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Optically detected magnetic resonance of a localized spin-triplet midgap center in GaAs

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A strong optically detected magnetic-resonance (ODMR) spectrum is obtained by the monitoring of a broad luminescence band peaking at 0.82 eV in as-grown Zn-doped GaAs. Our analysis firmly establishes a localized spin-triplet character of the spectrum and trigonal ⟨111⟩-oriented symmetry axis of the corresponding defect. This type of ODMR has only been tentatively identified in GaAs previously.

I. INTRODUCTION

Localized spin triplets are commonly observed for bound-exciton recombination at neutral (isoelectronic) defect complexes and strongly coupled donor-acceptor pairs in most semiconductors, such as GaP,[1,2] Si,[3] SiC,[4] and CdS.[5] Such triplets have often proven particularly suitable for optically detected magnetic-resonance (ODMR) studies.[1,2,4–6]

In GaAs, no isoelectronic complexes with hole affinity have been reported.[7] Since this type of center seems to account for most of the well-understood cases of electronic spin-triplet configuration,[1–3] ODMR investigations on such systems are accordingly absent. It has been argued that the electron in the case of hole-attractive centers is prevented from binding, in view of local strain at the complexes and the large effective mass ratio m_h^*/m_e^* of GaAs.[7]

For deep centers well beyond the simplified effective-mass theory such as the persistent midgap centers in GaAs, some of which give rise to deep photoluminescence (PL) bands,[8–10] there is no *a priori* reason not to expect a localized spin-triplet configuration for the excited two-particle states. However, previous studies of such midgap PL centers have given disappointingly scarce ODMR signals, and neither the $\mathrm{As_{Ga}}$ antisite luminescence[8] nor the 0.84-eV Cr luminescence[11] exhibit spin-triplet character.

In the preceding Rapid Communication, Kennedy and Wilsey reported evidence for a triplet excited state in the ODMR spectrum of a deep center in GaAs:Zn.[12] The interpretation was based on indications of a level crossing and a preliminary analysis of some branches in the angular dependence of the ODMR signal which suggested ODMR-active centers of ⟨110⟩ symmetry. A level crossing in the ⟨111⟩ direction also suggested that trigonal centers might be present.

We have investigated the ODMR spectrum of Zn-doped GaAs and find that the dominant signal originates from a trigonal ⟨111⟩-oriented center and not from a center with ⟨110⟩ symmetry. We present a detailed analysis of this spectrum which firmly establishes the symmetry and the localized spin-triplet character of the center. Evidence for a weaker ⟨110⟩-oriented center is present in our spectra as well, but largely obscured by the strong signal reported here. The ODMR is shown to originate from a deep photoluminescence band, centered around 0.82 eV, inherent in the as-grown material. The results presented in this paper are important, since they represent the first identification and analysis of a localized spin-triplet configuration in GaAs and give clues to the structure of a native midgap center in Zn-doped GaAs.

II. EXPERIMENT

The samples used were commercially available Horizontal Bridgman GaAs crystals obtained from MCP Electronic Materials and Wacker, Zn-doped to room-temperature hole concentration of $1–7\times10^{16}$ cm^{-3}. The signal was present throughout the bulk of the as-grown samples. Annealing of the samples was performed in sealed quartz ampoules at 520 °C. Cu doping was performed by including pellets of 99.9999% pure Cu in the ampoules.

ODMR measurements were made at 2 K in a 35-GHz $\mathrm{TE_{011}}$ cavity[13] using a modified Oxford Instruments SM-4 superconducting magnet. The measurements were made in the Faraday configuration $\mathbf{k}\parallel\mathbf{B}$. The photoluminescence was excited by the 5145-Å $\mathrm{Ar^+}$-ion laser line (<50 mW) or a Xe arc lamp. The PL signal was detected with a cooled North Coast Ge detector and dispersed with a $\frac{1}{4}$-m Jarrell Ash Mark X grating monochromator, blazed at 1 μm.

III. EXPERIMENTAL RESULTS

Figure 1 (curve *a*) shows the low-temperature spectrum of a typical GaAs:Zn sample with room temperature hole concentration $p_{300}=1.3\times10^{16}$ cm^{-3}. This sample was annealed in vacuum for 15 h at 520 °C, which enhanced the infrared (ir) luminescence relative to the band-edge PL band. In addition to the broad 0.82-eV ir luminescence (the PL is uncorrected for the spectral response of the detection system) a broad PL band is present, peaking at about 1.1 eV. This band is of unknown origin and was not present before the heat treatment. The Zn-doped samples always showed some degree of Cu contaminaton as evidenced by the 1.36 eV Cu-acceptor PL band.[14] The broad band around 1.47 eV is related to $\mathrm{Zn_{Ga}}$ acceptors (donor-acceptor pair emission).

The ODMR signal in Fig. 2 was measured by monitoring the total unpolarized ir luminescence for $\mathbf{B}\parallel[111]$. It is characterized by strong positive resonances (up to 5% increase of intensity in phase with microwave amplitude modulation). The resonances are very broad, of the order of 60 mT. The strong angular variation of the ODMR signal is also shown in Fig. 2 for the magnetic field in the $(1\bar{1}0)$ plane. All of the strong lines in the spectrum are accounted for by the computer fit included in the figure. Other weaker features in the spectrum are found to belong to different centers. Many of them occur with different intensities in different samples.

The spin Hamiltonian used for the analysis of the angular

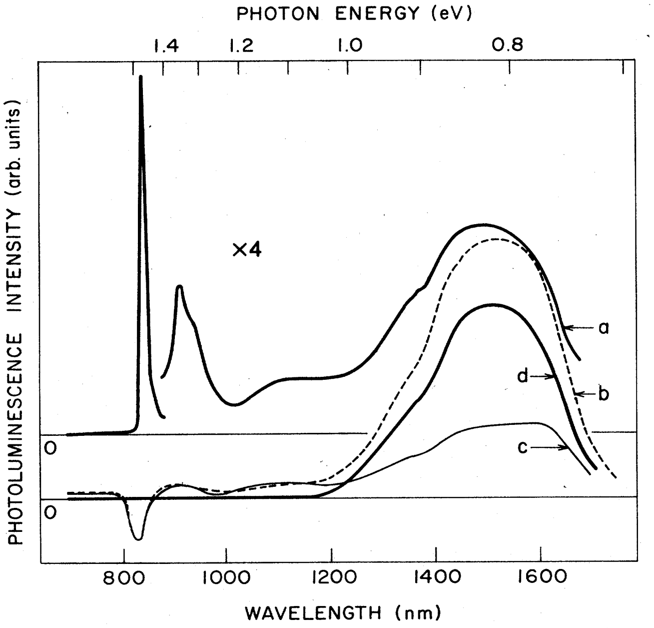

FIG. 1. Curve *a* : PL spectrum at 1.7 K of a Zn-doped GaAs, annealed in vacuum for 15 h at 520 °C. Curve *b* shows the spectral dependence of the ODMR signal for $B = 0.91$ T, $\mathbf{B} \parallel [111]$; curve *c* shows the spectral dependence of the background for $B = 0$. Curve *d* is obtained by subtracting the background (*c*) from curve *b* and represents the spectral dependence of the $\langle 111 \rangle$-triplet ODMR signal.

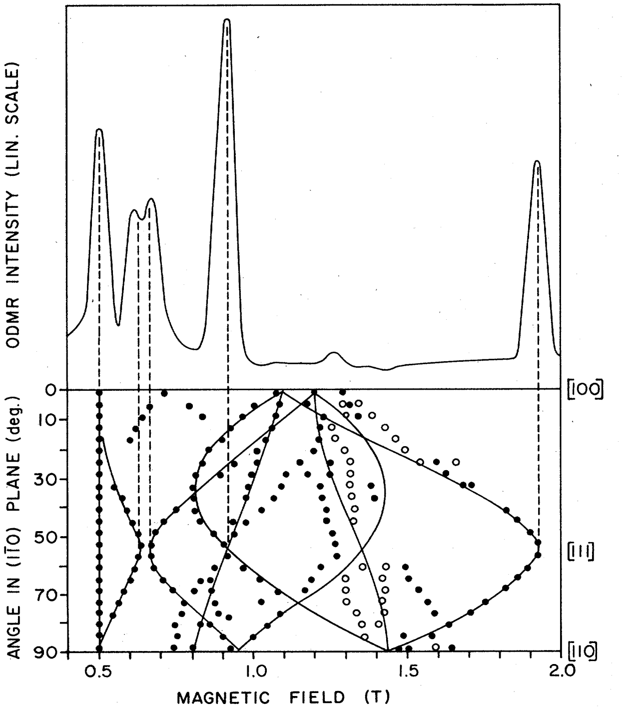

FIG. 2. ODMR spectrum with $\mathbf{B} \parallel [111]$ at $T = 1.7$ K, $\nu = 35.0$ GHz (upper part). The lower part shows the angular variation of the ODMR for $\mathbf{B}$ in the $(1\bar{1}0)$ plane. A computer fit based on a spin Hamiltonian for a $\langle 111 \rangle$-oriented spin-triplet system is included in the figure. Parameters are given in the text.

variation is given by

$$\mathcal{H} = \beta g_{\parallel} \hat{S}_1 B_1 + \beta g_{\perp} (\hat{S}_2 B_2 + \hat{S}_3 B_3) + D(\hat{S}_1^2 - \tfrac{1}{3} S^2) + E(\hat{S}_2^2 - \hat{S}_3^2) \ , \qquad (1)$$

where $S = 1$ (a spin triplet), $g_{\parallel} = 1.96 \pm 0.02$, $g_{\perp} = 2.17 \pm 0.02$, $D = +0.073 \pm 0.03$ meV, and $E = 0$. The computer fit was obtained by a direct diagonalization of the spin Hamiltonian (1), since the D term is too large to allow a perturbation treatment. The defect symmetry is trigonal C_{3v}, with a principal axis along each of the four equivalent $\langle 111 \rangle$ directions in the cubic lattice. The analysis leaves no doubt that the ODMR signal is of localized spin-triplet character. Measurements at different frequencies within the tuning range of the Gunn oscillator (frequency shift of ~ 1 GHz is obtainable) also confirm the triplet configuration.

Further, as shown in Fig. 3, polarization measurements prove this assignment. Here, the Zeeman splitting of the excited spin-triplet state is schematically shown for $\mathbf{B}$ along the defect axis $\mathbf{z}$. The possible microwave transitions are indicated in the figure, $\Delta M = \pm 1$ and $\Delta M = 2$. As the experimental curve *a* shows, all peaks are positive, representing increase in the total unpolarized intensity. This is characteristic for an unthermalized triplet with a bottleneck state

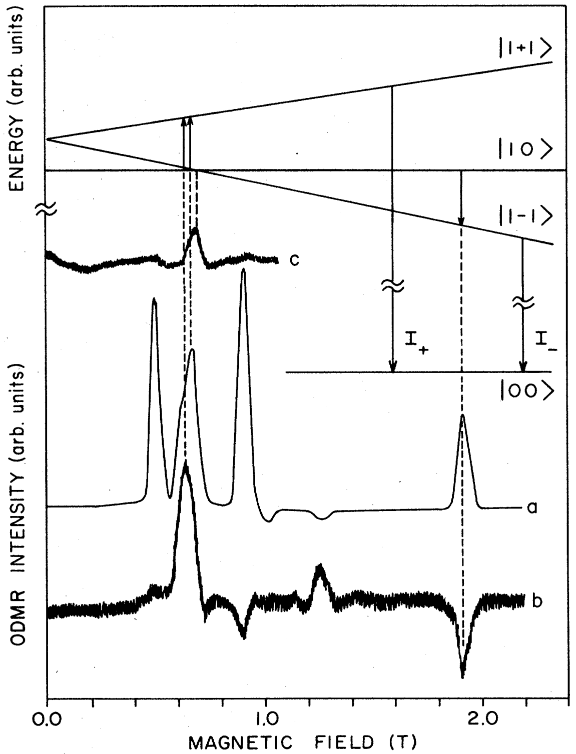

FIG. 3. Schematic Zeeman splitting for a spin-triplet with a large positive zero-field splitting for $\mathbf{B} \parallel \mathbf{z}$. Curve *a* shows the unpolarized ODMR signal for $\mathbf{B} \parallel [111]$. The two $\Delta M = 1$ microwave transitions corresponding to $\mathbf{z} \parallel [111]$ are indicated in the figure. Also shown is the $\Delta M = 2$ transition, partly overlapping the low-field $\Delta M = 1$ transition. Curve *b* shows the same as *a* but monitoring $I_+ - I_-$. Only the $\Delta M = 1$ transitions are observed, now with opposite sign. Curve *c* shows the level crossing signal without microwave excitation.

$|JM_J\rangle = |10\rangle$. If, as in curve *b*, the difference between the left- and right-hand polarized light $I_+ - I_-$ is monitored instead, using a double-modulation technique with a stress modulator and microwave modulation, the two $\Delta M = 1$ resonances have opposite sign. This establishes the sign of D as positive.

The level crossing signal in curve *c* was taken with magnetic field modulation without microwave excitation. It was observed in a narrow angular range around $\mathbf{B} \parallel \langle 111 \rangle$. The value of D deduced from the level crossing is $D = +0.077 \pm 0.005$ meV, in good agreement with the value obtained from the computer fit in Fig. 2. We see no level crossing signal for $\mathbf{B} \parallel \langle 110 \rangle$ as reported by Kennedy and Wilsey[12] in similar Zn-doped GaAs. (We have actually measured on samples kindly provided by Kennedy. These samples show almost identical ODMR spectra as ours. The interpretation of Kennedy and Wilsey[12] in terms of $\langle 110 \rangle$-oriented centers is based partly on other branches in the angular variation diagram than we use in our analysis.)

The spectral dependence of the ODMR signal was measured in different ways. First, the spectral dependence was measured directly by setting the magnetic field at resonance position scanning the wavelength with a monochromator. Curve *b* in Fig. 1 shows the spectral dependence for the magnetic field set at the strong 0.91-T peak for $B \parallel [111]$. The measurement shows that the signal originates from the deep 0.82 eV PL band. The negative intensity contribution around 1.475 eV at slightly higher energy than the corresponding PL peak derives from the considerable background always present in the ODMR measurements. This background signal is of unknown origin and does not show any significant variation with the magnetic field. All contributions to the ODMR signal for wavelengths shorter than 1200 nm (including the negative one) cancel out when the spectral dependence of the background signal (curve *c*) is subtracted from curve *b*. Thus curve *d* in Fig. 1 shows the resulting spectral dependence of the ODMR signal from the trigonal center. The ODMR signal was also measured monitoring different portions of the PL spectrum through a monochromator (large bandwidth, 40 nm) scanning the magnetic field. This measurement confirms the spectral dependence of Fig. 1. In particular, no ODMR is observed when directly monitoring the high-energy region, either through the monochromator or using filters.

The combination of both the above measurements confirms that the $\langle 111 \rangle$ resonances analyzed above indeed belong to the same PL center. Other weaker resonances found in the same samples originate from the same general spectral region, however. We have been able to correlate some of these (not included in the analysis) to a slightly higher energy region within the broad ir band. Further analysis of these resonances is in progress.

IV. DISCUSSION AND SUMMARY

The identification of midgap centers in GaAs is of considerable current interest. In our analysis of the luminescence related to one of these centers we are able to determine its electronic structure and symmetry. The chemical identity remains unknown, however, and is the subject of further study.

We have observed the $\langle 111 \rangle$ triplet ODMR signal in as-grown Zn-doped bulk GaAs from different independent sources. The signal is strong in the untreated starting material, but can be enhanced an order of magnitude by heat treatment. Cu is a persistent contaminant of most III-V compound semiconductors and particularly GaAs, and was present in all the Zn-doped material we studied as manifested by the 1.36 eV Cu-acceptor band.[14] For this reason and also because of the apparent similarity of the ODMR signal with signals from Cu-doped GaP,[15] the possible relation with Cu was investigated.

We find that gradually increased Cu diffusion always causes a corresponding decrease of the 0.82-eV PL band and thus the ODMR signal. The increased Cu doping can be monitored through the intensity of the 1.36 eV Cu-acceptor PL band. Heat treatment alone does not seem to affect this band, whereas the 0.82 eV PL band and the ODMR signal increase. These preliminary results argue against a direct correlation with Cu.

All samples that showed the 0.82 eV PL band were Zn doped and show a strong band-edge luminescence related to $\mathrm{Zn_{Ga}}$ acceptors. $\mathrm{Zn_{Ga}}$ is a shallow acceptor in GaAs [$E_A = 30.7$ meV (Ref. 16)] and cannot explain the deep center unless it forms a complex with other defects. It has been argued that Zn doping causes a considerably enhanced vacancy diffusion in GaAs,[17] suggesting a complex involving either V_{Ga} or V_{As} as a possible candidate for the defect associate.

On the other hand, we can rule out any correlation with the 0.8 eV PL band reported in semi-insulating GaAs and attributed to $\mathrm{As_{Ga}}$.[10] The lower symmetry of our center and different annealing behavior are in sharp contrast to Ref. 10. Instead of quenching of the 0.8 eV PL band upon annealing around 500 °C,[10] we observe the contrary. Further, ODMR measurements have been performed on the 0.8 eV PL band in semi-insulating GaAs without any strong signals detected.[8]

A luminescent center of trigonal symmetry giving rise to the 0.84 eV emission in GaAs:Cr (Ref. 11) has also been rejected as a candidate for the 0.82 eV ir band studied here. The Cr band has a characteristic zero-phonon structure and a sharp high-energy edge which are absent for the 0.82 eV band.

In summary, we have observed a strong ODMR signal from a deep photoluminescence band peaking around 0.82 eV in Zn-doped GaAs. Our analysis firmly establishes the symmetry of this center as trigonal and the electronic configuration of the excited state as a localized spin triplet with a large zero-field splitting *D*. Such spin triplets have only been tentatively identified in GaAs before. Possible candidates for the defect associate are neutral trigonal complexes involving Zn and a vacancy such as $\mathrm{Zn_{Ga}}V_{\mathrm{As}}$. Optically detected ENDOR measurements are planned to reveal the nucleus involved.

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