Transfer processes for excitons bound to complex defects in GaP studied by optical detection of magnetic resonance

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A comprehensive discussion of relevant transfer processes for excitons bound to complex defects in GaP is presented on the basis of experimental studies by optically detected magnetic resonance (ODMR). A new experimental procedure is applied for determination of the efficiency of the energy migration processes among complex defects in the GaP lattice. The role of phonon interaction in the transfer transitions is discussed, with the example of excitation-energy transfer from shallow donor-acceptor pairs in GaP to excitons bound at complex isoelectronic defects. It is explained that the sign of the sensitizer ODMR signal may relate to the nature of the phonon interaction. The relevant ODMR signal is positive for "purely" electronic transitions or for one-site phonon interaction and it may be observed as negative for two-site phonon interactions in the transfer process. The data presented prove the quenching action of the antisite-related complex defects on the GaP visible emission. The mechanism responsible for photoluminescence quenching in this case is shown to be excitation-energy transfer, probably due to phonon-assisted tunneling of bound excitons.

I. INTRODUCTION

Transfer processes for excitons bound to complex defects in GaP are studied in this work, by means of optically detected magnetic resonance (ODMR). These processes are of high interest since they can often limit the efficiency of radiative recombination processes, via energy transfer to nonradiative recombination centers. In addition, it is shown to be very important to understand the role of such transfer processes in order to interpret ODMR data for defects in semiconductors in a proper way.

If a light-emitting defect system is placed in a magnetic field the photoluminescence (PL) intensity may be affected, since the relevant recombination processes are subject to spin selection rules. This can be readily explained for a case of a recombining donor-acceptor pair (DAP) with two centers of $s=\frac{1}{2}$ configuration, or for the quite common spin triplet configuration of a bound-exciton (BE) system.[1] In both cases an excited state has a strongly emitting singlet configuration (antiparallel spins) and a slowly emitting spin triplet configuration. The basis of the optically-detected-magnetic-resonance technique is a change of the spin population of the sublevels of the excited (BE) state, by inducing magnetic resonance transitions between them. By such transitions some of the excess population of the slowly emitting states is transferred to fast emitting ones, and hence an increase of the emission intensity will be concomitant with the relevant magnetic resonance transition.[2-6] The above means that a magnetic resonance [electron-spin resonance (ESR)] of the excited state of an emitting center may be detected by observing changes of the PL in the resonance, either as a change of its total intensity or as a change of the polarization pattern. In ODMR, therefore, two powerful techniques are coupled—ESR and PL. In many cases the application of ODMR has allowed for direct identification of the nature of the emitting center, and of the recombination mechanism. The numerous successes of this technique have also unfortunately been accompanied by some evident misinterpretations.

It has been shown on several occasions that the ODMR signals observed may not be directly related to the emitting center, and that they may come from a ground state or an excited state of some other center, linked with the emitting one by a spin-dependent interaction.[7-14] Different spin-dependent mechanisms have been considered to explain such a linking.[8,11-13,15]

In this paper we utilize the common observation of an ODMR signal due to spin-dependent energy transfer to study the energy transfer processes between different BE systems, from DAP's to BE's and vice versa, and also the energy migration from radiative recombination centers to PL quenching centers, such as the antisite-related defects in GaP.

This paper is organized in the following manner. In Sec. II a short description of the experimental techniques used is presented. This is an important part of this paper, since a new approach to the studies of transfer processes is presented. We propose an extension of the standard ODMR measurements with studies of dye-laser-excited excitation spectra of the ODMR signals.

The relevant experimental results and their interpretation are given together in Sec. III (Discussion) of this paper. In this section the impact of efficient transfer processes between BE's or DAP's and BE's on the ODMR signals of the emitting centers is discussed. The new experimental approach to the studies of the electronic en-

ergy transfer is demonstrated on an example of our recent studies of BE's bound at complex defects in GaP.

The case of "purely" electronic and of phonon-assisted energy transfer processes is discussed, and related experimental results are presented. The discussion is supplemented by a short comment on the possible effects of the Zeeman energy transfer (spin cross-relaxation effects) on the ODMR data.

II. EXPERIMENTAL

The ODMR measurements have been performed on a modified Bruker 200D-SRC X-band (9 GHz) ESR spectrometer, equipped with an Oxford Instruments He-flow cryostat (Oxford ESR 10) and a cylindrical cavity, allowing for optical access from all directions. This system allowed for variation of sample temperatures down to 2 K, and a microwave power up to 600 mW could be used, chopped by a p-i-n diode at one of the chopping frequencies available (37.5 Hz, 375 Hz, 1.5 kHz, 6 kHz, and 12 kHz). An external oscillator could also be used, with a possibility of continuous change of this chopping frequency.

Optical excitation was obtained from an Ar^+ laser (Coherent Innova 100). The 5145-Å line has been standardly used for the GaP samples studied. A variety of optical detection systems has been applied, depending on the emission range. These have been S20- and S1-type photomultipliers or a nitrogen cooled North-Coast EO 817 Ge detector. Experiments could be performed in both the Faraday and the Voigt configurations.

For the spectral dependence of the ODMR signal (ODMR-PL) the magnetic field has been set at resonance and a Jobin-Yvon 0.25-m grating monochromator has been used to disperse the emission. In the measurements we detect the strength of the relevant ODMR signal as a function of the emission spectral region. Such an experiment allows for a precise determination of which emission a given ODMR signal is linked to.

The excitation spectrum of the ODMR signals (ODMR-PLE) has been measured by employing a Coherent 590 tunable dye laser as an excitation source, pumped by an Ar^+ laser. In this experiment the magnetic field has been set at resonance, and the emission has been selected either by an appropriate filter or a monochromator. The dependence of the ODMR signal strength has been measured as a function of the excitation spectral wavelength, and the results in this case have been corrected for the wavelength dependence of tunable laser output. This has been done by separate measurements of the PL intensity as a function of the excitation wavelength, performed in the same experimental setup as used for ODMR-PLE investigations. For the band gap or the near-band-gap excitations, corrections for the variation in the effective penetration depths may also be necessary. The information obtained from such an experiment is similar to the one obtained from the standard PL excitation (PLE) data, with an additional advantage of the possibility of direct determination of the recombination mechanism and the identity of the emitting center(s). We will show below that such an approach is especially a suitable tool for studies of energy transfer processes.

A variety of GaP samples have been used in the measurements. These have been either bulk or solution grown crystals doped by diffusion with copper, lithium, nitrogen, etc. Diffusion temperatures have been selected from the range of 400–1000 °C. More details on the sample preparation procedure can be found in the original papers referred to in the discussion below.

III. DISCUSSION OF DIFFERENT EXCITATION TRANSFER MECHANISMS IN RELATION TO EXPERIMENTAL DATA FROM ODMR

As indicated in the Introduction a transfer transition may lead to the observation of an ODMR signal from one center on the emission of another center. In what follows we shall discuss a possible application of the ODMR to studies of energy transfer processes. Two distinctly different cases of electronic energy transfer are discussed. First, the "purely" electronic transition is treated, followed by a discussion of phonon-assisted transfer.

A. Electronic energy transfer

A first theoretical approach to transfer effects in ODMR was given by Davies.[8] He indicated that the ODMR signal of the PL quenching center may not necessarily be observed as a decrease of the PL intensity in the resonance, as observed previously (e.g., Refs. 16 and 17), but positive signals (increase of the PL intensity in the resonance) may be observed as well.[18] This is a consequence of the similar selection rules ruling the radiative and energy transfer transitions, as can be easily demonstrated when classical models of Förster[19] and Dexter[20] are analyzed. For interaction times much longer than the characteristic quantum-mechanical frequency of the system (the time associated with the excitation transfer is much longer than the vibrational relaxation time), time-dependent perturbation theory can be applied.[19] In this approach the transfer probability per unit time is[19,20]

$$P_{\text{transfer}} = \frac{2\pi}{\hbar} |M_{\text{transfer}}|^2 \delta(E) , \tag{1}$$

where M_{transfer} of the form $|\langle \hat{H}_{\text{int}} \rangle|$ is the transfer transition matrix element and $\hat{H}_{\text{int}}$ is an interaction Hamiltonian, $\delta(E)$ is an energy δ function, ensuring the energy conservation during the transfer.

For complex defect systems various interactions can lead to an energy transfer between defect centers, and the identity of these interactions may, in general, not be known. An electric dipole-dipole mechanism is often assumed to be dominant. For this mechanism the interaction Hamiltonian takes the form

$$\hat{H}_{\text{DD}} = \frac{e^2}{4\pi\varepsilon\varepsilon_0 R^3} \left[\mathbf{r}_s \mathbf{r}_f - \frac{3(\mathbf{r}_s \cdot \mathbf{R})(r_f \cdot \mathbf{R})}{R^2} \right] , \tag{2}$$

where $\mathbf{r}_s = \sum_i \mathbf{r}_{si}$, $\mathbf{r}_f = \sum_i \mathbf{r}_{fi}$ are the summations over the positions of all electrons of energy transfer sensitizer and

fluorescer, respectively, measured from their nuclei. The transfer rate is

$$P_{DD}=\frac{3h^4c^4Q_f}{4\pi n^4\tau_R R^6\langle E^4\rangle}\int f_s(E)F_f(E)dE\ , \tag{3}$$

where τ_R is the radiative lifetime of the sensitizer, R is the separation between the sensitizer and fluorescer ions, Q_f is the integrated absorption cross section of the fluorescer in units of area times energy, n is the index of refraction of the host material, and the integral represents the area of the spectral overlap between emission and absorption of the transfer sensitizer and fluorescer ion, respectively. $f_s(E)$ and $F_f(E)$ are the normalized shape functions for the spectral emission and absorption, proportional to the following matrix elements: $|\langle\psi_s^*|\hat{r}_s|\psi_s\rangle|^2$ and $|\langle\psi_f|\hat{r}_f|\psi_f^*\rangle|^2$, respectively. $\psi_{s,f}^*$ and $\psi_{s,f}$ denote the excited and ground states of the sensitizer and fluorescer systems, respectively.

For further discussion it is important to note that the same matrix elements are obtained when calculating the transition rates for electric-dipole-induced emission of the sensitizer and absorption of the fluorescer. For this reason any magnetic resonance transition which promotes the emission of the energy sensitizer should also promote the energy transfer, if efficient.[8] In consequence, on the emission of the fluorescer a positive ODMR signal of the sensitizer may be observed. Such a possibility may lead to a misinterpretation of the ODMR spectra, as indicated by Davies.[8]

A similar result is obtained if one applies the more relevant theory of Schaffer and Williams.[21] These authors extended the model of Förster and Dexter to the case in which three centers (particles) are involved in the transfer transition, a situation typical for energy transfer from DAP's (discussed by Davies[8]) or for BE transfer processes discussed here. This also holds for higher-order multipole transfer mechanisms, and for the exchange-induced processes, also shown to be of importance.[22,23] It is tempting, therefore, to conclude that important information on transfer transitions may often be deduced from ODMR data. We will demonstrate this for the case of BE recombination processes for excitons bound at isoelectronic complex defects in GaP.

1. Experimental verification of energy transfer of bound electron-hole pairs in GaP

In Fig. 1 the ODMR spectrum of a GaP:Cu,Li crystal is shown. On the 2.172-eV BE emission due to an exciton bound at the isoelectronic so-called $(Cu\text{-}Li)_V$ defect[24,25] two positive ODMR signals are observed. A central part of the spectrum around $g\approx 2$ ($B\approx 0.33$ T) is found to be related to the exciton bound at another complex defect, the so-called 2.25-eV BE.[26] In Fig. 2 the spectral dependence (ODMR-PL) of this ODMR signal is shown. It can be seen that the ODMR signal is observed not only on 2.25-eV BE emission but on the $(Cu\text{-}Li)_V$ PL as well. This is a first indication that excitation transfer occurs between these two complex systems.[13] To verify this possibility the ODMR-PLE spectrum of the 2.25-eV BE ODMR signal has been measured. If the data shown in Fig. 2 are a fingerprint of transfer from the 2.25-eV BE to the $(Cu\text{-}Li)_V$ one, the $(Cu\text{-}Li)_V$-defect-related ODMR signal should be excited within the 2.25-eV BE PLE spectrum. The appropriate experimental results are shown in Fig. 3. The $(Cu\text{-}Li)_V$ ODMR-PLE shows an excitation spectrum from the $(Cu\text{-}Li)_V$ BE complex and another one (in fact stronger) rising above 2.25 eV, coming from 2.25-eV BE excitation. These data confirm that we deal with efficient transfer between these two BE systems. We believe that the complimentary use of the ODMR-PL and the ODMR-PLE experiments may be the only reliable way to verify if the relevant transfer processes are efficient.

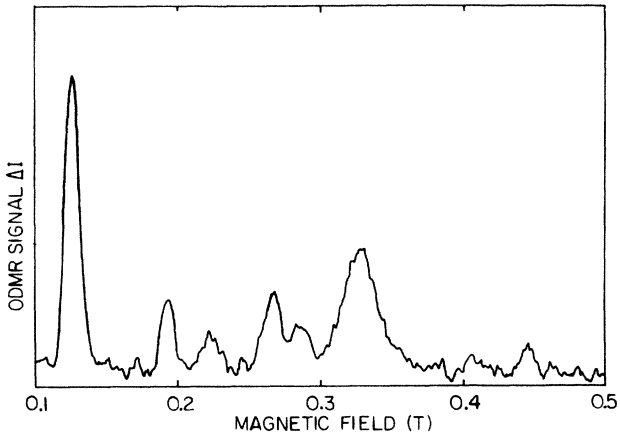

FIG. 1. The ODMR spectrum of GaP: Cu and Li at 4 K. The main structure of the spectrum is due to the spin triplet excited state of the $(Cu\text{-}Li)_V$ defect, with a no-phonon BE line at 2.172 eV. The single unresolved line at 0.33 T is due to the overlapping resonance lines of the spin triplet excited state of the 2.25-eV BE.

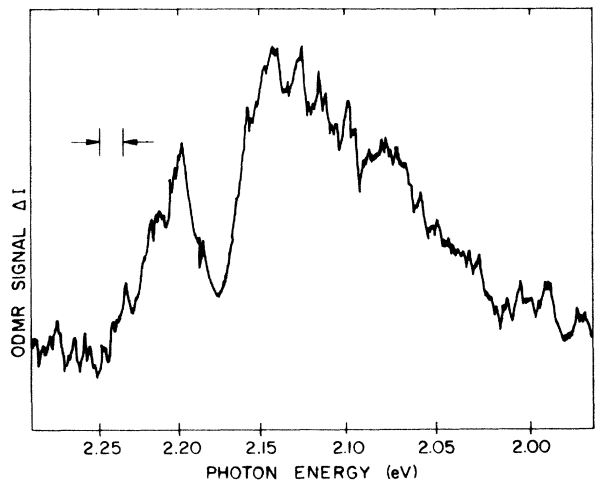

FIG. 2. The spectral dependence of the 2.25-eV BE resonance spectrum. The strong band for energies between 2 and 2.17 eV is identified with the $(Cu\text{-}Li)_V$ BE emission, indicating that strong excitation transfer occurs between the $(Cu\text{-}Li)_V$ and the 2.25-eV BE systems.

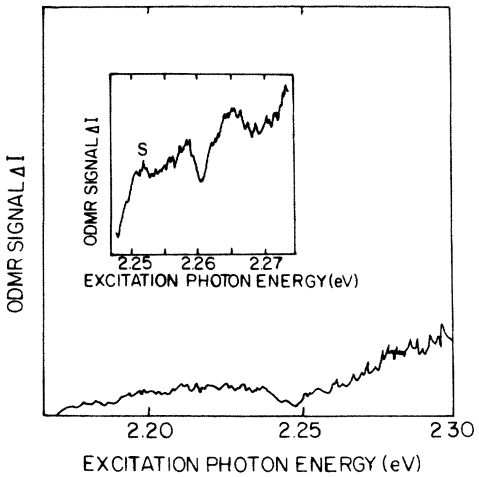

FIG. 3. The excitation spectrum of the $(Cu\text{-}Li)_V$ BE ODMR signal. In addition to a $(Cu\text{-}Li)_V$-related phonon-assisted excitation spectrum (2.15–2.25 eV) a stronger excitation band is seen with a no-phonon line at 2.25 (see inset) and with a quasi-localized phonon mode of about 7 meV (seen weakly in the spectrum shown in the inset). These features are a fingerprint of the 2.25 eV BE, confirming the energy transfer between the $(Cu\text{-}Li)_V$ and 2.25-eV BE systems.

The ODMR-PLE itself can be used also to measure the intracomplex excitation transitions, as discussed previously by one of the authors.[27]

B. Phonon-assisted energy transfer

In the "classical" models of Förster and Dexter a spectral overlap between the emission of the sensitizer and the absorption of the fluorescer was a prerequisite for an efficient energy transfer. However, if an energy mismatch occurs between these two spectra it must be taken away by phonons. A first extension of the transfer theory to the case of the phonon-assisted transfer has been presented by Miyakawa and Dexter.[28] For the case of phonon emission or absorption taking place at a single site formulas similar to Eqs. (1)–(3) are obtained, i.e., the transfer probability is proportional to an overlap of absorption and emission line shapes of the fluorescer and sensitizer, respectively. Both these transitions (absorption, emission) are phonon-assisted optical processes. For phonon interaction taking place at both sites active in the transfer process, the relevant transfer rate does not, however, relate directly to the spectral overlap. This means that if the transfer process is a phonon-assisted transition, the conclusions derived from Eq. (3) may no longer be valid.

The transfer rate for the phonon-assisted transitions is of the following form:[29]

$$P_{\text{transfer}}=\frac{2\pi}{\hbar}\sum_{s_1,q_1,s_2,q_2}|M_{\text{transfer}}|^2 \times\delta\left[\sum\Delta n_{s,q}\hbar\omega_{s,q}\pm\Delta E\right] \quad (4)$$

where summation in the δ function is over occupation numbers of phonons which can participate in the transfer process, s_i and q_i are the polarization indexes and phonon wave vectors of the initial (i) and final (f) states, $\Delta n_{s,q}$ is the change in the occupation number of the phonon of polarization index s and wave vector q in the i-f transition, and M_{transfer} is the transition matrix element of the form

$$M_{\text{transfer}}=\langle f|\hat{H}|i\rangle+\sum_{m_1}\frac{\langle f|\hat{H}|m_1\rangle\langle m_1|\hat{H}|i\rangle}{E_i-E_{m_1}+is} +\sum_{m_1,m_2}\frac{\langle f|\hat{H}|m_2\rangle\langle m_2|\hat{H}|m_1\rangle\langle m_1|\hat{H}|i\rangle}{(E_i-E_{m_1}+is)(E_i-E_{m_2}+is)} +\cdots, \quad (5)$$

where $\hat{H}$ is the interaction Hamiltonian which is a sum of a site-site coupling Hamiltonian (multipole interaction, exchange, etc.) and the sum of single-site phonon Hamiltonians $\sum_j\hat{H}_{(\text{ph})j}$, and s stands for a positive infinitesimal. The first term in formula (5) relates to the case of purely electronic transitions, the second describes the one-phonon-assisted transitions, etc.

A participation in the transfer transition of a variety of phonons with different polarization indexes means that a spin memory may be lost in such transitions, and the spin selection rules will no longer control the transfer efficiency. One should not, therefore, expect an observation of the ODMR signal of the transfer initial state on the PL of the transfer final state. Such a signal can, however, appear if the transfer processes efficiently compete with radiative recombination at the sensitizer center. The resonance transition which promotes the radiative recombination at the sensitizer, consequently reduces the transfer efficiency, and the ODMR signal of the initial state can be observed as a decrease of the fluorescer PL at resonance. This will be demonstrated below with an example of the DAP→BE transfer processes found to be active in Li-doped GaP crystals.

A description of the recombination process of DAP's for a case of weakly interacting pairs has been given by Dunstan and Davies.[30] The case where both donor and acceptor in the pair are spin $s=\frac{1}{2}$ centers has been discussed. The relative population of four possible sublevels of the excited state for a magnetic field different from zero depends on the pumping rate, spin relaxation times, and the recombination and transfer rates. In most cases the spin relaxation times are longer than radiative recombination times and the strongly emitting sublevels ($|+-\rangle$, $|-+\rangle$) will depopulate faster than the slowly emitting ones ($|++\rangle$, $|--\rangle$), where, e.g., by $|+-\rangle$ we denote the sublevel of the excited state of the DAP with electron-spin up, hole-spin down configuration of the donor and acceptor in the pair, respectively. This difference in the depopulation comes from quite different radiative recombination times for singlet ($|+-\rangle$, $|-+\rangle$) and triplet ($|++\rangle$, $|--\rangle$) sublevels of the DAP excited state. Due to the spin selection rules

the electronic multipole transitions to a spin singlet ground state are allowed only from singlet sublevels of the excited state. Transfer thus may come mostly from a triplet state of the DAP, whereas it can be weak compared to a radiative recombination for a singlet configuration of the pair excited state. As already indicated, the magnetic resonance transition of the sensitizer promotes its recombination and hence may be observed as a decrease of the fluorescer emission.

In the discussion given above we have shown first a case for which a positive ODMR signal from the sensitizer has been observed on fluorescer emission. For phonon-assisted transfer we have explained that the analogous signal could be negative as well. We will show here, for the first time, that in fact both cases may be realized for one system, and that depending on the experimental conditions the relevant ODMR signal may be either positive or negative. The above fact complicates considerably the interpretation of the ODMR data, but is, on the other hand, a source of important information on the nature of the transfer mechanism, whether it is a purely electronic transition or a one-site phonon-induced process, or if it is a phonon-assisted process in the sense that phonon interactions are important at both sites active in the transfer transition.

It is a well-known fact that the pair recombination rate for both radiative[31] and transfer transitions[19–21] depends on the separation of a pair in the first case and on the separation between the pair (pair acts as sensitizer) and fluorescer in the second case. It is a relatively easy task to select in the ODMR experiment signals coming from close and distant DAP's. This can be done simply by selecting the chopping frequencies.[32] For high chopping frequencies (in the range of 10 kHz) we detect mostly the resonance from closely separated pairs for which the radiative recombination is fast. For low chopping frequencies (≈ 100 Hz) more distant pairs become dominating in the ODMR spectrum. For such DAP's the transfer processes may compete with the radiative recombination, which is quite slow. The experimental results indicate that different mechanisms rule the transfer transitions for close and distant pairs. For close pairs Eq. (3) is relevant, whereas for distant pairs probably both radiative recombination and transfer transition are phonon-assisted processes described by formulas (4) and (5), i.e., phonon interactions are important at both sites taking part in the transfer transition.

Such a situation is shown for the first time for the interstitial lithium-related Li_A donor in GaP.[13] The ODMR signal from this donor has been observed not only on the appropriate DAP emission (Li_A donor, likely C_p acceptor pair), but on a range of BE spectra at lower energies as well. This example is a signature of efficient transfer transitions from "shallow" DAP's to "deeper" BE's. The ODMR-PL spectrum of the Li_A donor is shown in Fig. 4(b) together with the PL spectrum measured in the same experimental setup as used for ODMR measurement [Fig. 4(a)]. For higher chopping frequencies (1.5 and 6 kHz) the Li_A donor ODMR signal has been observed as an increase for the PL at resonance, not only for the DAP emission but for the (Cu-Li)$_{III}$, (Cu-Li)$_V$, and Li-Li-O BE spectra as well. By (Cu-Li)$_{III}$, (Cu-Li)$_V$, and Li-Li-O we labeled here the BE spectra with zero-phonon lines at 2.242 eV [(Cu-Li)$_{III}$ (Ref. 33)] 2.172 eV [(Cu-Li)$_V$ (Refs. 24 and 25)], and 2.087 eV Li-Li$_{Ga}$-O$_P$ (Ref. 34) commonly observed in our lithium- and copper-doped GaP crystals. For lower chopping frequencies (37.5 and 375 Hz), however, the Li_A donor ODMR changed its sign, and has been observed as a decrease of these BE's emissions at resonance. Such a behavior is naturally explained by the participation of phonons in the transfer transition at both sites, as discussed in detail above.

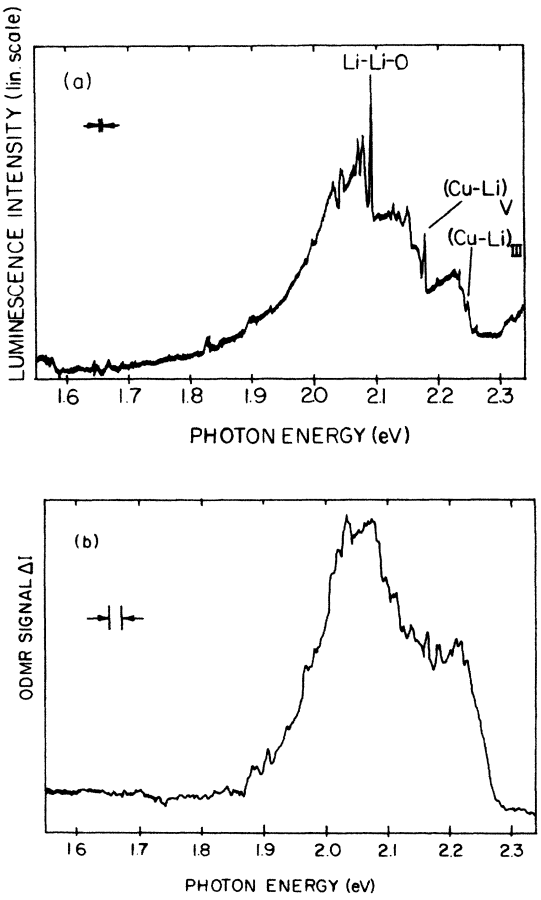

FIG. 4. High-resolution photoluminescence spectrum (a) at 2 K for a GaP:Cu,Li crystal showing the following spectra: the (Cu-Li)$_{III}$ BE (no-phonon line at 2.342 eV), the (Cu-Li)$_V$ BE (no-phonon line at 2.172 eV), and the Li-Li-O BE (no-phonon line at 2.078 eV), overlapping a shallow donor-acceptor pair (DAP) emission. In (b) the spectral dependence of the Li_A donor ODMR signal taken at 4 K is shown. In addition to the Li_A-related DAP emission with maximum at 2.22 eV, the Li_A signal is observed on the (Cu-Li)$_{III}$, (Cu-Li)$_V$, and Li-Li-O BE spectra. This indicates energy transfer from the DAP emission to lower-energy BE systems.

C. Phonon-assisted tunneling mechanism for the BE energy migration

A significant role of the phonons is especially expected in the transfer processes of the "shallow" BE's. The

large spatial extent of such BE wave functions promotes the BE tunneling over much larger distances than possible for the multipole interaction mechanism. This, for example, has been demonstrated for nitrogen bound excitons in the GaP,[35] as discussed further below.

The tunneling transfer rate can be estimated from the following formula:[36]

$$P_{\text{tun}} = \omega_0 \exp(-2R/a_{ij}) , \tag{6}$$

where ω_0 is in the range $10^{12}-10^{13}$ s^{-1}, R is the tunneling distance, and a_{ij} is an average radius of the initial and final BE states, which is about 40 Å for energy migration between N-related defects.[35] From these parameters it can be found that within the radiative recombination time for, e.g., the N-related BE at 2 K (≈ 1 μs), transfer can occur for distances as large as 200 Å and more, i.e., comparable to typical intercenter distances in the sample.

Similar to the case of the phonon-assisted transfer by the multipole interaction, a participation of phonons means that a spin memory is often lost in the transfer transition. Moreover, the N-related BE ODMR has not been observed so far. These two facts seemed to obscure the application of the ODMR for determination of transfer processes from the N-related BE's to other deeper complex defects. It means that transfer could not be verified in a standard way by observing the ODMR signal from the initial center (N) on the emission of the (final state) fluorescer. This problem is of a high practical importance because of the manufacture of the $GaAs_{1-x}P_x$:N based light-emitting devices (see, e.g., Ref. 37 for a discussion of the N-related BE's in GaP). It has been assumed that long-range energy migration processes by tunneling transitions provide a mechanism by which the BE energy is transferred to deep nonradiative centers.[37] We verify here this hypothesis, checking the efficiency of the energy transfer from the N-related BE with zero phonon line at 2.317 eV to the P_{Ga} antisite-related complex defects recently studied.[38,39] Three different P_{Ga}-Cu complex isoelectronic defects have recently been detected by ODMR via the "deep" BE emissions in the infrared with maxima at 1.0–1.1 eV.[38,39] The antisite-related defects in the III-V semiconductors are believed to be efficient eliminators of the band-edge emissions.[40] The observation of the P_{Ga}-related ODMR signals and of the appropriate infrared emissions enables us to verify a high efficiency of the transfer transitions from the N-related BE's to these complex defects by performing ODMR-PLE experiments. The experiment has been performed as explained in Sec. II above, i.e., the magnetic field has been set at one of the P_{Ga}-Cu resonance signals while the excitation energy has been scanned. The strength of the ODMR signal has been measured as a function of the excitation wavelength. The ODMR-PLE spectrum measured in this way is shown in Fig. 5. In the range of the nitrogen BE intracomplex absorption transitions a strong excitation of the P_{Ga}-Cu related ODMR signal (emission) is observed. These data are believed to be the first reliable proof that the antisite-related complex defects quench

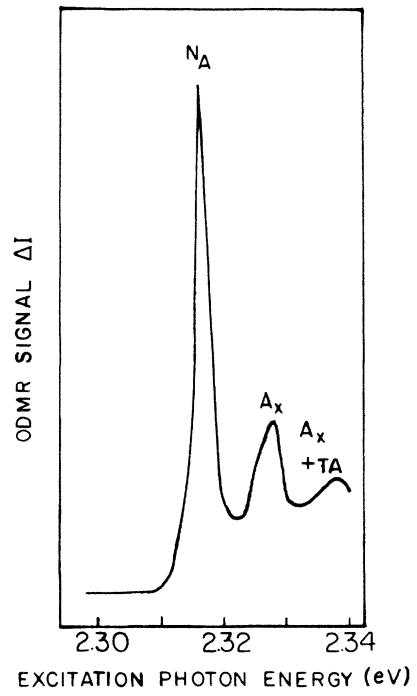

FIG. 5. The near-band-gap excitation spectrum of the P_{Ga}-related ODMR signal. This spectrum and that shown in Fig. 6 were obtained by setting the magnetic field at resonance condition, using a Coherent 590 dye laser with a Coumarin 540 dye. A clear fingerprint of the N-related PL excitation spectrum is seen, proving an efficient energy transfer from shallow N_P centers to deep P_{Ga}-related antisite complexes in GaP.

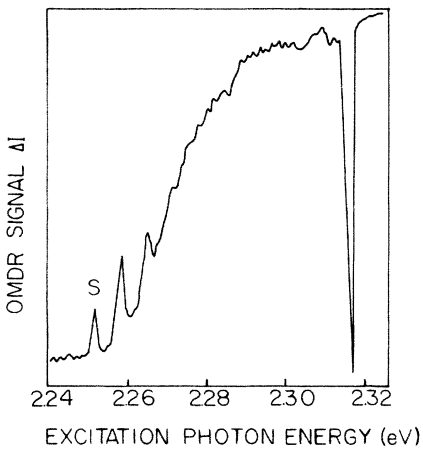

FIG. 6. The PLE-ODMR spectrum of the 2.25-eV BE system, taken at the same experimental condition as the data shown in Fig. 5. A strong reduction of the excitation efficiency occurs in the energy region coinciding with the PLE spectrum of the N_P center (2.317 eV). At lower energy a three-line structure is well resolved with the singlet (S) BE no-phonon line at 2.2508 eV. This part of the PLE-ODMR spectrum is a fingerprint of the 2.25-eV BE photoluminescence excitation spectrum (Ref. 26).

GaP visible PL due to the efficient energy migration from "shallow" BE's to these centers.[41]

For "shallow" BE fluorescence we found, however, that the energy migration processes from N centers are less efficient. This can be seen, e.g., in Fig. 6 where the ODMR-PLE spectrum is shown for 2.25-eV BE. In this case the excitation spectra of N and 2.25-eV BE's overlap and the appropriate N-related transitions are observed now as "dips" in the 2.25-eV BE ODMR-PLE spectrum. This is readily explained as being due to an efficient excitation of the N-related BE with a quite inefficient final recombination at the 2.25-eV BE system. This result is consistent with the general description of the energy migration processes. It has been assumed that the excitation migrates fast between various shallow BE complexes until it is trapped at a deep recombination center such as, e.g., the antisite-related complex at which either nonradiative or infrared recombination occurs. One should, therefore, expect strong effects in ODMR-PLE for a deep P_{Ga}-Cu complex acting as the energy trap, and a quite inefficient PLE influence for the N$\rightarrow$2.25-eV BE case, as in fact confirmed by our experimental data. This is the first direct proof of the above hypothesis for the energy transfer mechanism.

D. Cross relaxation

The discussion given above has been limited to the case of electronic energy transfer. A totally different situation arises when the spin cross relaxation is efficient. By cross relaxation we understand the exchange of a quantum of energy between two nearby centers, whose resonance frequencies coincide, so that they undergo a spin flip-flop transition. It is important in this case that the spin-spin relaxation times between the two close systems are much shorter than the spin-lattice relaxation times, and hence the cross relaxation may be a more effective process in removing energy from a "hot" spin system by transferring it to another "cold" spin system.[42] Hence, the cross relaxation is an exchange of the Zeeman energy between two centers, but without interchange of electronic excitation energy. In this process center 1 undergoes first a magnetic resonance transition, and then it exchanges its spin excitation energy with center 2 by a spin flip-flop process. In turn, a spin flop in center 2, if being in the excited state, may promote its radiative recombination. It is clear then that the exchange of Zeeman excitation energy may lead also to observation of the resonance signal of one center (in its ground or excited state) on the emission of another one. Kluge and Donecker[12] have shown that the cross-relaxation mechanism of transfer may lead to very strong effects in ODMR studies. The resonance signal of the Mn^{2+} ground state has been observed on every DAP emission in the visible range for Mn-doped ZnS and ZnSe crystals.[12]

It is natural to assume that the cross-relaxation processes should be of importance also in ODMR studies of BE emissions. In this case a triplet ($S=1$) spin configuration is often found[1] with magnetic resonance frequencies coinciding for different BE systems and DAP transitions, which is a requirement for efficient spin flip-flop transitions. Moreover, due to their large extent, the BE wave functions often may overlap, satisfying the second condition for fast mutual spin flips. It may be possible that efficient spin-spin interactions are one of the reasons for a large width of the resonance signals generally observed in ODMR experiments for III-V semiconductors. We believe that the common feature in our studies of the GaP PL, i.e., the observation of a shallow donor ODMR signal on different deep BE spectra, is evidence of the cross-relaxation link between donor and deep BE's. We emphasize this fact, because we can now distinguish quite easily between these two extreme cases of the energy-transfer–electronic-energy-transfer versus Zeeman energy transfer, by performing the ODMR PLE measurements introduced here. In the latter case (cross relaxation) the excitation spectra of relevant ODMR signals should be different since the electronic excitation energy is not transferred. Otherwise, the cross-relaxation processes may affect the ODMR spectra, and it should be emphasized that the observation of the ODMR signal from one center on the emission of another one may not necessarily mean that we deal with an electronic energy transfer between them, as erroneously claimed in many previous reports on ODMR data. The ODMR-PLE, as introduced in this paper, should be performed to verify the transfer hypothesis.

IV. CONCLUSIONS

We have introduced in this paper an experimental procedure enabling verification of the existence of the electronic energy transfer, and proof of its efficiency. It is shown that by extending the standard ODMR technique by the complementary ODMR-PL and ODMR-PLE measurements the required unambiguity of the experimental results can usually be obtained. Especially interesting is the possibility of determination of the role of phonon interactions in the transfer transitions. We discuss how to distinguish on the basis of ODMR data between "purely" electronic, eventually one-site phonon interaction transfer transitions, and two-site phonon interaction processes. Our recent ODMR results also prove that the ODMR yields precise information on energy migration processes between BE's bound at complex isoelectronic defects in GaP. We show, e.g., that the deep antisite-related complex defects act as energy sinks, and that energy transfer is the mechanism responsible for this effect. A fast energy migration from the N-related BE to P_{Ga}-Cu complex could be proved directly even if the ODMR signal of the N-related complex could not be detected. This is an important extension of the power of the ODMR technique.

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[1]B. Monemar, U. Lindefelt, and M. E. Pistol, J. Lumin. **36**, 149 (1986).

[2]S. Geschwind, in *Electron Paramagnetic Resonance,* edited by S. Geschwind (Plenum, New York, 1972).

[3]J. J. Davies, Contemp. Phys. **17**, 275 (1976).

[4]B. C. Cavenett, Adv. Phys. **30**, 475 (1981).

[5]J. J. Davies, J. E. Nicholls, and B. C. Cavenett, Semicond. Insulators **4**, 101 (1978).

[6]R. T. Cox, Rev. Phys. Appl. **15**, 653 (1980).

[7]M. Gal, B. C. Cavenett, and P. J. Dean, J. Phys. C **14**, 1507 (1981).

[8]J. J. Davies, J. Phys. C **16**, L867 (1983).

[9]K. P. O'Donnell, K. M. Lee, and G. D. Watkins, J. Phys. C **16**, L723 (1983).

[10]B. C. Cavenett, S. P. Depinna, I. G. Austin, and T. M. Searle, Philos. Mag. B **48**, 169 (1983).

[11]A. V. Malyavkin, Phys. Status Solidi B **115**, 353 (1983).

[12]J. Kluge and J. Donecker, Phys. Status Solidi A **81**, 675 (1984).

[13]M. Godlewski, W. M. Chen, and B. Monemar, Phys. Rev. B **33**, 8246 (1986).

[14]W. M. Chen and B. Monemar (unpublished).

[15]K. Morigaki, N. Kishimoto, and D. J. Lepine, Solid State Commun. **17**, 1017 (1975).

[16]K. Morigaki, D. J. Dunstan, B. C. Cavenett, P. Dawson, J. E. Nicholls, S. Nita, and K. Shimakawa, Solid State Commun. **26**, 981 (1978).

[17]J. L. Patel, J. J. Davies, J. E. Nicholls, and B. Lunn, J. Phys. C **14**, 4717 (1981).

[18]J. L. Patel, J. E. Nicholls, J. J. Davies, and B. Lunn, Solid State Commun. **43**, 385 (1982).

[19]T. Förster, Ann. Phys. (Paris) **2**, 55 (1948).

[20]D. L. Dexter, J. Chem. Phys. **21**, 836 (1953).

[21]J. Schaffer and F. Williams, Phys. Status Solidi **38**, 657 (1970).

[22]P. Kisliuk, N. C. Chang, P. L. Scott, and M. H. L. Pryce, Phys. Rev. **184**, 367 (1969).

[23]R. J. Birgeneau, J. Chem. Phys. **50**, 4282 (1969).

[24]H. P. Gislason, B. Monemar, M. E. Pistol, A. Kana'ah, and B. C. Cavenett, Phys. Rev. B **33**, 1233 (1986).

[25]W. M. Chen, B. Monemar, M. Godlewski, H. P. Gislason, and M. E. Pistol (unpublished).

[26]W. M. Chen and B. Monemar, Phys. Rev. B **36**, 7948 (1987).

[27]M. E. Pistol and B. Monemar, J. Phys. C **17**, L943 (1984).

[28]T. Miyakawa and D. L. Dexter, Phys. Rev. B **1**, 2961 (1970).

[29]T. Holstein, S. K. Lyo, and R. Orbach, in *Laser Spectroscopy of Solids,* Vol. 49 of *Topics in Applied Physics,* edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981), p. 39.

[30]D. J. Dunstan and J. J. Davies, J. Phys. C **12**, 2927 (1979).

[31]D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, Phys. Rev. **140**, A202 (1965).

[32]J. J. Davies and J. E. Nicholls, J. Phys. C **15**, 5321 (1982).

[33]H. P. Gislason, B. Monemar, M. E. Pistol, P. J. Dean, D. C. Herbert, S. Depinna, A. Kana'ah, and B. C. Cavenett, Phys. Rev. B **32**, 3958 (1985).

[34]P. J. Dean, Phys. Rev. B **4**, 2596 (1971).

[35]P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975).

[36]A. Miller and E. Abrahams, Phys. Rev. **120**, 745 (1968).

[37]P. J. Dean and D. C. Herbert, in *Excitons,* Vol. 14 of *Topics in Current Physics,* edited by K. Cho (Springer-Verlag, Berlin, 1979), p. 55.

[38]W. M. Chen, H. P. Gislason, and B. Monemar, Phys. Rev. B **36**, 5058 (1987).

[39]W. M. Chen, M. Godlewski, and B. Monemar, Phys. Rev. B (to be published).

[40]J. A. Van Vechten, J. Electron. Mater. **4**, 1159 (1975); *Handbook on Semiconductors,* edited by T. S. Moss (North-Holland, Amsterdam, 1982), Vol. 3, p. 1.

[41]W. M. Chen, B. Monemar, and M. Godlewski, Phys. Rev. B (to be published).

[42]A. Abragam and B. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970).