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Optically detected magnetic resonance in oxygen-doped GaP

M. Godlewski* and B. Monemar
Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden
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New results from optically detected magnetic resonance (ODMR) studies of oxygen-doped GaP are reported. We show that the previous attribution of a triplet resonance spectrum with a characteristic Ga-related four-line hyperfine splitting to the 841-meV oxygen-donor capture emission is incorrect. Careful measurements of the spectral dependence of the ODMR signals show that the triplet spectrum comes from a different emission, probably related to a Ga_i (gallium interstitial) complex, superimposed on the O-related 1.4-eV band. An Auger-type intersite energy-transfer process from the Ga_i complex to the deep neutral O donor explains the ODMR data.

The deep oxygen-related donor in GaP is one of the most extensively studied deep centers in any semiconductor, but also a quite controversial one.[1] Oxygen is known as an inadvertent impurity in GaP, but also efficient light-emitting diodes (LED's) are produced from zinc- and oxygen-doped GaP, utilizing bound-exciton (BE) recombination at close O_P-Zn_{Ga} pairs (O_P—oxygen on a phosphorus site, Zn_{Ga}—zinc on a gallium site).[2,3] For more distant pairs a structured donor-acceptor-pair (DAP) emission is observed,[4] in which oxygen acts as a 900-meV deep single donor.[5,6] One remarkable feature of the deep O donor is the existence of the second electron state (O_P^-), and the related observation of two different electron-capture photoluminescence (PL) spectra with electronic lines at 841 meV ($O^+ + e \rightarrow O^0 + h\nu$) and 528 meV ($O^{-1*} \rightarrow O^- + h\nu$), respectively.[1]

Recently, there have been two conflicting models attempting to account for the experimental results obtained for GaP:O. One of them, supported by Dean,[1,7,8] views the deep O-related neutral donor as a conventional P-site donor state with a strong central-cell potential. The second model—the molecular-orbital "weak-bonding" description—has been proposed by Morgan.[9–12] The two models require different explanations for the majority of optical data available for O in GaP.[7,11]

Previous optically detected magnetic resonance (ODMR) experiments of Gal *et al.*[13] and Dawei and Cavenett[14] have given quite confusing contributions to the controversy of the relation between optical spectra and charge states of the O_P donor.[1] A spin-triplet resonance spectrum has been reported in these experiments, showing a quartet hyperfine splitting arising from the spin interaction with a single gallium atom. This spectrum has been related to the 841-meV capture PL of oxygen [$O^+ + e \rightarrow O^0 + h\nu$, zero-phonon line at 841 meV (Ref. 15)], based on the observation of similarities between low-resolution PL spectra and the spectral dependence of the ODMR signal (ODMR-PL spectra). The explanation given for the earlier data requires that the 841-meV emission is related either directly, or indirectly, by spin-dependent recombination, to the O^- state.[13,14]

This interpretation of the previous ODMR data has been proposed disregarding many discrepancies with the experimental results. For example, even when taken at low spectral resolution the PL and ODMR-PL spectra clearly peaked at slightly different energies for the 1.4-eV band (see Fig. 2 in Ref. 14). Secondly, the characteristic decay time of the 841-meV PL and of the ODMR signal were found to be quite different. The lifetime measured in ODMR was about 1 order of magnitude longer than that observed for the 841-meV emission.[14] This was explained as follows:[14] There are two components of the 841-meV emission, and the ODMR signal comes from the weaker long-lifetime component of the PL spectrum. Another obvious possibility, namely, that the ODMR spectrum arises from a PL spectrum of a different origin coupled to the 841-meV O-related capture emission by efficient energy transfer, was not discussed. The spectral dependence of the $g = 1.99$ donor signal appearing in the ODMR spectra together with the $S = 1$ spectrum was not reported in the previous work either.

A triplet excited state for the 841-meV emission is only predicted if it is due to capture into the O^- state, which has recently been shown to be incorrect.[1] A proposition of Morgan[12] that the ODMR spectrum comes from a quartet spin system ($S = \frac{3}{2}$), which would then be consistent with the weak-bonding description, has not been confirmed by the ODMR experiments of Dawei and Cavenett.[14] To resolve this contradiction a model involving spin-dependent Auger recombination has been proposed.[7,14,16] In this model a spin-conserving Auger-recombination process occurs in the two-electron state (O^-)—the recombination of one electron with a hole leaves a remaining electron in the $1S(E)$ excited state of O^0, whereupon energy relaxation results in the 841-meV emission observed. This model requires that the memory of the two-electron triplet spin is conserved in the one-electron emission.[16]

In this Rapid Communication we offer a new explanation of the previous ODMR experiments. We show that the spin-triplet resonance arises from an emission different from the O-related band and is probably unrelated to oxygen. Further, an efficient spin-dependent energy transfer between Ga_i-related centers and the O donor explains the appearence of the $S = 1$ spectrum on the oxygen-related emissions.

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The ODMR results presented here have been obtained with a modified Bruker electron-spin-resonance (ESR) X-band spectrometer (Bruker 200D-SRC) equipped with an Oxford ESR 10 continuous-flow helium cryostat and a cylindrical cavity with optical access from all directions. Microwave power up to 500 mW and sample temperatures (regulated) down to 2 K could be obtained. The 5145-Å line of a Coherent Innova 100 Ar^+ laser has been used for the optical excitation. Optical detection has been done with a liquid-nitrogen-cooled North-Coast EO817 Ge detector in phase with the chopped microwave radiation. A Synchrotrack lock-in amplifier (vector voltmeter) has been used. The spectral dependencies of the ODMR signals have been measured through a 0.25-m Jobin-Yvon grating monochromator.

The GaP:O samples used in these studies were solution-grown high Ohmic n-type material, intentionally doped with oxygen. At room temperature the Fermi-level position was estimated from Hall measurements to be about 0.75 eV below the conduction-band edge.

In Fig. 1 we show the ODMR spectrum measured by detecting the intensity changes in the resonance for the phonon replica of the 841-meV oxygen-capture emission. This spectrum, taken for $\mathbf{B} \| [110]$, consists of two separate resonance spectra—a single isotropic resonance with $g = 1.99$ corresponding to the ESR signal of the oxygen donor [$g = 1.99$ (Ref. 17)], and a spin-triplet spectrum with a quartet splitting as reported previously by Cavenett and co-workers.[13,14] The low-field line of the $S = 1$ spectrum is here superimposed on a broad strong resonance, probably arising from formally spin-forbidden $\Delta m_S = 2$ transitions within the triplet sublevels.

The data shown in Fig. 1 seem to be consistent with the results of Gal *et al.* and Dawei and Cavenett[13,14]—the triplet resonance is observed on the 841-meV capture emission. This can, however, also indicate an efficient energy transfer between the system from which the resonance spectrum is observed and the deep O donor, as commonly observed in our recent ODMR experiment of BE emissions in GaP.[18] To verify this possibility the ODMR-PL spectra of the two observed resonances were measured.

In Fig. 2(a) the PL spectrum of the GaP:O crystals studied is shown, measured in the same experimental setup as used for the ODMR-PL investigations. This spectrum consists of two structured O-related bands, the 1.4-eV PL due to donor-acceptor-pair (DAP) recombination ($O^0 + A^0 \rightarrow O^+ + A^- + h\nu$) and the 841-meV capture emission ($O^+ + e \rightarrow O^0 + h\nu$).

In Fig. 2(b) the ODMR-PL spectrum of the $g = 1.99$ donor signal is shown. It is apparent that this spectrum is identical to that shown in Fig. 2(a)—the spectral region of the observed emissions and their relative intensities are identical to that measured in PL. We believe that this result strongly supports the explanation that the $g = 1.99$ signal is due to the deep oxygen single donor in GaP (O^0). The observation of this signal on both O-related emissions has a very simple explanation. By the resonance

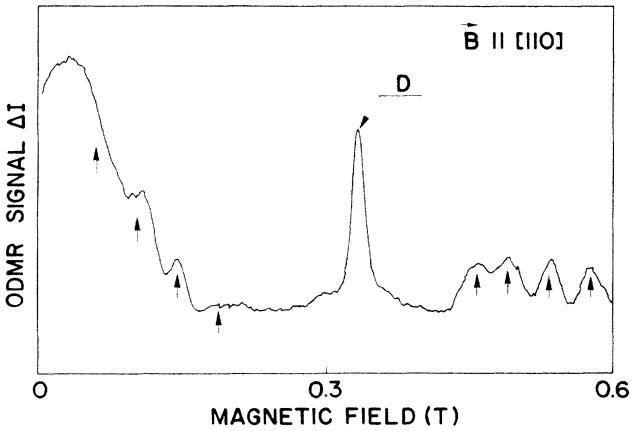

FIG. 1. The ODMR spectrum of GaP:O with 5145-Å Ar^+-laser excitation at 2 K. This spectrum was obtained as a total change of the intensity of the phonon replica of the 841-meV zero-phonon line of the oxygen-capture emission. The four-line structure of the resonances due to an interaction of an electron spin with a nuclear spin of a single Ga atom is clearly resolved and indicated by arrows.

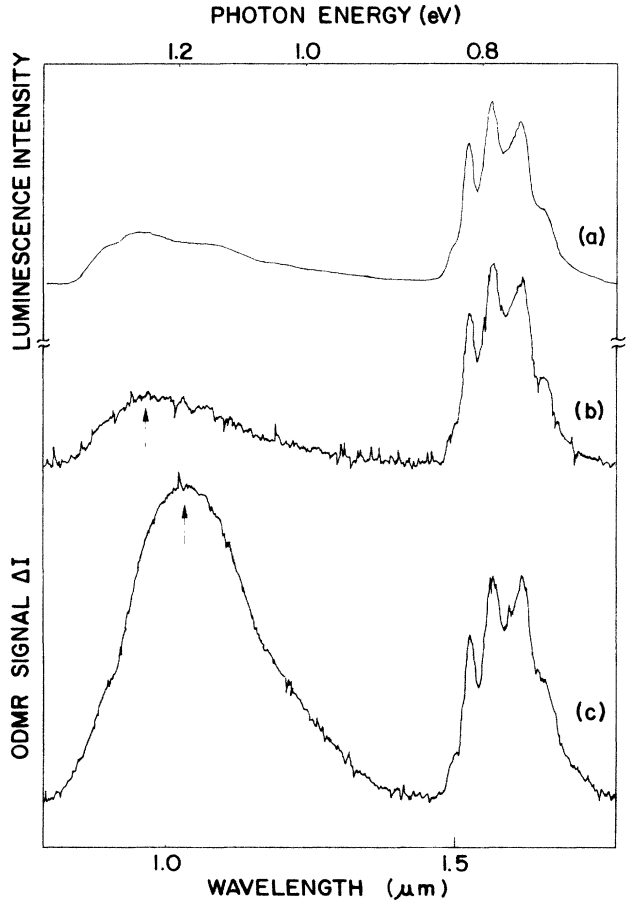

FIG. 2. The spectral dependencies of (a) the photoluminescence and (b),(c) ODMR spectra [(b) donor signal and (c) the $S = 1$ state]. The spectra were measured at the same experimental conditions in the ODMR setup through a 0.25-m Jobin-Yvon grating monochromator and with the 5145-Å line of Ar^+-laser excitation at 2 K. The position of the maxima of the 1.2-eV band and of the O-related 1.4-eV DAP emissions are indicated by arrows.

transition-induced spin flip at the donor site, we can stimulate DAP recombination ($O^0+A^0 \rightarrow O^+ + A^- + h\nu$), which in turn, increases the amount of oxygen centers in the O^+ state active in the 841-meV capture emission ($O^+ + e \rightarrow O^{0*} \rightarrow O^0 + h\nu$). Shallow-acceptor resonance signals were not observed in these ODMR experiments. This is typical for all our studies of recombination processes in GaP.

In Fig. 2(c) we show the ODMR-PL spectrum related to the $S=1$ resonance spectrum. This ODMR-PL spectrum is distinctly different from that shown in Figs. 2(a) and 2(b). It consists of a strong emission peaked at 1.2 eV, superimposed on a much weaker O-related 1.4-eV emission. The 841-meV O-related emission is also observed, but is of lower intensity than the 1.2-eV band. It is apparent that the argument used by Cavenett and co-workers[13,14] for correlation of the $S=1$ spectrum to the O-related capture emission, i.e., similarities of PL and ODMR-PL spectra, is not valid. This triplet resonance comes from a different emission peaking at 1.2 eV, underlying the strong 1.4 eV in the PL experiments. The observation of this triplet spectrum, which as indicated by hyperfine structure is Ga-related, on O-related bands indicates a strong energy transfer between a Ga complex and the O donor.

A strong spin-dependent energy-transfer process has been commonly observed in our recent studies of recombination processes in GaP.[18] One of the prerequisites for a phonon-assisted transfer to occur is a spectral overlap between the PL emission band of the "energy-donor" system and the absorption band of the "energy-acceptor" system. It is noticed that the 1.2-eV PL band overlaps strongly with the photoionization spectrum σ_{n^0} ($O^0+h\nu \rightarrow O^+ + e_{CB}$) (CB denotes conduction band), which indicates that the energy transfer between the two systems may, in fact, be very efficient. This is illustrated in Fig. 3, where it is shown that an Auger transfer process directly promotes the 841-meV PL band. The free electrons produced in the Auger process may also migrate and get recaptured at other O_P sites, having an acceptor at a closer distance, thus stimulating also the 1.4-eV DAP emission. No resonance in the O^- system[13,14,16] is therefore needed to explain the experimental data.

The nature of the 1.2-eV PL and the identity of the complex for which the ODMR spectrum is observed are not known. The spin-triplet configuration of the initial state in the recombination is consistent with a BE at an isoelectronic center.[19-21] The observed hyperfine structure suggests that the defect contains one Ga atom, and a Ga interstitial as the donor part of the complex is the most probable choice. Then an acceptor must also be part of the complex to form an isoelectronic center. The nearly isotropic g tensor with all components close to 2 shows that the hole angular momentum is quenched, i.e., the hole attractive potential from one constituent of the complex defect must also be fairly strong.[19] Therefore, at the moment, the most natural candidate for the 1.2-eV PL complex is one including the Ga interstitial as a donor part, and some deep-acceptor impurity as a charge compensator. It is very likely that this complex does not include oxygen at all.

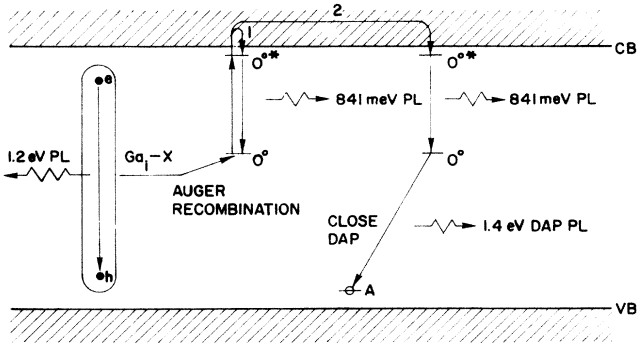

FIG. 3. Model for the recombination of the 1.2-eV Ga-related BE in GaP. The competition of the radiative recombination (1.2 eV) and the Auger-type energy-transfer processes leads to (1) enhancement of the 841-meV capture emission, and (2) also the 1.4-eV DAP PL emission when the electron induced in the CB is recaptured by an oxygen center close to a populated acceptor.

In conclusion, the ODMR-PL experiments show that the $S=1$ ODMR spectrum attributed previously by Cavenett and co-workers[13,14] to the 841-meV oxygen-capture emission comes from a different Ga-related PL band with maximum at 1.2 eV. The ODMR-PL data indicate that a very efficient energy-transfer process takes part between these Ga-related complexes and the oxygen donor. The transfer process is an Auger-type σ_{n_0} process ($O^0+\Delta E \rightarrow O^+ + e_{CB}$), as verified by the simultaneous enhancement of both the 841-meV capture emission and the 1.4-eV DAP emission for the oxygen donor. The ODMR data are explained in detail by this simple transfer process, and neither "weak-bonding" models[22] nor complicated Auger-recombination processes in the O^- state[16] are needed.

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*Permanent address: Institute of Physics, Polish Academy of Sciences, 02-668 Warsaw, Al. Lotnikow 32/46, Poland.

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