Spin-dependent interdefect change transfer in the GaP:(Mn,S) system

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Optically detected magnetic resonance (ODMR) is observed on the internal $^4T_1$-$^6A_1$ emission of Mn^{2+} in GaP. From an investigation of the photoluminescence excitation spectrum, the photoluminescence intensity as a function of temperature, and the ODMR properties, it is concluded that the spin resonance occurs in shallow sulfur donors present in the sample. A model describing the spin-dependent interdefect transfer mechanism is suggested.

I. INTRODUCTION

A Mn impurity on the Ga site in the GaP lattice introduces a deep acceptor level at $E_V+0.4$ eV.[1] The $^6A_1$ ground state of the ionized acceptor, $Mn^{2+}(3d^5)$, has been identified from the well-known electron-paramagnetic-resonance (EPR) spectrum, with six resolved $^{55}Mn(I=\frac{5}{2})$ hyperfine lines (I is the nuclear spin).[2] In the wide-gap ionic crystals and II-VI compound semiconductors, adsorption and emission between crystal-field-split states of Mn^{2+} are well-known features.[3,4] This is in contrast to most III-V compounds, where the Mn^{2+}-related emissions have been identified as band-acceptor and donor-acceptor recombinations.[5–7] In GaP, however, the radiative emission originates in the internal transition between the excited state, $^4T_1$, and the ground state, $^6A_1$, of Mn^{2+}.[8]

The optically detected magnetic-resonance (ODMR) technique is often used to obtain detailed information on the electronic properties of the states involved in radiative recombination.[9] Such ODMR investigations on the internal transitions of transition-metal impurities have previously been successfully performed in ionic crystals.[4] However, ODMR on the internal transitions of transition-metal impurities in III-V semiconductors has, to the best of our knowledge, never been reported. Because of its fairly long radiative lifetime of 1 ms,[8] resulting from the spin-forbidden $^4T_1 \rightarrow {}^6A_1$ transition, GaP:Mn seems to be a promising system in which to study the excited state properties using the ODMR technique.

In this paper we report on photoluminescence, photoluminescence excitation, and ODMR investigations of the $Mn^{2+}(^4T_1 \rightarrow {}^6A_1)$ emission in GaP.

II. EXPERIMENTAL DETAILS

We used the same GaP:Mn crystals on which the luminescence investigations reported by Vink and Van Gorkum were carried out.[8] Briefly, these n-type crystals were grown by the slow cooling of molten Ga to which GaP, Mn, and S were added. Electron-spin-resonance measurements (Bruker ESP 300, X band) at 4 K revealed the presence of isolated Mn^{2+} ions in the concentration range $(1-2)\times 10^{18}cm^{-3}$.[2] An additional EPR spectrum, presumably due to Mn-S pairs[10] at a lower concentration, was also detected.

In the present study, photoluminescence (PL) spectra were recorded with a grating double monochromator (Spex 1681) in combination with a liquid-nitrogen-cooled Ge detector (North Coast). The sample was cooled using a helium gas-flow cryostat (8–300 K). Excitation was induced by an Ar^+ laser (above-band-gap excitation) or a dye laser (below-band-gap excitation). Photoluminescence excitation (PLE) spectroscopy was carried out using either a dye laser, or a tungsten-halogen lamp in combination with a double monochromator. For the ODMR investigations, a 4-T superconducting magnet in combination with a 24-GHz microwave system was used at a temperature of 1.6 K. The measurements were performed either by detecting the total $Mn^{2+}(^4T_1 \rightarrow {}^6A_1)$ luminescence changes induced by the chopped microwaves, or by selecting a part of the luminescence with the monochromator. The microwave power could be varied up to 3 W (using a Gunn diode amplified by a Hughes traveling wave tube); the measurements presented here were performed with ≤ 500 mW of microwave power. An optimum signal-to-noise ratio for the ODMR was observed for microwave chopping frequencies around 350 Hz. Both Ar^+ and dye-laser excitation were used in the ODMR studies.

III. EXPERIMENTAL RESULTS

A. Photoluminescence and ODMR investigations

The PL spectrum of the internal $Mn^{2+}(^4T_1 \rightarrow {}^6A_1)$ emission obtained at 9 K using 5145-Å excitation (≈ 0.5 W/cm^2) is shown in Fig. 1. It consists of a slightly asymmetric Gaussian band centered at 1.3 eV. With increased resolution the fine structure of the luminescence, previously reported in Ref. 3, is visible (see inset in Fig. 1). The zero-phonon line transition at 1.534 eV is followed

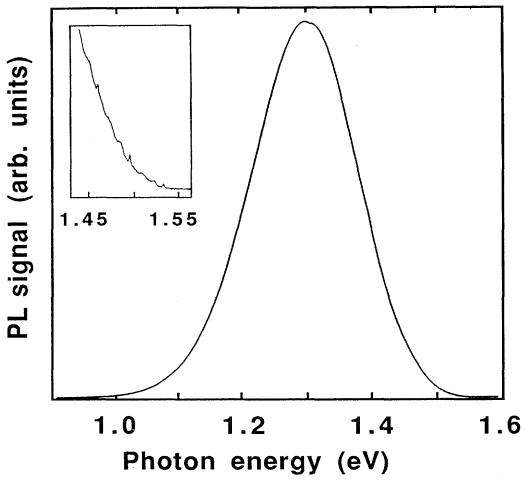

FIG. 1. Photoluminescence spectrum of $Mn^{2+}({}^4T_1 \rightarrow {}^6A_1)$ in GaP obtained at 9 K using 5145-Å excitation (≈ 0.5 W/cm^2). The inset shows the zero-phonon line at 1.534 eV, followed by phonon replicas and Mn local modes.

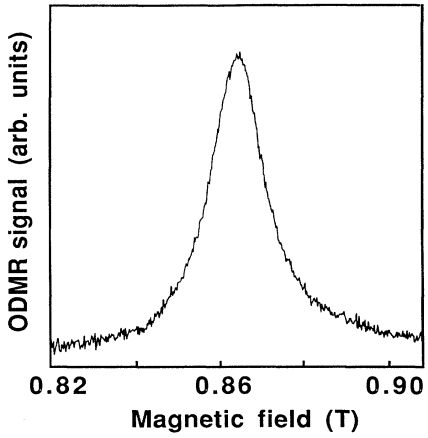

FIG. 2. ODMR spectrum measured on the GAP:$Mn^{2+}({}^4T_1 \rightarrow {}^6A_1)$ emission at $T = 1.6$ K ($\Delta I/I \approx 5\%$, where I is the PL intensity) with a microwave frequency of 24 GHz (200 mW). From the arguments presented in this paper, it is concluded that the ODMR signal originates from the S donor.

by TA-phonon replicas spaced by intervals of 11 meV (the weak broad lines in the inset) and Mn local modes spaced by intervals of 39.5 meV (the sharp lines in the inset).

Using above-band-gap excitation and detecting the microwave-induced changes of the PL in phase with the chopped microwaves during the ODMR experiments, we observe an isotropic spin-resonance signal at $g = 1.99 \pm 0.01$ with a half-width of 150 G (see Fig. 2). Using 200 mW microwave power, the ODMR signal appears as $\approx 5\%$ increase of the total luminescence.

Besides the Mn^{2+} emission, above-band-gap excitation showed only a weak PL band centerd at 1.9 eV with an intensity of a factor of 100 lower than that of the internal Mn^{2+} PL band, but no S-related exciton- or donor-acceptor recombination in the near-band-gap region could be observed. The PL band at 1.9 eV, which is absent using below-band-gap excitation, is probably due to recombination involving the neutral charge state of the phosphorus antisite.[11,12]

Below-band-gap excitation in the 1.95–2.0-eV range did give rise to a strong Mn^{2+} PL signal. The same ODMR signal is observed for below-gap as for above-gap excitation (see Fig. 2).

B. Photoluminescence excitation

In the PLE experiments, the Mn^{2+} emission was detected at fixed energy (1.3 eV), while the excitation wavelength was scanned. As shown in Fig. 3 (data obtained with the lamp-monochromator system), the internal Mn^{2+} luminescence can be excited with below-band-gap energy, with the first onset at approximately 1.95 eV, followed by a second onset at approximately 2.2 eV. Above 2.3 eV (not shown in Fig. 3) the intensity decreases, probably due to increased adsorption near and above the band gap (the band-gap energy of GaP is 2.35 eV at 4.2 K). The increased absorption causes an increased excitation density in the near-surface region where the influence of nonradiative capture processes dominate.

C. Temperature dependence of the emission

More insight into the Mn^{2+} emission process can be gained from a study of the temperature dependence of the emission, since the thermal quenching of the emission very often gives information on the binding energy of the bound particles (electron, hole, or exciton) or, alternatively, on the properties of the corresponding excited states.

The temperature dependence of the luminescence intensity was studied from 9 up to 218 K. For higher temperatures the intensity was too low to be detected. The PL intensity decreases slowly from 9 to 100 K, while a

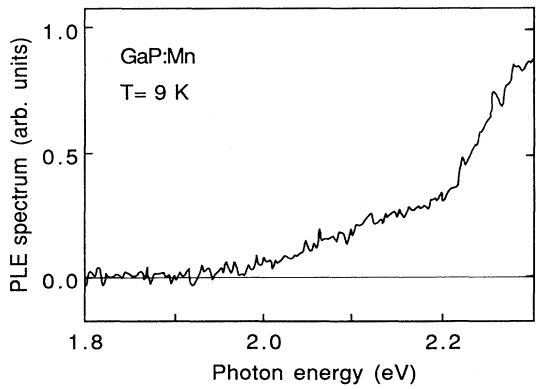

FIG. 3. PLE spectrum of the GaP:$Mn^{2+}({}^4T_1 \rightarrow {}^6A_1)$ emission obtained at $T = 9$ K using a tungsten-halogen lamp-monochromator system. The emission energy was fixed at 1.3 eV.

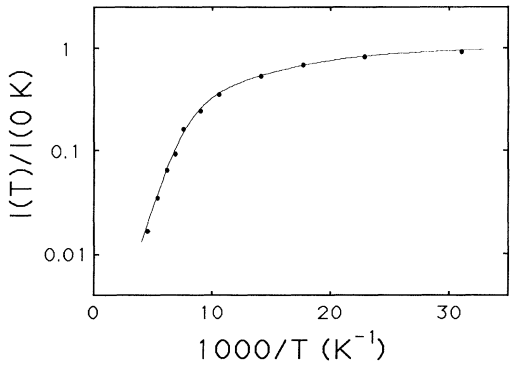

FIG. 4. Arrhenius plot of the luminescence intensity of the internal ($^4T_1 \rightarrow {}^6A_1$) transition of Mn^{2+}. The solid line is a fit to the experimental data (solid circles) using the expression given in the text.

more rapid decrease is observed at temperatures above 100 K, as shown in the Arrhenius plot in Fig. 4. The temperature dependence was analyzed using the following expression:[13]

$$I(T)/I(0)=1/(1+C_1 e^{-T_1/T}+C_2 e^{-T_2/T}) ,$$

where $I(0)$ and $I(T)$ are the intensities at 0 K and temperature T, C_1, and C_2 are constants and $k_B T_1$ and $k_B T_2$ are activation energies. The behavior of the PL intensity over the whole temperature range was fitted with $C_1=2.2\times10^3$, $k_B T_1=74$ meV, $C_2=8.4$, and $k_B T_2=14$ meV.

IV. DISCUSSION

The two pronounced onsets in the PLE spectrum (Fig. 3) are suggestive of photoionization transitions. From the EPR results we can infer that the Fermi level is above the Mn^{2+}/Mn^{3+} level at $E_V+0.4$ eV.[1,14] For an ionization transition from Mn^{2+} to the lowest conduction-band (CB) minimum at X_1 ($Mn^{2+} \rightarrow Mn^{3+}+e_{CB}$), an energy of 1.95 eV is needed. This is in agreement with our experimental observation and gives an independent confirmation of the position of the Mn^{2+}/Mn^{3+} acceptor level at 0.4 ± 0.05 eV above the valence band. The second onset at 2.2 eV could in principle originate from an ionization transition to a higher conduction-band minimum, e.g., X_3. The energy separation between X_1 and X_3 is 0.355 eV (Ref. 15) and, therefore, the threshold for such a transition should be close to the band-gap energy at 2.3 eV, which is clearly higher than the experimental value of ≈2.2 eV. The value of the binding energy of the S donor is, however, 107 meV below the conduction band.[15] It is therefore more likely that the transition at ≈2.2 eV arises from a valence-band to shallow-donor transition. This interpretation is also consistent with the temperature dependence (see below).

The observed activation energy of 74 meV in the temperature dependence of the emission intensity is clearly not the same as the binding energy (400 meV) of the acceptor. This is in contrast to GaAs:Mn (Ref. 16) and InP:Mn (Ref. 17), where the thermal quenching of the emission is activated by an energy equal to the ground-state binding energy. Instead, it is very close to the ground-state thermal binding energy of S.[15]

From the PLE and thermal quenching results a model for the recombination can be constructed. For below-band-gap excitation (from 1.95 to 2.2 eV) Mn^{2+} is photoionized by the excitation light,

$$Mn^{2+}+h\nu \rightarrow Mn^{3+}+e_{CB}+ \rightarrow Mn^{3+}+e_D ,$$

where e_D is a donor-bound electron. The system relaxes to equilibrium by the electron capture of Mn^{3+}, thus creating Mn^{2+} in the excited $^4T_1$ state. In the intermediate step the electron is captured by the shallow donor S. The behavior of the emission at low temperature, with the quenching activation energy of 14 meV, might be a result of the fact that the electron capture proceeds via Rydberg excited states of the donor.[18] From there, via the ground state of the donor, a transfer to the excited state of $Mn^{2+}(^4T_1)$ proceeds. This transition may be radiative (but outside the range of the Ge detector; ≤0.65 eV) or nonradiative. Based on the time dependence of the photoluminescence of Fe^{2+} in n-type InP:Fe, a very similar model, including a shallow level, was discussed.[19] The shallow level was tentatively ascribed to an electron weakly bound to Fe^{3+} by the central-cell potential. The capture from the shallow level to the deep-level $Fe^{2+}(^5T_2)$ would involve the recombination of the weakly bound electron with the hole tightly bound to the Fe^{3+} core. The exciton composed of a weakly bound electron and tightly bound hole has indeed been observed in recent absorption measurements.[20] In the case of Mn in GaP, we suggest that the S donor plays this role.

For excitation energies between 2.2 eV and the band gap, Mn is excited by the valence-band to shallow-donor transition,

$$Mn^{2+}+h\nu \rightarrow Mn^{2+}+e_D+h_{VB} \rightarrow Mn^{3+}+e_D ,$$

the hole being trapped by Mn^{2+}, thus creating Mn^{3+}. The donor electron is subsequently transferred from the shallow-donor state to the excited state of Mn^{2+}, where the PL originates.

For above-band-gap energy, photoexcited electrons and holes are created, followed by hole capture by Mn^{2+} and the subsequent capture of the electron by Mn^{3+} in a two-step capture process involving the shallow donor, as described above:

$$Mn^{2+}+h\nu \rightarrow Mn^{2+}+e_{CB}+h_{VB} \rightarrow Mn^{3+}+e_{CB} .$$

The ODMR results remain to be explained. Based on the similarities between the spin-resonance properties studied here and those of shallow donors (S,Se,Te) in GaP,[21,22] the involvement of S in the recombination mechanisms discussed above, and previous findings on indirect spin-resonance mechanisms in III-V and II-VI semiconductors,[22,23] it is concluded that the ODMR signal detected on the Mn^{2+} internal emission originates from the S donors. As noted in previous studies of ZnSe:Fe (Ref. 24) the magnetic resonance might modulate not only the luminescence transition itself, but also

the energy-transfer mechanisms. The spin-dependent transfer mechanism in the GaP:(Mn,S) system cannot be directly inferred from the experiments, but the increase of the PL intensity at resonance can be qualitatively explained with a simple model. The five d electrons in the ${}^6A_1(S=\frac{5}{2})$ ground state of Mn^{2+} all have their spins oriented in the same direction, for example, spin up, along the magnetic field. In the excited ${}^4T_1(S=\frac{3}{2})$ state, one of the five electrons has a spin of opposite direction (spin down). As the ${}^4T_1$ state is populated preferentially via the S donor, spin-down electrons are required, assuming that no spin flip occurs in the electron transfer from S to Mn. This would lead to a depletion of the S donors with spin-down electrons, which would in turn limit the emission from the ${}^4T_1$ state. At spin resonance, spin-up electrons bound to the S atoms will be converted to spin-down electrons, thus increasing the rate of excitation transfer to the $Mn^{2+}({}^4T_1)$ state and hence the internal Mn^{2+} luminescence.

V. CONCLUSIONS

The internal $({}^4T_1 \rightarrow {}^6A_1)$ luminescence of Mn^{2+} in GaP was investigated by PL and PLE spectroscopy, temperature-dependent PL quenching, and ODMR. All the experimental results can be explained by a model of spin-dependent excitation transfer from a S shallow donor state to the ${}^4T_1$ excited state of Mn^{2+}. GaP:(Mn,S) thus presents an unusually clearcut case of a system in which ODMR arises from spin-dependent excitation transfer between two impurities.

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