unresolved lines at zero field, where the weak lines only appear as shoulders. Another observation is the negligible quadratic Zeeman shift of the center of gravity of these lines, at least an order of magnitude smaller than for shallow donorlike electrons in GaAs.[6,7]

The full angular dependence of the Zeeman splitting of the electronic lines was recorded, and is shown in Fig. 2(b) for a rotation in the $(1\bar{1}0)$ plane. A theoretical fit is also included in Fig. 2(b) according to the following perturbation Hamiltonian for a BE consisting of one electron and one hole, both bound in a localized neutral potential of low symmetry,[8,9]

$$H'=H_{\mathrm{ex}}+H_{\mathrm{LCF}}+H_{\mathrm{LZ}}\ ,$$

where

$$H_{\mathrm{ex}}=-a\mathbf{S}_h\cdot\mathbf{S}_e-b(S_{hx}^3S_{ex}+S_{hy}^3S_{ey}+S_{hz}^3S_{ez})$$

denotes the $e$-$h$ exchange interaction.

$$H_{\mathrm{LCF}}=-D[S_{h\zeta}^2-\tfrac{1}{3}S_h(S_h+1)]$$

is the axial strain perturbation on the hole states from the local crystal field (LCF) at the defect,[8] while

$$H_{\mathrm{LZ}}=\mu_B[g_e\mathbf{S}_e\cdot\mathbf{H}+K\mathbf{S}_h\cdot\mathbf{H}+L(S_{hx}^3H_x+S_{hy}^3H_y+S_{hz}^3H_z)]$$

is the linear Zeeman (LZ) term.[9] $\mathbf{S}_e$ is the electron spin, $\mathbf{S}_h$ the effective hole spin (including angular momentum), and $\mu_B$ the Bohr magneton. $x$, $y$, and $z$ refer to the usual cubic axes of the zinc-blende lattice, while $\zeta$ refers to the defect axis. The possible influence of localization on the symmetry of the bound electron state as well as quadratic Zeeman effects are neglected. The major effect of both the $e$-$h$ exchange and the low-symmetry crystal field are included in this perturbation Hamiltonian $H'$.

In the theoretical simulation of experimental data [Figs. 2(a) and 2(b)] the above three contributions to $H'$ are treated on the same level, and are diagonalized simultaneously. The best fit to the data partly shown in Fig. 2 is

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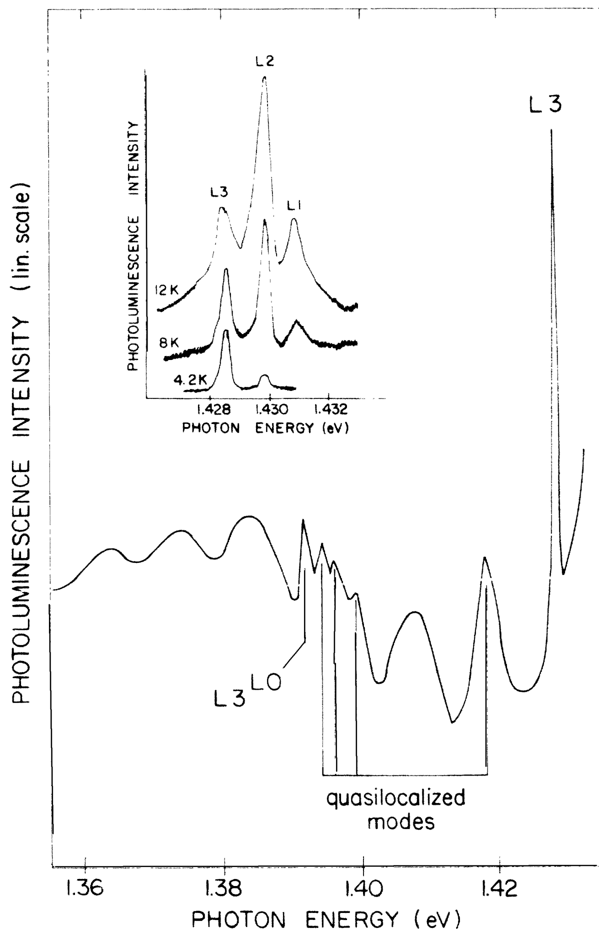


FIG. 1. Photoluminescence (PL) spectrum at 2 K for a Zn-doped horizontal Bridgman-grown (HB) bulk GaAs sample ($[Zn] \approx 1.3 \times 10^{16}$ $cm^{-3}$), Cu diffused at 500 °C for 19 h, and rapidly quenched in water. Only the lowest-energy energy electronic line $L3$ at 1.4285 eV is seen at 2 K, together with a phonon wing towards lower energies. In the inset PL spectra are also shown for higher temperatures, where three electronic lines can be resolved.

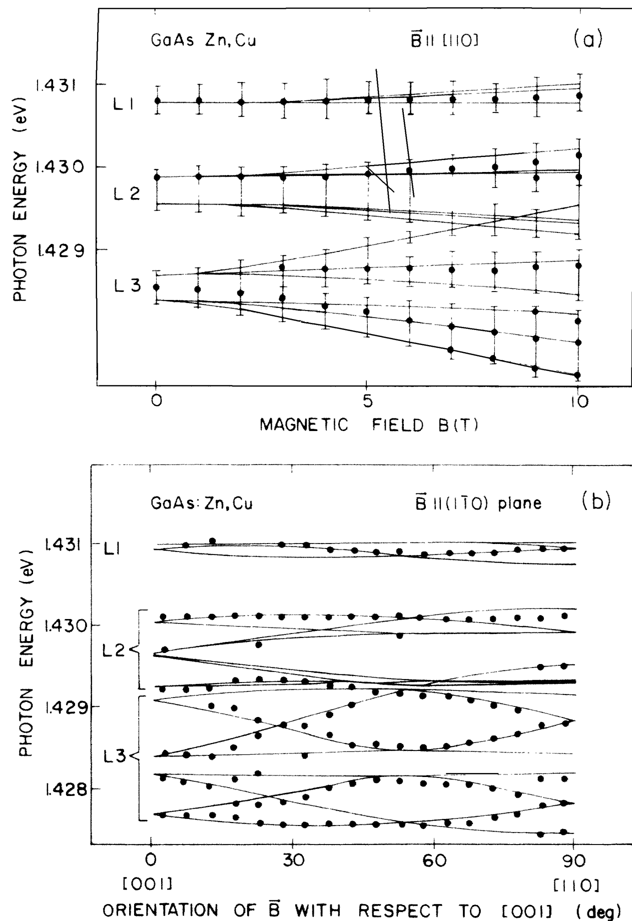


FIG. 2. Fit of Zeeman data for the 1.429-eV PL emission, taken in the Voigt configuration at 5 K, to the Hamiltonian described in the text. In (a) a fan diagram is shown for fields up to 10 T, for **B**‖[110]. No significant quadratic Zeeman shift is seen, and $L2$ and $L3$ are split even at zero field. In (b) the angular dependence of the lines at 10 T is shown, together with the fit to the model Hamiltonian. Lines with no experimental points are seen as weak shoulders experimentally, and they are also expected to be weak from theory (Ref. 4).

obtained with the following parameters: $a = 1.75 \pm 0.05$ meV, $b = -0.30 \pm 0.05$ meV, $D = 1.15 \pm 0.05$ meV, $g_e = +0.90 \pm 0.02$, $K = 0.80 \pm 0.02$, and $L = 0.04 \pm 0.02$. Further, the symmetry of the defect is determined as being $C_{1h}$ from Fig. 2(b), i.e., the defect is linear with a [110] axis.

As a consequence of the above theoretical fit [full lines in Figs. 2(a) and 2(b)] the zero-field lines $L1$–$L3$ in Fig. 1 are identified as deriving from the "$J = 2$" quintuplet of a BE, as expected for the case of a large $e$-$h$ exchange interaction and as found previously for electron-attractive neutral complexes in GaP, e.g., in the cases of GaP:Zn,O (Refs. 10 and 11) and GaP:Li,Li,O.[12] In the present case with low $C_{1h}$ symmetry, the entire degeneracy of the quintuplet is already lifted at zero magnetic field. The lowest line $L3$ is identified as the $|\overline{2, \pm 2}\rangle$ pair in the $|J,m_J\rangle$ notation,[13] consistent with a tensional local strain field ($D > 0$). Here the notation $|\overline{J,m_J}\rangle$ means that we no longer have a pure $|J,m_J\rangle$ state, but a mixed one in this low symmetry.[4] $L3$ is split even at zero magnetic field due to the anisotropic exchange interaction [parameter $b$ above, see Fig. 2(a)]. A similar splitting occurs for the $L2$ line, identified as the $|\overline{2, \pm 1}\rangle$ pair, while the high-energy singlet line $L1$ is assigned to the $|\overline{2,0}\rangle$ state. The $J = 1$ triplet is expected to be well above the $J = 2$ lines, and not seen in low-temperature PL spectra due to thermalization.

The electronic structure of the 1.429-eV BE is summarized in Fig. 3. The dominant perturbation is the $e$-$h$ exchange interaction (as evident from the parameters evaluated above), which leaves the $J = 2$ quintuplet at lowest energy. The effect of the local [110]-oriented axial tensional strain field is comparable, though, and gives rise to the five zero-field lines. The value $g_e = +0.9$ is drastically different from $g_e = -0.46$ observed for a shallow donorlike electron in GaAs.[6] This proves the strong localization of the bound electron; a limiting value of $g_e = +2$ is expected when the effect of the conduction-band structure is lost because of strong localization, as observed, e.g., for $O_{Te}$ in ZnTe.[14] The absence of a quadratic Zeeman shift is further evidence for strong localization of the bound electron.

The $K$ and $L$ values for the bound-hole state are rather close to the values found for previously studied acceptor hole states in GaAs, such as the Sn acceptor.[6] The ob-

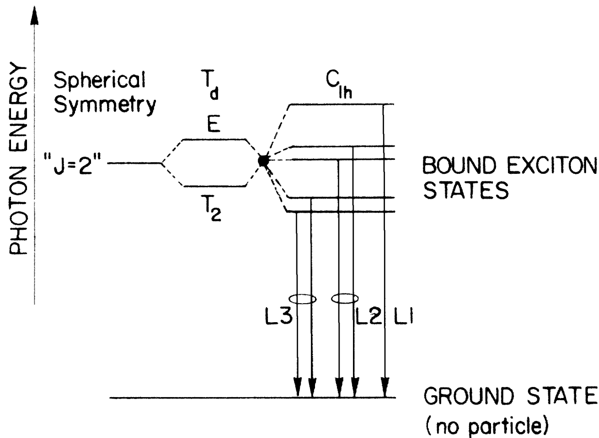


FIG. 3. Perturbation scheme at zero magnetic field for the experimentally observed lowest $J=2$ quintuplet of the bound exciton, showing the lifting of electronic degeneracy by the $C_{1h}$ crystal field. The experimentally observed PL transitions $L1$-$L3$ are indicated.

served anisotropy of the Zeeman-split components is fully derived from the bound-hole,[8] since the electron $g$ factor is isotropic. This indicates an effective-mass-like bound hole state, but with a moderate amount of localization to maintain the observed value of the $e$-$h$ exchange splitting (factors $a$ and $b$ above).

On the other hand, a dominantly hole-attractive local potential, would be expected to have strong effects on the $g$ factors of the bound hole, as has recently been observed for hole-attractive Cu-related complex defects in GaP.[15-19] A completely quenched hole angular momentum is observed in this case for low-symmetry defects, with an approximately isotropic hole $g$ value $g_h = +2$.[15-19] The lowest BE state would behave as an isotropic triplet in this case.[15-19]

The proposed identity of the defect responsible for the 1.429-eV BE spectrum has to be consistent with the [110] axial direction, a tensional local strain field, and a local strongly electron-attractive neutral potential. An activation energy of about 1.65 eV for the creation of this defect,[5] together with the involvement of both Cu and Zn, suggest a slow defect reaction during the long-term Cu diffusion, where $Zn_{Ga}$ is replaced by $Cu_{Ga}$, i.e., $Zn_{Ga}+Cu_i \rightarrow Cu_{Ga}+Zn_i$. A $Cu_{Ga}Zn_i$ pair would presumably create a compressive local strain field. In addition, a [110] axial symmetry for a $Cu_{Ga}Zn_i$ pair is most unexpected. The $Zn_i$ may migrate away after the Cu-Zn exchange has been completed on a Ge site, however.

The [110] symmetry of the neutral complex is suggestive of a Ga-site pair, i.e., a pair of $Cu_{Ga}$-$D_{Ga}$, where $D_{Ga}$ is a deep Ga-site double donor compensating the $Cu_{Ga}$ double acceptor. The only deep intrinsic Ga-site double donor known so far is the $As_{Ga}$ antisite defect,[20,21] which has deep states at midgap in GaAs. Such an $As_{Ga}$ donor could be produced in this case via local defect reactions involving both Ga- and As-site vacanices $V_{Ga}$ and $V_{As}$.[22] It has recently been shown that Zn-doping induces a remarkable enhancement of vacancy diffusion in GaAs,[23] so that transport of $V_{Ga}$ and $V_{As}$ to the sites of formation of the 1.429-eV defect is facilitated (during 20 h at $\approx 500\,^{\circ}\mathrm{C}$). Clearly, the strongly electron-attractive $As_{Ga}$ donor potential would dominate the moderately deep $Cu_{Ga}$ acceptor [0.15 eV (Ref. 24)], so that the total $Cu_{Ga}$-$As_{Ga}$ defect potential would be strongly electron attractive, as observed. The observed $g$ value $g_e = +0.9$ for the electron bound to $Cu_{Ga}$-$As_{Ga}$ is consistent with a reduction of the electron-attractive $As_{Ga}$ potential by the adjacent $Cu_{Ga}$, as compared to the isolated $As_{Ga}$ donor, where a $g$ value $g_e = 2.04$ has been reported.[25]

In summary, we have reported the first detailed study of a neutral defect binding an exciton in GaAs. An appropriate perturbation Hamiltonian is employed for the analysis of Zeeman data of this 1.429-eV bound exciton, showing a very good fit to the data. The defect is electron attractive, with an anomalous $g$ value $g_e = +0.9$ for the deeply bound electron, while the hole is effective-mass-like. The established [110] symmetry of the defect suggests a Ga-site pair, probably $Cu_{Ga}$-$As_{Ga}$, as the identity of this complex.

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[1]The notation neutral defect is used here as a synonym of "isoelectronic" defects. Such defects have no electronic particles in the ground state, and a bound electron-hole pair ("bound exciton") as the lowest-energy electronic excitation at low temperature.

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