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Optically detected magnetic resonance of triplet excited states in GaAs

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Optically detected magnetic resonance of a triplet excited state of a native defect in GaAs:Zn is reported. Strong enhancement signals are observed in a photoluminescence band centered at 0.8 eV. Angular dependence studies taken at 24 and 35 GHz reveal that the state has monoclinic symmetry with spin Hamiltonian parameters $D = 0.58 \pm 0.01$ cm^{-1}, $E = 0.09 \pm 0.01$ cm^{-1}, $g_x = g_y = 2.03 \pm 0.01$, and $g_z = 1.93 \pm 0.01$ with axes x, y, and z being $[11\bar{2}]$, $[\bar{1}10]$, and $[111]$, respectively. Because there is no resolved hyperfine structure, assignment of the spectra to specific chemical species is difficult. However, correlations involving the 1.36-eV Cu luminescence suggest that Cu is a part of the defect.

Optical detection of magnetic resonance (ODMR) in semiconductors is of high current interest because it can provide information on both the structure and optical properties of deep levels. Although many defects have been studied with ODMR in the II-VI compounds and in GaP in the last few years,[1] results in technologically important GaAs have been few. First, chromium ODMR was reported on luminescence at 0.84 eV.[2] Second, the As antisite defect, As_{Ga}, has been studied through magnetic-circular-dichroic absorption at 1.05 and 1.29 eV in semi-insulating GaAs (Ref. 3) and through luminescence at 0.7 eV in electron-irradiated GaAs.[4] In related work, semi-insulating GaAs and Mn in GaAs have been shown to exhibit nonresonant spin-dependent recombination through optical pumping studies.[5] Some of the difficulties in performing ODMR in GaAs are discussed in Ref. 5.

In this work strong photoluminescence ODMR signals due to magnetic resonance of triplet spin states of a native defect in a bulk GaAs:Zn sample are reported. The ODMR is observed on emission bands at 0.8 eV with an angular dependence which indicates that the state has symmetry lower than tetrahedral. Hyperfine structure is not resolved and thus the chemical identity of the defect is not revealed. However, some external evidence indicates that the defect contains Cu. To the best of our knowledge, these results are the first example of triplet-state ODMR in GaAs.

The Zn-doped GaAs used in these experiments was obtained from Wacker Chemitronic and has a room-temperature hole concentration of $(4–7) \times 10^{16}$ cm^{-3}. Samples with no surface preparation exhibit the same ODMR as polished wafers indicating that the defects are in the bulk of the material. Spectrometers operating at two different microwave frequencies were used. The 24-GHz ODMR system operated in the Voight configuration in a 9-in. electromagnet which gave a maximum field of 1.1 T with a 3-in. gap. A Kr-ion laser provided optical excitation at 647.1 nm with typically 75 mW at the sample. Luminescence was detected with a North Coast cooled, intrinsic Ge detector. A 50-mW Gunn oscillator provided microwave power to the 24-GHz TE_{011} cylindrical cavity which contained 12.5-mm-wide slots for optical access. The sample and cavity were immersed in liquid He at 1.6 K in a Janis 6DT optical Dewar. Additional data were taken with the 35-GHz spectrometer operated in the Faraday geometry. This system is built around a 6.5-T Oxford Instruments superconducting magnet (SCM) with $f/4$ optical access and variable temperature insert. The laser and detector are the same as for the 24-GHz system.

The GaAs exhibits a strong broad luminescence band peaking at about 0.9 eV (see Fig. 1). This band (or bands) is not easily identified, but it is typical of the bands which exhibit ODMR. Resonance spectra were obtained by detecting all the deep luminescence with a Si filter in front of the Ge detector. Data obtained at 24 GHz for the major symmetry directions with the microwaves switched on and off at 1 kHz are shown in Fig. 2. Strong lines are observed over the entire available field range with a linewidth of about 60 mT. The lines tend to weaken with increasing magnetic field.[6]

The angular dependence of the ODMR peak positions in

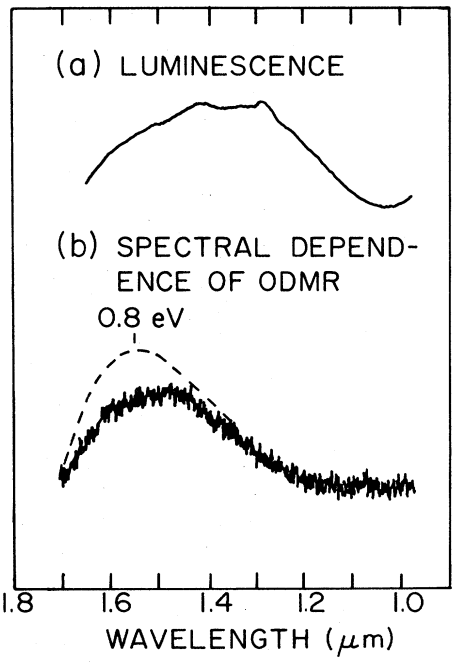

FIG. 1. Deep photoluminescence and spectral dependence of the ODMR. Trace (a) is the deep photoluminescence taken with 20-nm resolution. Trace (b) is the spectral dependence of the 0.23-T line taken with 40-nm resolution. The dashed line in (b) has been corrected for detector and grating response.

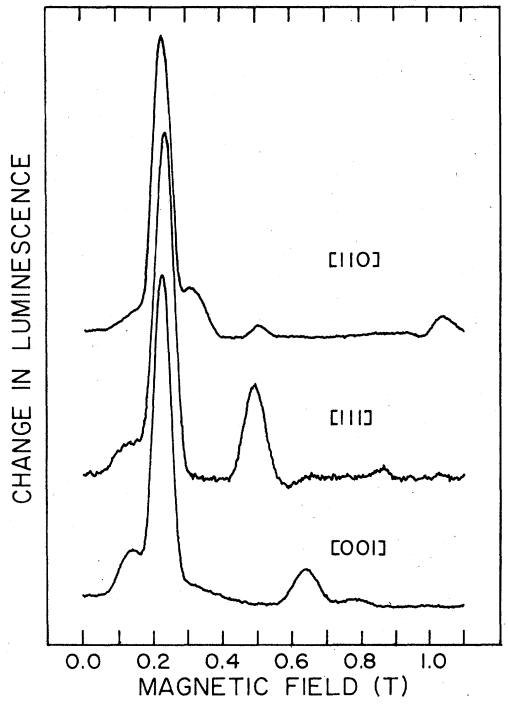

FIG. 2. Optically detected magnetic resonance for the major symmetry directions. The microwave frequency is 24.10 GHz.

the $(\bar{1}10)$ plane are shown in Fig. 3. The strong peak at 0.23 T is very nearly isotropic in the $(\bar{1}10)$ plane and ancillary studies in the (112) plane confirm that it is very nearly isotropic in all crystal directions. Points near [110] suggest that there are resonances above the available maximum field. The presence of many branches in the angular dependence signifies low symmetry, while the large splittings indicate interactions with stengths comparable in magnitude to the Zeeman interaction. Additional data taken with the 35-GHz spectrometer are shown in Fig. 4. The second microwave frequency clarifies the field and/or frequency dependences and the SCM provides enough magnetic field to reveal the entire spectrum.

The strength of the signals, the high optimal power modulation frequency and the large anisotropic splittings all point to the conclusion that the ODMR arises from a spin triplet excited state. Changes in the emitted intensity without microwaves, taken with magnetic field modulation, were observed over narrow angular ranges around the [111] and [110] and indicate level crossings. These are at the fields 0.65 T for [111] and 0.35 T for [110] and confirm that the ODMR arises from a spin triplet.

The existence of the two level crossings and the turning points for [111] and [110] axes in the ODMR angular dependences lead to the following spin Hamiltonian for the excited states:

$$\mathcal{H} = g_{\parallel}\mu_B B_z S_z + g_{\perp}\mu_B (B_x S_x + B_y S_y) + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \ . \quad (1)$$

The first two terms describe the Zeeman interaction and the last two terms the fine-structure interaction. Approximate parameters were obtained by fitting the turning points in the spectra. The final parameters, obtained from the simulation to be described below, are $g_{\parallel} = 1.93 \pm 0.01$, $g_{\perp} = 2.03 \pm 0.01$, $D = 0.58 \pm 0.01$ cm^{-1}, and $E = 0.09 \pm 0.01$ cm^{-1} with principal axes x,y,z being $[11\bar{2}]$, $[\bar{1}10]$, and [111]. The symmetry of the state is monoclinic (C_s). Thus there are twelve equivalent centers, three for each [111] direction.

The full angular dependence of the ODMR for this model has been calculated numerically and is shown by the solid lines in Figs. 3 and 4. In all calculations it is necessary to use the exact eigenvalues of the Hamiltonian [Eq. (1)] since

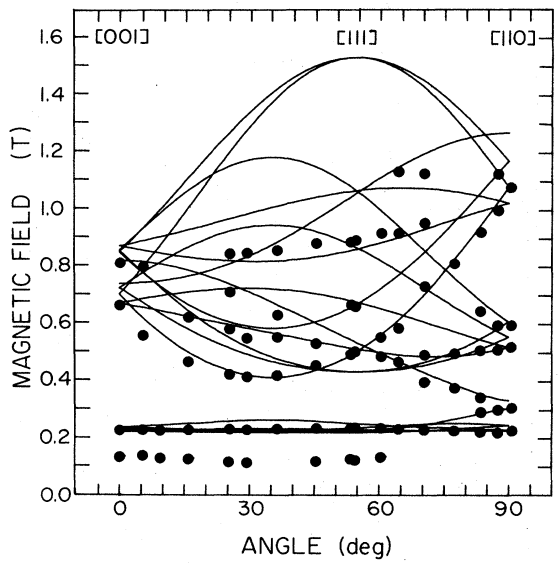

FIG. 3. Angular dependence of the 24-GHz ODMR in the $(\bar{1}10)$ plane. Experimental data are denoted as circles. The lines denote the simulation calculated using the Hamiltonian given in the text.

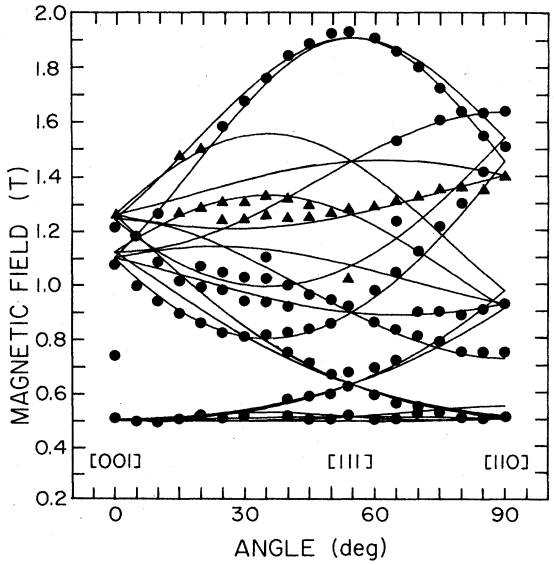

FIG. 4. Angular dependence of the 35-GHz data in the $(\bar{1}10)$ plane. The circles denote resonances which were increases in the photoluminescence. The triangles denote resonances shifted in phase due to different radiative lifetimes.

the microwave quanta of 0.80 and 1.16 cm^{-1} are comparable to the fine-structure interaction $D = 0.58$ cm^{-1}. The simulations are very good at reproducing the overall symmetry of the patterns and the values at the turning points for the data at both 24 and 35 GHz. Changing magnetic field and sample orientation strongly affect the lifetimes of the spin states when the Zeeman and fine-structure terms are comparable. The changing lifetimes produce signals of different intensity and temporal response. The missing branches and slight discrepancies between theory and experiment are attributed to the changing lifetimes. The high-field branches are also much weaker for the case of Ga^+ in alkali halides.[6] The low-field branch in the 24-GHz data and the point with **B** along [001] in the 35-GHz data are not understood.

Further confirmation of the model comes from the fit to the level crossings. The existence of two crossings indicates that the symmetry is lower than axial—that is that E is not equal to zero. For the parameters given, the model predicts level crossings with $\mathbf{B} \| [111]$ at 0.64 T and with $\mathbf{B} \| [110]$ at 0.37 T. These compare favorably with the observed crossings at 0.65 and 0.35 T. Overall there is excellent agreement between the model and experiment.

The signal strengths for some of the ODMR lines are sufficient to study their spectral dependence. Figure 1(b) shows the result for the 0.23-T line for $\mathbf{B} \| [111]$ and 24 GHz. The ODMR arises from the longer-wavelength region of the deep luminescence and thus shows that more than one band is present. The still rather broad ODMR-active band peaks at 0.8 eV.

Triplet ODMR is usually attributed to either two-electron states of deep donors such as O (Ref. 7) or P_{Ga} (Ref. 8) in GaP or bound excitons at isoelectronic centers such as the complex Cu centers in GaP.[9,10] Often the identification of the responsible defects follows from their chemical identity as revealed through hyperfine interactions. In the case of deep donors, the defects may be isolated and thus the lowered symmetry derives from a Jahn-Teller effect in the excited two-electron state leading to a "relaxed excited state."[7,8,11] In terms of symmetry and size of fine-structure term D, the ODMR reported here is similar to previously reported triplet ODMR. The wide lines, which suggest strong central hyperfine interactions, do not reveal a chemical identity since there is no resolved structure. Furthermore, the defects are native to the as-grown material. Thus, assignment of the spectra to specific defect structures is necessarily indirect.

Because of the similarity of these GaAs results to the results reported for Cu in GaP (Refs. 9 and 10) and because Cu is a common contaminant in GaAs, special efforts were made to look for correlations with Cu. Thus, the near-band-gap luminescence was studied at high resolution. The spectrum is dominated by a peak at 1.473 eV, which is deeper than expected for the Zn free-to-bound transition or the Zn-bound exciton.[12] A second, very weak band is observed at 1.36 eV, the position of the zero-phonon line of the band generally attributed to substitutional Cu in GaAs. Many other bands, including some deep bands, have been attributed to Cu complexes.[13,14] Thus, there is evidence for Cu in the as-grown GaAs:Zn material. The ODMR of an undoped GaAs sample which exhibited a strong 1.36-eV luminescence following a 700 °C anneal was also studied. It exhibited a clear resonance at 0.23 T for 24-GHz microwaves and some weaker lines which seem to correspond to those of the GaAs:Zn sample. Overall the ODMR was much weaker than in the Zn-doped sample, however. These studies provide evidence that the ODMR does arise from a Cu complex,[15] although probably not involving substitutional Cu.

Further work is planned to clarify the chemical identity of the defect. Optically detected electron-nuclear double resonance (ODENDOR) can resolve the hyperfine interactions responsible for the very wide lines and identify the nucleus. With these results, it should be possible to determine whether the ODMR is due to a two-electron center or a bound exciton and to determine what chemical species are present.

In summary, strong triplet excited state ODMR has been observed from a native defect in GaAs:Zn. The state has a strong fine-structure interaction and low (monoclinic) symmetry. Correlations with the 1.36-eV Cu luminescence suggest that Cu is a part of the defect. These results confirm that ODMR detected through luminescence is valuable in studying defects in GaAs.

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