Optically detected magnetic-resonance observation of spin-dependent interdefect electron transfer in the GaP:(V,S) system

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A strong, optically detected magnetic-resonance (ODMR) signal at $g=1.99$ is observed on the internal $^3T_2 \rightarrow {}^3A_2$ emission of V^{3+}. The ODMR excitation spectrum is identical with the emission spectrum. From the analysis of the experimental data it is nevertheless concluded that the spin resonance does not arise from the V but is due to shallow S donors present in the sample. A model accounting for the spin-dependent electron-transfer mechanism is suggested. An unidentified photoluminescence emission centered at 1.35 eV with an isotropic $g=2.06$ ODMR line is also observed.

I. INTRODUCTION

The substitutional transition metals in III-V semiconductors are probably among the best studied impurity systems.[1-4] However, there are still unresolved questions of importance for a complete understanding of their electronic structure. One such question is the reason for the lack of observations of spin resonance in the excited states of the crystal-field-split energy levels. Earlier it was suggested that substitutional vanadium (V_{Ga}) in GaAs gives rise to a midgap energy level.[5] Since such a deep energy level could be of importance for semi-insulating GaAs, intensive research on vanadium-doped III-V semiconductors was initiated.[6,7] Besides showing that there were no appropriate energy levels for the creation of semi-insulating material, an important result was that a fairly unified picture of V in GaAs, InP, and GaP emerged. For GaP it was concluded that V_{Ga} gives rise to two energy levels in the band gap, the V^{4+}/V^{3+} donor located at $E_v+0.35\pm0.10$ eV and the V^{3+}/V^{2+} acceptor located at about $E_c-0.58$ eV.[8] Proofs of the occurrence of the V^{3+} and V^{4+} were given by electron paramagnetic resonance (EPR).[9,10] Furthermore, from absorption and luminescence measurements it was possible to identify the crystal-field-split excited states for V^{3+}.[8,11-13] The present understanding of the energy-level structure of GaP:V_{Ga} is shown schematically in Fig. 1.

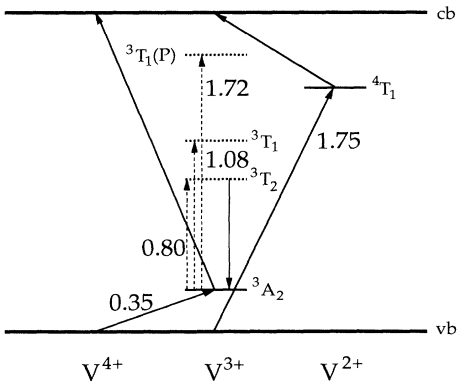

FIG. 1. The energy-level diagram of GaP:V_{Ga}. It should be noted that the assignment of the V^{2+} ground state as a $^4T_1$ state is controversial. It may instead be ^2E. Energies are in eV.

The intense luminescence from the V^{3+} ($^3T_2 \rightarrow {}^3A_2$) transition, which was studied in Refs. 11 and 12, consists of two zero-phonon lines at 0.791 and 0.793 eV (denoted as *A* and *B* in Refs. 11 and 12) and a pronounced phonon replica structure. Zeeman splitting investigations of this luminescence, and of the corresponding luminescence in InP:V,[13] revealed the designation of the transition $\{V^{3+}\ (^3T_2 \rightarrow {}^3A_2)\}$, and for GaP:V, showed that the *g* value of the ground $^3A_2$ state is ≈ 2.0, in agreement with earlier EPR data.[9]

The optically detected magnetic resonance (ODMR) technique is often used to obtain detailed information on the electronic properties of luminescent states.[14] Such ODMR investigations on the internal emission of transition-metal impurities have previously been successfully performed in ionic crystals.[15] However, ODMR arising from spin resonance within the electronic excited states of transition-metal impurities in III-V semiconductors has, to the best of our knowledge, never been reported. Recently, it was shown that the ODMR signal observed on the internal $^4T_1 \rightarrow {}^6A_1$ emission of Mn^{2+} in GaP was actually caused by spin resonance in shallow sulfur donors.[16] A spin-dependent, interdefect charge-transfer mechanism between the shallow sulfur donor and the Mn^{2+} defect was suggested to be responsible for the effect. In this paper, we further explore the existence of such interdefect charge-transfer mechanisms by investigating the $V^3(^3T_2 \rightarrow {}^3A_2)$ luminescence in GaP using the ODMR technique.

II. EXPERIMENTAL DETAILS

The GaP samples used in this work are grown by the liquid encapsulated Czochralski technique, and the principal growth procedure has been described in Ref. 11. The samples are *n* type, contaminated with S, and, there-

fore, the vanadium in these samples is in the V^{2+} state in the absence of illumination. Zn-doped, *p*-type GaP:V samples were also investigated.

The photoluminescence (PL) measurements were performed at $T=1.5$ K. The following lasers were used to excite the PL: an Ar-ion laser ($\lambda=514.5$ nm, or 2.410 eV); an Ar-ion pumped dye laser (500–900 nm, or 1.4–2.5 eV); and a Nd:YAG laser (where YAG denotes yttrium aluminum garnet) (1.064 μm, or 1.165 eV). The emission was dispersed by a Spex 1681 monochromator and detected by a liquid-nitrogen-cooled Ge detector (North Coast).

Most of the ODMR measurements were done at 24 GHz, but measurements were also performed at 9 and 14 GHz. Here we describe the 24-GHz system. The computer-controlled ODMR equipment consists of a 4-T superconducting magnet and a microwave system with an output power $P<0.5$ W. The TE_{110} microwave cavity, which has large openings for excitation and luminescence collection, can be tuned to resonance at the measuring temperature ($T\geq 1.5$ K) by adjusting both the length of the cavity and the microwave frequency. The ODMR signals were observed either by detecting the change in the total $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence intensity induced by the chopped microwaves or by detecting the change in intensity of a small part of the spectrum which was selected with the monochromator.

III. EXPERIMENTAL RESULTS

A. Photoluminescence

The well-known infrared PL spectrum of GaP:V^{3+} as observed in both *n*-type and *p*-type samples is shown in Fig. 2. This spectrum, which is measured at $T=1.6$ K, using above-band-gap excitation ($\lambda=514.5$ nm or 2.41 eV), is dominated by the *A* line of the ${}^3T_2\rightarrow{}^3A_2$ transition and its phonon replicas. The weaker zero-phonon line, the *B* line at 0.793 eV, is, however, not resolved from the stronger zero-phonon line, the *A* line at 0.791 eV, in this low-resolution measurement.[8,11,12] For above-band-gap excitation the holes generated in the valence band are captured by the V^{2+} ions, transferring them first to V^{3+} and then to V^{4+}. The electrons in the conduction band are captured by the V^{4+} ions, thus creating highly excited V^{3+}. These highly excited V^{3+} relax to the ${}^3T_2$ states, from which they decay to the ${}^3A_2$ ground states with the emission of photons (see Fig. 1).

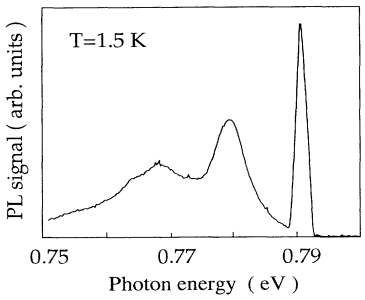

FIG. 2. The GaP:$V^{3+}({}^3T_2\rightarrow{}^3A_2)$ photoluminescence spectrum.

The same PL emission spectrum obtained for above-band-gap excitation is also obtained for below-band-gap excitation with $h\nu>1.4$ eV. A PL excitation (PLE) measurement (see Fig. 3) allows the optical cross section of the excitation process to be determined; the optical cross section is shown as an inset in Fig. 3. An interpretation of the excitation mechanism will be given in the discussion. As was already observed in Ref. 8, Nd:YAG laser excitation (1.064 μm or 1.165 eV) produces an identical PL emission spectrum with much higher intensity than 1.4-eV excitation, and with approximately the same intensity (see Fig. 3) as for above-band-gap excitation (514.5 nm or 2.41 eV). The explanation is straightforward, if the absorption spectrum of the GaP:V^{3+} system is considered.[8] The emission energy of the Nd:YAG laser is centered at the absorption peak of the GaP:V^{3+} (${}^3A_2\rightarrow{}^3T_1$) transition, and, consequently, the V^{3+} excited state is reached by internal excitation. In *n*-type samples, the excitation process has to occur in two steps due to the position of the Fermi level. First the V^{2+} ion is transferred to the $V^{3+}({}^3A_2)$ state by electron emission; then a second photon excites the V^{3+} ion to the ${}^3T_1$ state, from which the same light-emission process as described for above-band-gap excitation takes place.

For above-band-gap excitation a new, broad luminescence band is observed [see Fig. 4(a)]. The new PL band is located at about 1.35 eV, and seems to be a superposition of two broad bands centered at ≈ 1.28 and ≈ 1.42 eV. Assuming strong phonon-electron coupling, the estimated positions of the zero-phonon lines corresponding to these bands are ≈ 1.4 and ≈ 1.65 eV, respectively.

B. ODMR investigations

An ODMR investigation of the ${}^3T_2\rightarrow{}^3A_2$ luminescence, using either above-band-gap excitation ($h\nu=2.41$ eV) or below-band-gap excitation with $h\nu>1.4$ eV,

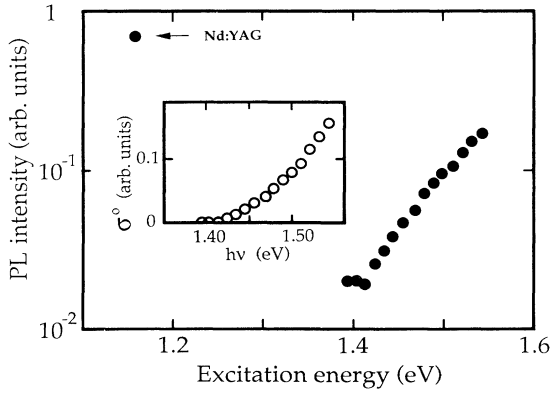

FIG. 3. The excitation spectrum of the GaP:$V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence obtained at $T=1.5$ K. For comparison, the PL intensity using a Nd:YAG ($\lambda=1.064$ μm or 1.165 eV) laser for excitation is also shown. The V^{3+} PL is excited much more efficiently at 1.165 eV than at 1.4–1.5 eV (because of resonant excitation of the ${}^3T_1$ state, as discussed later). The inset shows the corresponding optical cross section.

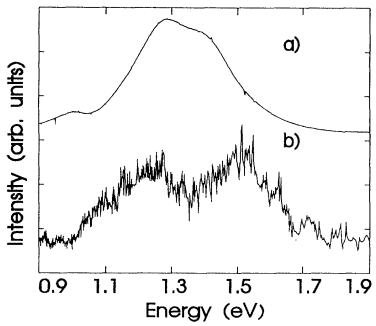

FIG. 4. (a) A photoluminescence spectrum of unknown origin obtained in GaP:V. (b) The excitation spectrum of the $g=2.06$ ODMR signal.

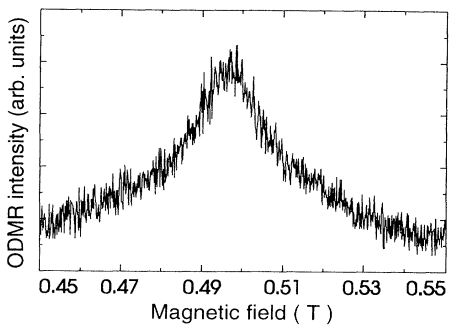

FIG. 6. The ODMR line as observed on the $h\nu=1.35$ eV line. $T=2.0$ K and the microwave frequency is 14.3 GHz.

shows an isotropic resonance signal at $g=1.99\pm0.01$ with a half-width of 120 G (Fig. 5). The ODMR signal is obtained by a phase-sensitive detection technique in which the effect of the modulated microwaves on the $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence intensity is measured. The phase shift of the ODMR signal relative to the modulating microwave pulses shows that the characteristic relaxation time for the spin resonance signal is $\tau_r\approx5$ ms. Using a low modulation frequency ($\tau_{\rm mod}=60$ ms $\gg\tau_r$) the ODMR signal is detected as an $\approx1\%$ increase of the total luminescence signal, regardless of whether the whole or only a part of the luminescence spectrum is detected.

The ODMR signal has a different sign for resonant PL excitation within the ${}^3A_2\rightarrow{}^3T_1$ absorption band than for above-band-gap PL excitation or for below-band-gap PL excitation with $h\nu>1.4$ eV. The ODMR signal is observed as a 1% *decrease* of the total luminescence. The g value and the linewidth of the ODMR signal are very close to the values observed using above-band-gap excitation [see Fig. 5(b)].

The ODMR excitation spectrum, i.e., the intensity of the ODMR signal measured as a function of the detected luminescence photon energy, exactly reproduces the $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ PL spectrum. Such agreement between the ODMR excitation spectrum and the PL spectrum has in many cases been taken as a convincing argument that the spin resonance originates from the same defect that gives rise to the PL band. That this is not the case for V^{3+} in GaP will be shown below.

An ODMR study of the 1.35-eV PL band reveals a new, isotropic ODMR signal (see Fig. 6). The g value is determined to be $g=2.06$. The ODMR excitation spectrum has a similar but not identical spectral shape to the 1.35-eV PL spectrum [see Fig. 4(b)].

Finally, it should be mentioned that the ODMR signals on the $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence were observed only in the n-type sample. No ODMR signal was observed in the p-type samples investigated.

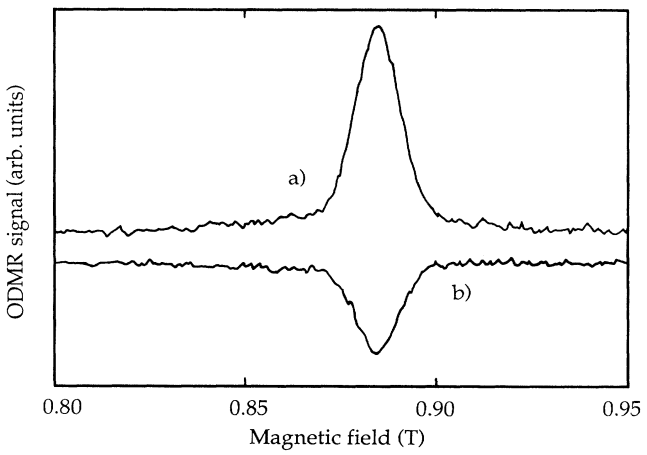

FIG. 5. The ODMR signals obtained on the GaP:$V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence using (a) above- or below-band-gap ($h\nu\geq1.4$ eV) excitation, or (b) excitation within the internal GaP:$V^{3+}({}^3A_2\rightarrow{}^3T_1)$ absorption line. $T=1.5$ K and the microwave frequency is 24 GHz. Note that the ODMR signal is positive in the former case and negative in the latter case.

IV. DISCUSSION

The exact correspondence between the $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ PL spectrum and the excitation spectrum obtained on the $g=1.99$ ODMR line shows that V^{3+} is involved in the pumping or the recombination cycle leading to spin resonance. It might, therefore, be tempting to suggest that the ODMR signal observed on the $V^{3+}({}^3T_2\rightarrow{}^3A_2)$ luminescence originates in a spin resonance transition in one of the excited states of V^{3+}. We can, however, immediately exclude the possibility that the spin resonance takes place in the ${}^3T_2$ level since, according to the Zeeman spectroscopy data (Ref. 12), the spin resonance in this state would occur above $B=2$ T for 24-GHz microwaves ($g<1$). Therefore, the observed ODMR spectrum can, in such a model, only occur within the ${}^3T_1$ state, and the origin of the ODMR signal would be in the spin-dependence transitions ${}^3T_1\rightarrow{}^3T_2\rightarrow{}^3A_2$. Most experimental observations, including the negative sign of ODMR in 1.064-μm excitation, can be explained in this model. However, the fact that the measured g factor is very close to 2 seems to be inconsistent with the model. The lowest spin-orbit state of ${}^3T_1$ of cubic $V^{3+}(3d^2)$ is a $J=2$ state which, by second-order spin-orbit interaction, splits into E and T_1. The g factor of the $J=2$ state is 1.5 in the pure static crystal-field case and approaches 1.0 in the case of a strong dynamic Jahn-Teller effect. The g factors of the E and T_1 states may be

different, but it is unlikely that the g factors are 2.0. Furthermore, the absence of an ODMR signal in p-type samples is also an argument against this model.

Therefore, we suggest another model to explain the observed data. In this model the electron-spin resonance occurs in the S donors, but the effect can be readily observed in the $V^{3+}({}^3T_2 \rightarrow {}^3A_2)$ luminescence due to a spin-dependent interdefect, electron-transfer mechanism. In the following we give the detailed arguments in favor of this model.

The full width of half maximum of the $g=1.99$ ODMR signal is 120 G. This corresponds to a peak-to-peak derivative linewidth of 70 G for a Lorentz-broadened line, and 100 G for a line with Gaussian broadening. The former value corresponds exactly to what is observed by electron paramagnetic resonance for the shallow, sulfur donor in GaP when the S concentration is about 10^{16} cm^{-3}. Furthermore, the g value is also consistent with that for S. Since our n-type crystals are doped with S (probably in the 10^{16}-cm^{-3} range), this suggests that the spin resonance is actually occurring within the neutral sulfur S^0. However, how the spin resonance of S^0 can be detected on the $V^{3+}({}^3T_2 \rightarrow {}^3A_2)$ emission remains to be explained.

In the case of 1.17-eV (Nd:YAG laser) excitation, the starting condition is $V^{2+}({}^4T_1)$, i.e., the negative charge state. The photons will, initially, ionize vanadium to the $V^{3+}({}^3A_2)$ ground state

$$V^{2+}({}^4T_1)+h\nu_{ex} \rightarrow V^{3+}+e_{cb} \tag{1}$$

and once in the V^{3+} state, a second photon can be absorbed according to

$$V^{3+}({}^3A_2)+h\nu_{ex} \rightarrow V^{3+}({}^3T_1) \rightarrow V^{3+}({}^3T_2) \rightarrow V^{3}({}^3A_2)+h\nu\ , \tag{2}$$

thus creating the PL channel. There is also a certain probability that the $V^{3+}({}^3A_2;S=1)$ state will capture electrons. If the capture is at least partly due to direct charge transfer from S^0 ($S=\frac{1}{2}$), the following spin-dependent process can occur. Because the $V^{3+}({}^3A_2;S=1)$ state has two spin-up electrons, transitions to $V^{2+}({}^4T_1;S=\frac{3}{2})$ occurs via the capture of another spin-up electron from S^0 ($S=\frac{1}{2}$). The result is that the population of spin-up electrons in S^0 will be depleted. At S^0 spin resonance, the spin-up population will increase and the transition rate of $V^{3+} \rightarrow V^{2+}$ will increase. Thus, the number of V^{3+} defects that can participate in the PL process decreases, and a negative ODMR signal results.

Above-band-gap excitation (Ar-ion laser) generates electron-hole pairs. The holes can be captured according to

$$V^{2+}+2h_{vb} \rightarrow V^{4+}\ . \tag{3}$$

Note that V^{2+} and V^{3+} correspond to the negative and neutral charge states, respectively, which means that the assumed hole capture is reasonable. Once in the V^{4+} state, which corresponds to the positive charge state, electron capture will dominate. Again, if the capture is partly from the neutral donors,

$$V^{4+}(S=\tfrac{1}{2})+S^0(S=\tfrac{1}{2}) \rightarrow V^{3+}({}^3T_1;S=1)+S^0(S=0) \tag{4}$$

and

$$V^{3+}({}^3T_1;S=1) \rightarrow V^{3+}({}^3T_2;S=1) \rightarrow V^{3+}({}^3A_2;S=1)+h\nu\ , \tag{5}$$

the positive ODMR signal can be explained with the same model as above. In order to create the excited V^{3+} state, a spin-up electron has to be captured from S^0 ($S=\frac{1}{2}$). This will depopulate the S^0 ($S=\frac{1}{2}$) spin-up states. At spin resonance the concentration of S^0 ($S=\frac{1}{2}$) with spin-up will increase, thus increasing the V^{3+} population and thereby increasing the luminescence intensity, and the ODMR is observed as a positive signal.

For below-band-gap excitation, but with $h\nu > 1.4$ eV, the same process as for above-band-gap excitation takes place. The electron-hole generation is, however, produced in a two-step excitation process via a deep energy level. This will transfer the vanadium into the V^{4+} state and the same spin-dependent recombination process as described above takes place. It is interesting to note that there is an unidentified, deep energy level in the band gap, which is located at ≈ 1.4 eV, according to the PL and PLE investigation. This defect, and others, could serve as the excitation channel in the generation of electron-hole pairs. The optical cross section for the excitation process (inset in Fig. 3), as determined on the ODMR signal, is, in such a case, one of the optical ionization cross sections for the new defect.

The proposed model resembles in many respects the model proposed for the interdefect charge transfer in the GaP:(S,Mn) system, even though the details are different. These examples show that even when the ODMR excitation spectrum is identical to the PL spectrum, the spin resonance does not necessarily occur at the same defect that gives rise to the PL. Despite the excitation spectra, which apparently point to the identification of the ODMR signal as originating in the V defect [or to Mn in the case of GaP:(S,Mn)], the spin resonance signal originates in a shallow donor. Such an indirect ODMR detection of a shallow donor resonance has also been made previously, viz., on the Pb PL signal in CdTe.[17]

V. CONCLUSIONS

We have observed an isotropic ODMR signal with $g=1.99\pm0.01$ on the $V^{3+}({}^3T_2 \rightarrow {}^3A_2)$ luminescence. The signal is observed as an increase of PL for excitation energies >1.4 eV and as a decrease for 1.71-eV excitation. The experimental data can be explained as a spin resonance in the shallow S^0 donor, which is observed in the vanadium PL because of a spin-dependent, interdefect, charge-transfer mechanism. Furthermore, an unidentified PL signal, located at about 1.35 eV with an ODMR signal with $g=2.06$, is also reported.

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