

Optical-pumping study of spin-dependent recombination in GaAs

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Optical-pumping techniques provide a convenient way to study spin-dependent recombination (SDR) processes at deep impurity centers in semiconductors. Indeed, by changing the polarization of excitation light, it is possible to modify the photoelectron spin polarization in a controlled way. This produces a change in luminescence intensity if the recombination is spin dependent and if the centers are spin polarized. The basic physical ideas which govern this type of study are discussed. Two different experimental situations are presented which show the possible effect of the external magnetic field parallel to the excitation direction. In semi-insulating GaAs, we find from an analysis of the effect on the luminescence band attributed to the EL2 center that this center is dynamically polarized by the photoelectrons, and that the spin-dependent character of the recombination at this center modifies both the free-electron concentration and polarization. These effects strongly increase with magnetic field and are approximately a factor of 3 larger than those calculated from a simple model. Possible reasons for this are discussed. The second situation we consider is the recombination on manganese acceptors in GaAs. These centers are thermodynamically polarized by the magnetic field and the corresponding SDR is conveniently monitored from the intensity of manganese emission since the photoelectron concentration is not modified by SDR. This shows the paramagnetic character of the manganese level in GaAs. The nature of this level is discussed. We emphasize that the present method can be used as a preliminary step to find the appropriate magnetic field and luminescence wavelength for optical detection of magnetic resonance.

I. INTRODUCTION

The fact that the efficiency of a recombination process may depend on the spin of the recombining electron comes from the fact that the total spin of the electron and of the center must be conserved in the recombination, at least if the spin-orbit coupling is not too large. If one assumes, for simplicity, that the center has a spin one-half, the only initial state for which recombination is allowed is the singlet state, since the final state is a spin zero. Thus, the cross section which characterizes the recombination for a given paramagnetic center is expected to be much larger for the singlet state than for the triplet state.

The existence of spin-dependent recombination (SDR) processes in semiconductors is now well established, and has been used to obtain a tremendous amount of information on paramagnetic recombination centers by monitoring the change at resonance of photoconductivity,^{1,2} luminescence,³ or more recently deep-level transient capacitance spectroscopy,⁴ (DLTS) or photovoltaic⁵ signals. However, in most of these cases, more attention was given to the information which was obtained on the relevant centers than on the spin dependence of the recombination process. We think, however, that such information is important for future studies. Indeed, in a compound such as GaAs, optical detection of magnetic resonance of deep paramagnetic centers (ODMR) seems to be difficult,⁶⁻⁸ for reasons which are not very clear (absence of sensitive light detectors beyond a wavelength of 1.7 μm , large hyperfine broadening of the resonance line,^{9,10} or efficient spin-lattice relaxation). It can then be very useful to be

able to study SDR processes in a nonresonant way, in order to find appropriate conditions for ODMR.

It was previously shown that optical-pumping techniques can be conveniently used for this application.^{11,12} Indeed, by changing the degree of circular polarization of the excitation light, it is possible to change the spin polarization of the photoelectrons.¹³ This is expected to modify the luminescence intensity if the recombination is spin dependent, provided the relevant centers are spin polarized. This has been observed in two different cases. First there is the work of Weisbuch and Lampel¹¹ (WL) in $\text{Ga}_{1-x}\text{Al}_x\text{As}$ alloys. The second study of SDR was done in multilayers of GaAs and $\text{Ga}_{1-x}\text{Al}_x\text{As}$.¹² In both of these cases the centers were polarized due to the spin-dependent character of the recombination of spin-polarized electrons. However, although very large ($\sim 200\%$ of relative variation of luminescence intensity), these SDR effects were observed in a very small number of samples and for a very high excitation density. Moreover, in none of the above cases could the centers be identified, so that the hypothesis of spin polarization of valence holes, which explains the results without requiring any deep center to be present, cannot be ruled out.^{14,15}

We have performed a study of SDR effects in GaAs in a magnetic field parallel to excitation light direction. We have obtained the following results. (i) SDR effects of the order of several percent are observed in a wide range of samples and even for very low excitation intensities. (ii) The application of the external magnetic field is crucial for observation of these effects, either because the centers are thermodynamically polarized by the magnetic

field according to the usual Curie law, or because their dynamic polarization increases with magnetic field. (iii) We have been able to identify the relevant centers from an analysis on the various luminescence lines. We then believe that the present method can be widely used to study SDR in semiconductors.

In the present work we explain the physical ideas underlying the optical-pumping study of SDR, and we experimentally illustrate several limiting cases of interest. We present the experimental results obtained in semi-insulating GaAs where the relevant center responsible for SDR is identified with EL2,¹⁶⁻¹⁸ and in GaAs:Mn where the recombination on manganese acceptors is spin dependent. From these results, we show that the centers may be thermodynamically polarized by the magnetic field or dynamically polarized by the recombining electrons, and we show the two cases where the SDR channel is, respectively, more efficient or less efficient than the non-SDR channel in recombining the photoelectrons. In the following section we present the principles of the optical-pumping study of SDR; the results obtained in semi-insulating GaAs and in GaAs:Mn are explained, respectively, in Secs. III and IV.

II. PRINCIPLES

The main feature of the optical-pumping study of SDR is that one modifies, in a controlled way, the polarization of the photoelectrons by a change of the polarization of the excitation light. We monitor the resulting variation of *steady-state* luminescence intensity that occurs if an SDR channel exists.

In order to give the basic principles underlying the optical-pumping study of SDR in semiconductors, we first recall that circularly polarized excitation of the crystal allows us to create spin-polarized electrons.¹³ Furthermore, in all cubic crystals, the initial polarization of the photoelectrons, that is, the polarization at the instant of creation in the conduction band, is ± 0.5 for σ^\mp -polarized light and zero for a linearly polarized excitation (π) or a nonpolarized excitation. Therefore, by using optical-pumping techniques, it is possible to change the sign, or to cancel the mean photoelectronic spin, by simply changing the excitation-light polarization from σ^\pm to σ^\mp or from σ^\pm to π . In the present work we are concerned with the resulting change of luminescence intensity that occurs if the recombination is spin dependent.

The calculation of the relative variation $\Delta I/I$ of the luminescence intensity, which we shall refer to in the following as the SDR signal, can be done straightforwardly in the framework of a model where we neglect the recombination of the triplet state formed by the electron and by the center. This implies that the center has a spin $\frac{1}{2}$. The behavior of the system in the case of a spin larger than $\frac{1}{2}$ is essentially the same. Thus, the recombination rate is proportional to $\text{Tr}(\rho P_s)/\text{Tr}\rho$, where ρ is the density matrix of the electron-center system and P_s is the projection operator for the singlet state. This rate could then be calculated exactly by using a quantum treatment similar to that of Haberkorn and Dietz.¹⁹ For simplicity, we shall not follow this formalism and we shall limit ourselves to a

classical treatment involving the resolution of rate equations. In Sec. II A we shall first consider the recombination of free electrons. The recombination within a pair, where the correlation between the electron and the center has been shown to play an important role,²⁰ will be discussed later.

A. Recombination of free electrons

The rate equations which govern the recombination of free electrons can be written in the following form:

$$\frac{dn_{\pm}}{dt} = g_{\pm} - \frac{1}{2T_1}(n_{\pm} - n_{\mp}) - \frac{1}{2}\sigma_s v N_{\mp} n_{\pm} - \frac{n_{\pm}}{\tau'}, \quad (2.1)$$

where g_{\pm} is the rate of creation of electrons of spin $\pm \frac{1}{2}$, n_{\pm} (N_{\pm}) is the concentration of electrons (centers) of spin $\pm \frac{1}{2}$, σ_s is the singlet recombination cross section, and v is the free-electron thermal velocity. This rate equation is very similar to that used by WL.¹¹ The main difference is that here we suppose that the SDR channel is not the only recombination channel, thus allowing for the existence of a non-SDR channel of characteristic time τ' . Indeed, it will be seen below that the experimental results strongly depend on the relative efficiency of these two channels. Steady state of this equation allows us to find the total electron concentration $n = n_+ + n_-$,

$$n = g \left[\frac{1}{4}\sigma_s v N (1 - p_c p) + 1/\tau' \right]^{-1}, \quad (2.2)$$

where $N = N_+ + N_-$ is the concentration of centers available for trapping an electron, $g = g_+ + g_-$. The quantity p_c given by

$$p_c = (N_+ - N_-)/(N_+ + N_-) \quad (2.3)$$

is the center polarization. The quantity $p = (n_+ - n_-)/(n_+ + n_-)$ is the electronic polarization. The above equation simply shows that the electronic steady-state concentration depends on the product $p_c p$, because the effective recombination speed due to the SDR channel is of the usual form

$$\frac{1}{\tau_{\text{SDR}}} = \frac{1}{4}\sigma_s v N (1 - p p_c). \quad (2.4)$$

This is a well-known effect which has allowed detection of magnetic resonance by photoconductivity.^{1,2} The same equation (2.1) allows us to find the value of the electronic polarization. This quantity is given by

$$p = p_0 \frac{1 + p_{\text{eff}}/p_i}{1 + p_0 p_{\text{eff}}}, \quad (2.5)$$

where p_i given by

$$p_i = \frac{(g_+ - g_-)}{(g_+ + g_-)} \quad (2.6)$$

is the initial polarization of free electrons, at the instant of creation, and is equal to ± 0.5 for σ^\mp excitation light and zero for linearly polarized (π) excitation light. The quantity p_0 , which will be referred to in the following as the optical-pumping polarization of the electrons, is the value of p in the absence of SDR and is given by

$$p_0 = p_i \frac{T_1}{T_1 + \tau}, \quad (2.7)$$

where T_1 is the electronic spin-lattice relaxation time and τ is the electronic recombination time in the absence of SDR, given by

$$\frac{1}{\tau} = \frac{1}{4} \sigma_s v N + \frac{1}{\tau'}. \quad (2.8)$$

The quantity p_{eff} is the effective polarization of the centers, and is given by

$$p_{\text{eff}} = \beta p_c, \quad (2.9)$$

where β , given by

$$\beta = \frac{\tau'}{(\frac{1}{4} \sigma_s v N)^{-1} + \tau'}, \quad (2.10)$$

gives the relative efficiencies of the SDR and of the non-SDR recombination channels. With the use of the above definitions and of Eq. (2.2), the electronic concentration n can be found to be of the form

$$n = g\tau(1 - pp_{\text{eff}})^{-1}, \quad (2.11)$$

where the term pp_{eff} is usually small since the optical-pumping polarization is generally of a few percent. Therefore, in the following we shall use the approximate formula

$$n = g\tau(1 + pp_{\text{eff}}). \quad (2.12)$$

Equations (2.5) and (2.12) are the basic equations of our system. We point out that, in the same way as the electronic concentration, the electronic polarization p depends on the polarization of the centers. This effect has two distinct origins. (i) The change in the total recombination time of the electrons due to SDR produces a modification of the usual optical-pumping polarization p_0 since the value of this last quantity is determined by the relative values of relaxation time and recombination time [Eq. (2.7)]. This effect is responsible for the term in the denominator of Eq. (2.5). (ii) The fact that the polarized centers do not trap the electrons of opposite spin with the same speed results in an accumulation of electrons of one spin (up or down) with respect to the other. This is the explanation of the term in the numerator of Eq. (2.5). In other words, the polarized centers act as a "spin filter" for the free electrons.

We now calculate the variation of luminescence intensity produced by a change of excitation-light polarization. The intensities corresponding to the two recombination channels, which are supposed to be radiative, are given by

$$I' = n / \tau' \quad (2.13)$$

and

$$I_{\text{SDR}} = n / \tau_{\text{SDR}} \quad (2.14)$$

for the non-SDR channel and the SDR channel, respectively. The variations $\Delta I'$ and ΔI_{SDR} of these intensities produced by a change in excitation-light polarization can

then be calculated straightforwardly. These quantities have opposite signs since the sum $I' + I_{\text{SDR}}$ is in steady-state conditions equal to the rate of creation g of free electrons. The ratio $(\Delta I_{\text{SDR}} / I_{\text{SDR}}) / (\Delta I' / I')$ can then be calculated straightforwardly. This ratio is quite generally not the same for σ^+ / σ^- and for σ / π modulation of excitation-light polarization, and depends on the value of the electronic polarization p and the center polarization p_c . However, if we assume that these polarizations are small with respect to unity, the above ratio is given quite simply by

$$\frac{\Delta I_{\text{SDR}}}{I_{\text{SDR}}} / \frac{\Delta I'}{I'} = \frac{\beta - 1}{\beta} \quad (2.15)$$

and becomes independent on excitation-light polarization. Since β is between 0 and 1, one sees that the two signals observed on the SDR luminescence line and on the non-SDR luminescence line have opposite signs and are, respectively, proportional to $1 - \beta$ and β . In order to discuss the above results in more detail, we now examine two limiting cases of physical significance.

1. Weak-SDR effects

If the SDR channel is not the dominant channel so that the quantity β is much smaller than unity, then both n and p are expected to be unmodified by SDR. This situation is very simple since the relative variation of luminescence intensity on the SDR channel produced by a change in excitation-light polarization is simply equal to the change of the corresponding effective recombination time given by Eq. (2.4),

$$\frac{\Delta I_{\text{SDR}}}{I_{\text{SDR}}} = \frac{\Delta \tau_{\text{SDR}}}{\tau_{\text{SDR}}} = -pp_c. \quad (2.16)$$

In this same case the intensity of the non-SDR channel does not depend on excitation-light polarization, at least in zero-order approximation. In this case, the spectroscopic study of SDR effects as a function of wavelength allows unambiguous identification of the SDR processes.

2. Strong-SDR effects

In the extreme opposite case where the SDR channel is the dominant recombination channel ($\beta \approx 1$), photoelectron concentration and polarization are modified by SDR and are therefore dependent on center polarization. An important point is that no SDR effects are expected to be observed on the SDR luminescence line, at least in zero-order approximation, since one has $I_{\text{SDR}} \approx g$. This indicates, as seen from Eq. (2.14), that a change of the recombination time produces an equally large change of photoelectron concentration. In the same conditions the intensity of the non-SDR luminescence lines reflects the modification of n .

We now discuss the value of the polarization of the centers p_c that we have introduced in the present section. Quite generally, this polarization is the sum of three terms and can be written

$$p_c = \alpha_{\text{th}} p_{\text{th}} + \alpha_{\text{h}} p_{\text{h}} + \alpha p, \quad (2.17)$$

where α_{th} , α , and α_h are numerical coefficients smaller than unity and p_{th} , p_h , and p are, respectively, the usual thermodynamic polarization of the centers by the external magnetic field according to the Curie law, the valence-hole spin polarization, and the photoelectron polarization, given by Eq. (2.5). The fact that the center polarization depends on the hole polarization simply comes from the trapping on these centers of the holes thermodynamically polarized by the magnetic field. We recall that due to their fast spin-lattice relaxation time, the valence holes have a very small optical-pumping polarization. The dependence of the polarization of the centers on the polarization of the photoelectrons, due to the third term of Eq. (2.17), simply accounts for the fact that, due to the spin-dependent character of the recombination, the electrons are able to transfer their polarization to the recombining centers. A possible mechanism for this effect, which will be referred to in the following as a dynamic polarization of the centers, is that the captured electron is of a spin antiparallel to that of the center, whereas the electron released to the valence band after capture is of either spin.^{11,12}

B. Discussion

The preceding model, summarized by Eqs. (2.5), (2.12), (2.13), and (2.14), allows us to calculate the SDR signal as well as the electronic polarization in the simple case of the recombination of free electrons on centers. In order to examine the generality of this model, we now briefly discuss two different cases of interest, where the physical picture of the system is likely to be different. The first case is the recombination within a pair such as excitonic or donor-acceptor pair. Numerous ODMR studies have shown the spin-dependent character of this recombination.³ Furthermore, Kaplan, Solomon, and Mott (KSM) have shown that in such a case, the correlation between the electron and the hole can lead to drastically larger SDR effects.²⁰ However, this type of effect is not expected to occur in our case, since the KSM model supposes that the distribution of the electron spin individually keeps its random character. Thus the effects do not depend on the electron polarization p so that this last model cannot be used to predict the dependence of recombination rate on this polarization. Furthermore, the exchange interaction which exists between the electron and the hole does not modify the spin-dependent character of the recombination, since the exchange Hamiltonian commutes with the projector P_s on the singlet state. In order to analyze the effects of correlation between electron and hole in optical-pumping conditions, we have solved the rate equations for such a system in the more specific case of a donor-acceptor pair. The rate equation for electrons of spin $\pm \frac{1}{2}$ involved in a pair where a hole is trapped on the nearby acceptor is of the form

$$\begin{aligned} \frac{dn_{\pm}}{dt} = & \sigma_e v N_h n_{f\pm} + \frac{1}{\tau_h} n_{t\pm} \\ & - \frac{1}{2T_1} (n_{\pm} - n_{\mp}) - \frac{1}{\tau'} n_{\pm} - \frac{N_h}{4\tau_s} (1 \mp p_c^{\pm}) n_{\pm}, \end{aligned} \quad (2.18)$$

where N_h and $n_{t\pm}$ are, respectively, the concentrations of pairs with no electrons, and with no hole and an electron of spin $\pm \frac{1}{2}$. The quantity $n_{f\pm}$ is the concentration of free electrons of spin $\pm \frac{1}{2}$ and σ_e is their capture cross section. The times τ_h and τ_s characterize, respectively, the trapping of valence holes on the pair and the recombination within a pair in the singlet state. Owing to the correlation between electrons and holes, we find that the polarizations p_c^{\pm} of holes involved in pairs with an electron of spin $\pm \frac{1}{2}$ are, in general, not the same.

In the extreme case where the holes are only thermodynamically polarized by the magnetic field and not dynamically polarized by the electrons, one has $p_c^+ = p_c^-$. One can see by comparing Eqs. (2.18) and (2.1) that the case of a pair combination is equivalent to the recombination of a delocalized electron, provided that one replaces p_i by the actual value of the initial polarization p_i' for electrons involved in pairs. This polarization is related to the free-electron polarization p_f and to the polarization $p^* = (n_{t+} - n_{t-}) / (n_{t+} + n_{t-})$ of electrons involved in pairs with no hole, and is given by

$$p_i' = (\tau_h \sigma_e v p_f + \alpha p^*) / (\tau_h \sigma_e v + \alpha), \quad (2.19)$$

where α is the ratio $(n_{t+} + n_{t-}) / N_h$. Thus, in this last case, the only particularity of the pair recombination lies in the difference between the optical-pumping polarizations p_0 for the two cases, and is in fact a trivial effect that can be checked independently.

In the opposite case where the hole spin-lattice relaxation time is long, so that the holes are dynamically polarized by the electrons, the effects of correlation play a role and modify the picture of the system. In order to analyze this effect quantitatively, we have solved the rate equations for this system. The final results are intricate and will not be explained in detail. We find that the concentration of electrons involved in pairs is given by an equation that is of the same form as Eq. (2.12). The only difference between the present case and the case of free-electron recombination lies in the values of the hole polarization p_c and of the modified value β^* of the parameter β , given by Eq. (2.10). The hole polarization p_c could in fact be higher than in the preceding case, since the exchange interaction between the electron and the hole provides a further process for dynamic polarization of the centers.²¹ However, we find quite generally that p_c is always smaller than the electronic polarization. Furthermore, the maximum value of the parameter β^* is found to be equal to 2,²² which is comparable with the maximum value of β which is 1. Thus, if we neglect this small enhancement, we see that the case of the pair recombination is essentially identical to the case of the free-electron recombination. Thus, in our optical-pumping conditions, the large enhancement predicted by KSM does not occur.

The second physical case which we now discuss is that where the recombination of the free electron on the center goes via the excited state of this center. Such an excited state could be an eigenstate bound by the Coulombic part of the potential created by the defect,²³ or the ground state of the defect before lattice relaxation takes place.²⁴ Recombination through an excited state of the center is probably the reason for the existence of large capture

cross sections shown in Fe for InP,²⁵ and irradiation defects in GaAs,²⁶ and is thus believed to be frequent in semiconductors. We make the assumption that the relevant SDR is that of the free electron on the excited state. If we suppose that this state is shallow and thus can be reexcited to the conduction band, for example, by impact ionization, the resulting variation of free-electron concentration is

$$\frac{\partial n}{\partial t} = \epsilon \sigma_i v N_{\text{exc}} n, \quad (2.20)$$

where N_{exc} is the concentration of centers in the excited state, σ_i is the impact ionization cross section, and ϵ is the fraction of the photoelectron population with a sufficient energy for impact ionization. The quantity v is the velocity of these electrons. One can show that, in the presence of impact ionization, the previous equations are still valid, provided, however, that the coefficient β is replaced by

$$\beta^* = \eta \beta, \quad (2.21)$$

where η given by

$$\eta = (1 - \epsilon \sigma_i v N_{\text{exc}} \tau)^{-1} \quad (2.22)$$

can be found to be a positive quantity and is a measure of the increase of n due to reexcitation of the shallow state. Thus, the quantity β^* is no longer smaller than unity, and the present effect provides an alternative mechanism for amplification of SDR effects, which does not involve pairs.

C. Experimental study of SDR effects

In order to describe the experimental method for the optical-pumping study of SDR effects, we first recall that a change of the excitation-light polarization from σ^+ to σ^- produces a change of the sign of the initial electronic polarization p_i given by Eq. (2.6), whereas a linearly polarized excitation produces nonpolarized electrons ($p_i = 0$).¹³ The comparison of results obtained by σ^+/σ^- and by σ^\pm/π modulation of excitation-light polarization allows us to determine whether the centers are dynamically polarized by the electrons, or thermodynamically polarized by the magnetic field. This comes from the fact that if the centers are only dynamically polarized by their coupling with the photoelectrons, so that p_c is proportional to p , all the relevant quantities (electron concentration and absolute value of polarization, luminescence intensities) are unchanged by a σ^+ to σ^- change of the excitation-light polarization, since the sign of $p_c p$ is not affected. On the other hand, in this last case a change of the excitation-light polarization from σ^+ to π will produce a modification of n and of p that can be monitored from the luminescence experiments. In the general case, we find from Eqs. (2.12), (2.13), and (2.14) that the SDR signals on the two lines are given by

$$\frac{\Delta I}{I} \Big|_{\sigma^+/\sigma^-} = 2ap(\alpha_{\text{th}} p_{\text{th}} + \alpha_h p_h), \quad (2.23)$$

$$\frac{\Delta I}{I} \Big|_{\sigma/\pi} = app_c \quad (2.24)$$

where $a = \beta$ for the non-SDR channel and $(\beta - 1)$ for the SDR channel. The two above equations are the fundamental equations for optical-pumping analysis of SDR. We recall that they are valid provided the polarizations of electrons and centers are weak. Another implicit assumption is that the concentration N of empty centers [Eq. (2.4)] remains constant, a condition which is fulfilled at low excitation power. The form of Eqs. (2.23) and (2.24) shows indeed that (i) dynamically polarized centers ($\alpha_{\text{th}} = \alpha_h = 0$) produce a signal for σ/π modulation, but not for σ^+/σ^- modulation of excitation-light polarization; (ii) in the case of thermodynamically polarized centers ($\alpha = 0$), the signal in the σ/π modulation is one-half the one obtained for σ^+/σ^- modulation.

We now describe the setup, situated at Ecole Polytechnique, that we have used for most of the experiments. This is a usual luminescence setup where the light source was the 7525-Å line of a krypton laser, and the luminescence detection and analysis were done by a Spex monochromator and a GaAs or Si-type photomultiplier. The samples that we used were kindly supplied by Mircea-Roussel of Laboratoires d'Electronique et de Physique Appliquées. These samples were placed in a strain-free manner on a holder in a variable temperature Dewar. The magnetic field was produced by an electromagnet for which holes in the pole pieces allowed light excitation and luminescence detection along the magnetic field direction. The maximum value of the magnetic field was 11.4 kG. In order to sensitively measure the change in luminescence intensity produced by a modification of the excitation-light polarization, we modulated this polarization from σ^+ to σ^- and from σ^\pm to π , and monitored the corresponding change of luminescence intensity with synchronous detection. This was done by a Lasermetrics Pockels cell placed on the excitation beam, which had the advantage of producing a vanishingly small modulation of the intensity of the laser light. The modulation frequency was 75 Hz. In order to minimize spurious intensity modulation effects, care was taken to place the sample normal to excitation-light direction, for which the transmission of the sample surface does not depend on polarization.

In summary, we have explained in this section the basis which allows us to analyze the spin-dependent character of free-electron recombination as well as pair recombination using optical-pumping techniques. Quite generally, SDR is likely to introduce a spin coupling between the center and the photoelectron spin reservoir, due to which the center polarization and the photoelectron polarization are interdependent. This does not happen in the case where the center spin-lattice relaxation time is sufficiently large so that the centers are mostly thermodynamically polarized by the magnetic field. We have also distinguished the strong-SDR case where the SDR channel is the dominant recombination channel for the photoelectrons and the opposite weak-SDR case.

In this work we shall present experimental illustrations for the above cases. We consider in the following section

a strong-SDR case where the centers are dynamically polarized by the photoelectrons.

III. STRONG SDR AND DYNAMICALLY POLARIZED CENTERS

A. Evidence for SDR effects

The experimental results which we shall now present were obtained in a bulk Czochralski-grown GaAs sample (No. CZ28). The luminescence of this sample at 5 K with an excitation intensity of approximately 1 W/cm^2 is shown in Fig. 1(a). The detector is a GaAs photomultiplier. One finds the donor-acceptor pair recombination peaking at 8310 \AA . The luminescence band at 8200 \AA is due to recombination of shallow states to the valence band, but no precise identification can be done due to the large width of this band. Finally, the weak line at 8520 \AA is probably a phonon replica of the donor-acceptor line, whereas no clear interpretation can be given for the $8450\text{-}\text{\AA}$ line.

The SDR results are shown in Fig. 1(b), which presents the relative variation of luminescence intensity produced by σ/π modulation of excitation-light polarization. An external magnetic field of 11.4 kG was applied parallel to the excitation-light direction. One sees that on all luminescence lines the modulation of excitation-light polarization produces a variation of ΔI of luminescence intensity. The corresponding relative variation $\Delta I/I$ is 2.3% for the donor-acceptor ($D-A$) line and 3.0% for the line at 8200 \AA . As explained in the preceding section, it is

straightforward to show the existence of centers dynamically polarized by the photoelectrons by comparing the effects of σ^+/σ^- modulation and of σ/π modulation of excitation light. Figure 1(c) presents the effects observed in the same conditions as Fig. 1(b), but for a σ^+/σ^- modulation of excitation-light polarization. In the case of the $D-A$ line, one observes a small variation ΔI , of the order of 0.3% of the luminescence signal, which changes its sign between the high-energy side and the low-energy side of the line. This shows that the observed modulation affects the position of the line rather than its intensity. This can be shown to be due to the modulation of the Zeeman energy of the electron-hole pair that occurs when the polarization of the electron is changed,²⁷ and is not due to SDR. Thus, we conclude that, in the case of the $D-A$ luminescence, the σ^+/σ^- modulation of excitation polarization does not produce any detectable SDR signal. This means that, as explained in the preceding section [Eqs. (2.23) and (2.24)], the SDR effects on this line are due to the recombination on centers which are dynamically polarized by the photoelectrons. Further analysis of the SDR results presented in Fig. 1 shows that the behavior of the two lines at 8450 and 8520 \AA is essentially the same as that of the $D-A$ line, since for these two lines the σ^+/σ^- effects are vanishingly small. The case of the line at 8200 \AA is more complicated. First, the σ^+/σ^- modulation results of Fig. 1(c) show, for this line, a signal which is comparable with that of Fig. 1(b), which proves the occurrence of centers which are thermodynamically polarized by the external field. More precise analysis as a function of the position on this line is presented in Fig. 2. This analysis shows that (i) the second SDR signal is only present at a wavelength above 8180 \AA that does not involve free electrons. (ii) The recombination of free electrons, at a wavelength below 8160 \AA , exhibits a SDR sig-

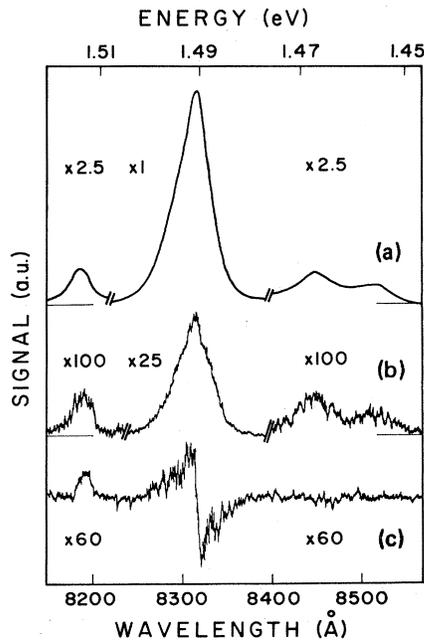


FIG. 1. Summary of the SDR effects obtained in a semi-insulating GaAs sample at 5 K. Curve (a) shows the luminescence of the sample. Curve (b) shows the variation ΔI of this luminescence, in a magnetic field of 11.4 kG , produced by a circular σ to linear π modulation of excitation-light polarization. Curve (c) shows the same variation, but for the case of a σ^+ to σ^- modulation.

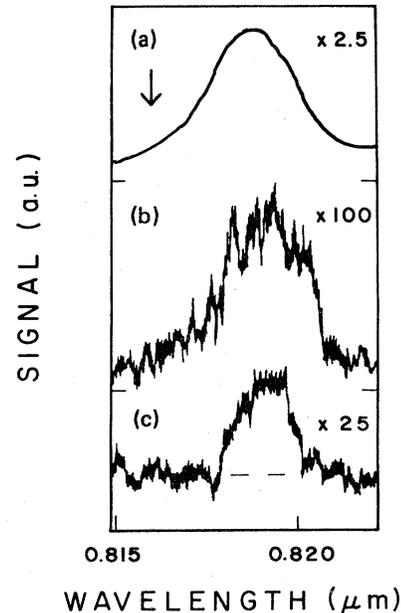


FIG. 2. Same results as Fig. 1, shown more precisely for the case of the $8200\text{-}\text{\AA}$ luminescence line. The arrow shows the position of the band gap.

nal of the same nature as that of the $D-A$ line.²⁸

In summary, the results presented in Figs. 1 and 2 reveal the existence of at least two distinct SDR channels. First, the line at 8200 Å shows the existence of centers thermodynamically polarized in the external field. These results will not be discussed further in this work. On the other hand, we have also found that centers exist, which are dynamically polarized by the photoelectrons, that allow us to observe SDR effects on the $D-A$ line, on the free-electron emission, and on the two weaker lines at lower energy.

B. Identification of the centers responsible for SDR

In this section we analyze the origin of the centers that are dynamically polarized by the photoelectrons, and which give rise to SDR. The magnitude of this SDR signal at 11.4 kG is 2.3% for the $D-A$ line. For the 8200-Å line, by subtracting the effect of the thermodynamically polarized centers discussed in the preceding subsection, we find a value of 1.9% that is comparable to that observed on the $D-A$ line. Furthermore, the field-dependence of this SDR signal, which will be discussed in Sec. III C, is the same for the various luminescence lines. Thus, we conclude that the dynamically polarized centers which give rise to the SDR signal are the same for all these lines. Their effect is to modify the free-electron concentration, which produces a corresponding variation of the intensity of all luminescence lines shown in Fig. 1.

Identification of these centers can be done straightforwardly by using Eq. (2.15). This equation predicts that if the relevant SDR recombination is radiative, the signal observed on the corresponding luminescence line should have a sign opposite to the one observed on the non-SDR luminescence lines. This shows, in particular, that shallow acceptors are not the relevant centers, since in this case this signal on the $D-A$ line should have a sign opposite to the one found on the line at 8200 Å. This is in agreement with the fact that these acceptors are unlikely to be dynamically polarized by photoelectrons, due to their short spin-lattice relaxation time.

We now show that the dominant recombination center EL2 is at the origin of the observed effects.¹⁶ This center is believed to give rise to the broad luminescence band of composite structure peaking around 0.65 eV.^{17,18} Since the recombination on EL2 is known to be the dominant recombination channel, the change of the corresponding recombination time due to SDR produces a corresponding modification of the photoelectron concentration, which is reflected in the intensity of the various luminescence lines shown in Fig. 1.

In order to verify this hypothesis, we have monitored the SDR effects on the luminescence line associated with EL2. This was done at the Naval Research Laboratory using a lead-sulfide detector. This line has an intensity at least one order of magnitude larger than that of the luminescence shown in Fig. 1. The results are shown in Fig. 3. The SDR signal observed on this line has the same polarization dependence and field dependence as those discussed in Fig. 1, and is therefore of the same origin. The relative variation $\Delta I/I$ is found to be constant

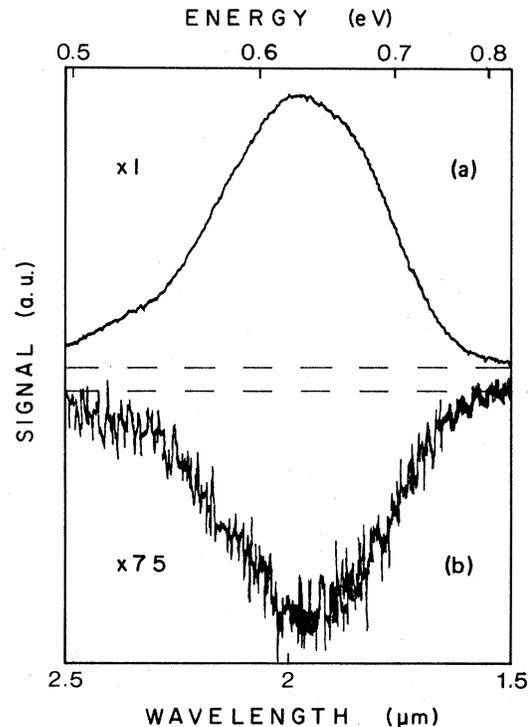


FIG. 3. SDR results obtained on the luminescence band associated with EL2. The value of the external magnetic field is 6 kG. Curve (a) shows the intensity of the luminescence. Curve (b) shows the SDR signal for σ/π modulation of excitation-light polarization. This signal has a sign opposite to the one of Fig. 1(b).

throughout the luminescence line and is of the order of 1.1%. An important result is that this signal has a sign that is opposite to the one observed on the $D-A$ line, as well as on the various luminescence lines which exhibit this effect. This is a strong indication that the EL2 centers are indeed the relevant recombination centers responsible for the observed SDR signal. If this were not the case, the intensity of the EL2 luminescence would simply reflect the modification of the photoelectron concentration, and would show an SDR signal of the same sign as the luminescence lines shown in Fig. 1. Thus, we have been able to identify unambiguously the relevant centers for SDR with the EL2 center. The effects shown in Fig. 1 simply reflect the modification of photoelectrons due to the spin-dependent character of this recombination.

C. Role of the magnetic field

Here we analyze the fact that the presence of the external magnetic field is important in order to give rise to the SDR effects on the dynamically polarized centers. Indeed, in zero external field, none of the SDR effects can be observed. This effect is analyzed in Fig. 4, which shows as a function of magnetic field the SDR signal observed on the $D-A$ line ($\lambda = 8310$ Å) in the conditions of Fig. 1(b). One sees that the characteristic field of the increase of this signal is of the order of 1 kG. However, there seems to be an effect at higher fields, since the signal slightly increases between 6 and 10 kG. Also shown

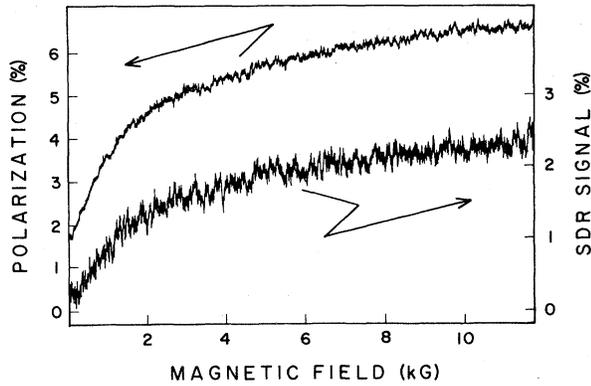


FIG. 4. Magnetic field dependence of the SDR signal $\Delta I/I$ obtained at a wavelength of 8310 Å for σ/π modulation of excitation-light polarization, and of the electronic polarization p measured at the same wavelength from the degree of circular polarization of the luminescence.

in the figure is the variation of the photoelectron polarization p , as obtained from an analysis of the degree of circular polarization of the luminescence.¹³ The interrelation between the variation of the two quantities is striking. Note that in zero field there remains a small SDR signal of 0.2%. This signal is believed to be of a different origin, since it is only observed at the maximum and on the low-energy side of the $D-A$ line and could explain why the SDR signal at this wavelength is slightly higher than that found on the other luminescence lines.

In order to demonstrate the effect of the external magnetic field, we point out that the influence of the magnetic field can be either on the spin of the photoelectrons, which could change the optical-pumping polarization p_0 defined by Eq. (2.7), or on the spins of the centers that could result in a modification of p_{eff} given by Eq. (2.9). In each of these two cases, as shown by Eq. (2.5) and (2.12), one should expect a change of both the photoelectron polarization p and the electronic concentration n , since we have shown that the photoelectron and the center spin reservoirs are reciprocally coupled by the existence of SDR. We shall now show that the effect of the magnetic field is on the centers rather than on the recombining electrons. Since, as shown by the experimental results, the centers are dynamically polarized, the value of the center polarization given by Eq. (2.17) can be written in the simple form

$$p_c = \alpha p. \quad (3.1)$$

Then, the electron polarization p and the relative variation $\Delta n/n$ of electron concentration due to σ^\pm/π modification of excitation-light polarization can be expressed as a function of the optical-pumping polarization without SDR effects p_0 and of the quantity γ given by

$$\gamma = \alpha\beta, \quad (3.2)$$

where β is given by Eq. (2.10) and expresses the relative efficiencies of the SDR and of the non-SDR channels. We then find straightforwardly

$$\frac{\Delta n}{n} = \gamma p^2, \quad (3.3)$$

$$p_0/p = pp_i \left[pp_i + \frac{\Delta n}{n} \right]^{-1}. \quad (3.4)$$

With the use of the two equations above, it is, in principle, possible to determine the values of γ and of p_0 since the two quantities $\Delta n/n$ and p are known (see Fig. 4). In doing this, care should be taken to use the correct value of electronic polarization since the polarization on the 8200-Å line is larger than that of the $D-A$ line by a factor of 1.6. As mentioned before, the relevant SDR is probably that of the capture of free electrons, since the SDR signal is the same on all luminescence lines, including those involving free electrons. Thus, for this treatment, we have used the polarization on the 8200-Å line. This polarization is found to be constant throughout this line, including its high-energy side which involves free electrons. The SDR signal was measured on the high-energy side of the $D-A$ line ($\lambda=8300$ Å) where it is not perturbed by the small signal of different origin shown in low field in Fig. 4. The variation of γ as a function of magnetic field is given in Fig. 5. One sees that γ increases up to a value of 3. The characteristic field of this increase is of the order of 1 kG which is comparable with that of the SDR signal. This shows unambiguously that this increase is due to the effect of the magnetic field on the centers and not on the photoelectrons. Since γ is constant for B higher than 2 kG, we conclude that the slight increase of SDR signal above this value of the magnetic field is due to a field dependence of the optical-pumping polarization p_0 . Therefore, we expect the quantity p_0 to slightly increase with magnetic field in order to account for the field increase of SDR signal and polarization above 2 kG. However, if one takes $p_i=0.5$, we find that p_0 strongly in-

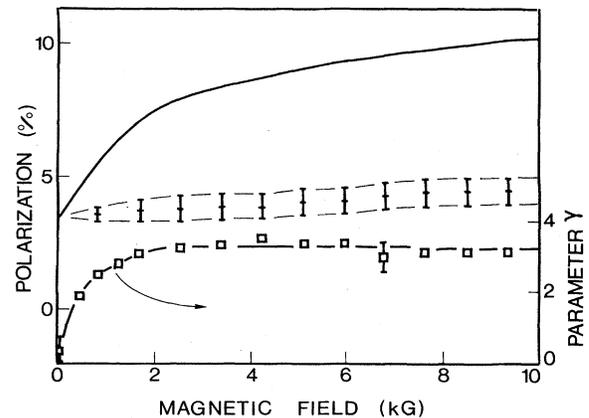


FIG. 5. Analysis of the field dependence of the SDR signal obtained at 8300 Å, using Eqs. (3.3) and (3.4). The value of the parameter γ (\square) is found to increase with magnetic field which shows that application of magnetic field increases the center dynamic polarization. The difference between the measured polarization (solid curve) and the calculated value of the optical-pumping polarization (+) is the increase of electronic polarization due to SDR effects. This last value was calculated using $p_i=0.25$ and the error bars were determined using $p_i=0.3$ and $p_i=0.2$.

creases in a field of 1 kG, which is contradictory with the above results. This contradiction can be resolved because (i) p_i can be smaller than 0.5 due to loss of electron polarization during thermalization at the bottom of the conduction band and (ii) the electronic polarization p can be higher than the measured value if the relevant recombination involves hot electrons. As seen from Eq. (3.4), this can in our case decrease the experimental value of p_i since the relevant quantity is pp_i . Consistency between the variations of γ and p_0 is achieved for $p_i \approx 0.25$ for which one obtains a smooth increase of p_0 over the whole magnetic field range (see Fig. 5). For $p_i = 0.3$, one still observes an increase of p_0 in a field for 1 kG, whereas for $p_i = 0.2$ the value of p_0 is constant up to 4 kG and increases at higher magnetic fields. We point out that the value of p_0 at large magnetic fields is one-half the actual value of electronic polarization. This shows that, as explained in Sec. II, the SDR at polarized centers indeed produces a strong increase of electronic polarization since these centers act as a "spin filter."

In summary, we have shown very clearly from our quantitative analysis that the application of an external magnetic field of several kilogauss strongly enhances the dynamic polarization of the centers by the free electrons, and that this produces a significant increase of the photoelectronic polarization since the polarized centers selectively trap the electrons depending on their spin. The unambiguous demonstration of this last effect leads us to the two following conclusions. (i) The present effect provides an alternative explanation to the field increase of photoelectron polarization, which is frequently observed in optical-pumping conditions and is generally attributed to a field dependence of the free-electron spin-lattice relaxation time.²⁹ (ii) The existence of SDR recombination processes could lead to the production of highly spin-polarized electrons, which could be used fruitfully, after extraction outside the sample, for a wealth of nuclear physics or atomic physics experiments.³⁰

D. Discussion

The results obtained in the present work show that the level responsible for the broad luminescence at 0.65 eV is paramagnetic. The precise discussion of the nature of this level is beyond the scope of this work and requires more extensive studies on a large number of samples, as well as magnetic resonance experiments. In this section we discuss mainly the origin of the field dependence of the center polarization and the very large magnitude of the SDR effect. These two features are summarized in Fig. 5.

1. Field dependence of the center dynamic polarization

Strongly field-dependent SDR has already been reported previously in amorphous silicon.³¹ We have shown in the present case that this is due to a field dependence of center polarization. This effect has two possible explanations. The first one is connected with the part of the hyperfine coupling between the electron trapped on the center and the lattice nuclei that does not commute with the Zeeman Hamiltonian. The resulting motion of the electron should decrease its spin polarization in an exter-

nal field smaller than the hyperfine nuclear field. This has been calculated by D'yakonov and Perel' by taking into account only the hyperfine coupling with the central nuclear spin.³² This picture can explain the magnitude of the observed increase of γ and also the characteristic width of this increase which is comparable with hyperfine fields in GaAs. The second possible interpretation for the field dependence of γ is the field increase of the spin-lattice relaxation time T_{1l} of the centers. Indeed, γ can be found straightforwardly by solution of rate equations to be

$$\gamma = \beta \frac{T_{1l}}{T_{1l} + T_{1e}} . \quad (3.5)$$

The dynamic polarization time T_{1e} only depends on the characteristic times for electron trapping and hole trapping on the center. This time could increase with the magnetic field if the centers are dynamically polarized by exchange interaction with the photoelectrons.²¹ However, this leads to a decrease of the SDR effects with magnetic field, and thus does not account for the experimental results. Therefore, it is reasonable to suppose that T_{1e} does not depend on magnetic field. The field increase of T_{1l} can explain the observed results. Indeed, at low external magnetic fields, T_{1l} is short with respect to the dynamic polarization time T_{1e} , so that the centers cannot be dynamically polarized. On the other hand, in high external magnetic fields, the centers are isolated from the lattice, since T_{1l} is larger and can be dynamically polarized. Further experiments are necessary in order to choose between the two above hypotheses. However, the relevance of the hyperfine interaction seems more reasonable since this explains the magnitude of the field characteristic of the observed increase of γ . Furthermore, in the present case of a center with strong coupling to the lattice, one could expect the spin-lattice relaxation to be due to phonons, for which the relaxation time would decrease with magnetic field,³³ whereas interpretation of the experimental results would require a field increase of this last quantity.

2. Magnitude of the SDR effects

The SDR effects which we have obtained in the present work are approximately one-half an order of magnitude larger than the predictions of our simple model. Indeed, the maximum value of γ at high field obtained in Fig. 5 is of the order of 3, whereas in the model of Sec. IIA this value should be smaller than unity. The purpose of the present section is to discuss the possible origin of this effect. We point out first, that as already mentioned in Sec. IIB, the case of a pair recombination cannot account alone for such a large value of γ . This value can be due to three different effects. (a) There is first the arguments already given in previous works in order to interpret large SDR effects without involving pairs, such as surface effects¹ or the relevance of spins larger than $\frac{1}{2}$.³⁴ (b) As already proposed in the preceding subsection, the relevant SDR could involve hot electrons for which p is larger than the measured value. As seen from Eq. (3.3), this could explain the large value of γ . (c) The third type of

argument involves, as discussed in Sec. II B, the relevance of a shallow excited state of the relevant centers. For the case of EL2, this has been shown from transport³⁵ experiments. Further experiments are necessary to verify the relevance of such an effect. However, this argument is reasonable, since by taking $\epsilon = 10^{-3}$,³⁶ $\sigma_i = \pi a_0^*{}^2$ where a_0^* is the effective Bohr radius,³⁷ and $\tau = 5$ ns as measured in the present sample by using standard optical-pumping techniques,³⁸ we find that the relevant parameter of Eq. (2.22), $\epsilon \sigma_i v N_{\text{exc}} \tau$, is equal to 1 for $N_{\text{exc}} = 5 \times 10^{15} \text{ cm}^{-3}$ which is of the order of usual EL2 concentrations in semi-insulating samples.

IV. WEAK-SDR CASE AND THERMODYNAMICALLY POLARIZED CENTERS: MANGANESE IN GaAs

In this section we present a situation which is opposite to that of the preceding section, i.e., where (i) the centers are thermodynamically polarized by the external magnetic field and, (ii) the efficiency of the SDR process is weak with respect to that of other recombination processes, so that the photoelectron concentration is not modified by SDR. These results have been obtained in several manganese-doped GaAs samples. Since all these samples gave similar results, here we shall only present the case of a bulk chromium-doped GaAs sample which had been diffusion doped with manganese for 24 h at 750 °C.

A. Demonstration of the SDR effects

The experimental setup and conditions have been described in detail in Sec. II. The experimental results obtained at a temperature of 7 K and for an excitation intensity of 1 W/cm^2 are summarized in Fig. 6. The various luminescence lines are shown in Fig. 6(a). The main line at 8330 Å is the usual donor-to-shallow-acceptor (*D-A*) line, with a shoulder at 8300 Å attributed to the recombination of free electrons with the same shallow acceptors (*e-A*).^{39,40} The line at 8800 Å is the usual zero-phonon manganese emission, with its TA phonon replica at 8850 Å.⁴¹⁻⁴⁵ In agreement with previous work, we have observed the other phonon replicas at lower energy. These replicas are not represented in Fig. 6 for the sake of clarity. Note the complex structure of the luminescence at 8200 Å. This luminescence has been found to be composed of four different lines labeled *A*, *B*, *C*, and *D*. This structure is not observed before manganese diffusion, and is thus probably of the same origin as found by Bilac *et al.*⁴⁶

The SDR effects are shown in Fig. 6(b), which presents the variation ΔI of the intensity of the luminescence produced by a σ^+/σ^- modulation of excitation-light polarization in an external magnetic field of 11.4 kG. The change of sign observed on the *B* line at 8198 Å is connected with the modulation of the position of this line and not of its intensity. As already observed in Fig. 1, this is due to the modulation of the Zeeman energy of the corresponding electrons and is not due to SDR. On the other hand, one observes a strong variation ΔI on the Mn line as well as on the *D-A* line and on the *A* line. The relative variation $\Delta I/I$ is equal to approximately 10% for the Mn

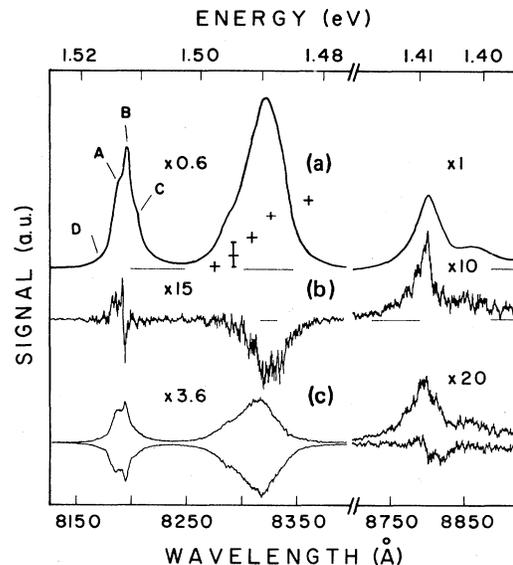


FIG. 6. SDR effects on a GaAs:Mn sample at 7 K. The resolution is 2 Å. Curve (a) is the luminescence spectrum. The luminescence band at 1.409 eV is the usual manganese emission with a phonon replica at 1.400 eV. Curve (b) is the variation of luminescence intensity produced by σ^+/σ^- modulation of excitation-light polarization in a magnetic field of 11.4 kG. The relative variation of intensity between 1.48 and 1.50 eV (+) is found to be strongly dependent on wavelength. Curve (c) shows the usual optical-pumping results, obtained by monitoring in the same conditions as curve (b) the variation of the σ^+ and σ^- components of the luminescence.

line and 1.5% for the *D-A* line and the *A* line. Also note the difference of the sign of ΔI observed for the Mn line and the *D-A* line.

These effects are due to SDR on centers polarized thermodynamically in the external magnetic field *B*. Indeed, in agreement with Eqs. (2.23) and (2.24), the reported effects are not observed if $B = 0$ and their sign is changed if the sign of *B* is changed. Furthermore, we have observed that the value of the variation ΔI of the luminescence produced by a σ/π modulation of excitation-light polarization is exactly one-half of the variation obtained above for a σ^+/σ^- modulation. As shown by Eq. (2.24), this means that in our case the dynamic polarization of the centers is negligible so that p_c only depends on the value of the external field and not on that of the photoelectrons. Thus we conclude that, in the present case, the relevant centers are thermodynamically polarized by the magnetic field.

Finally, we have verified that in the present case, the circularly polarized excitation of the sample creates spin-polarized electrons. This is shown in Fig. 1(c) which presents, in the same condition as Fig. 1(b), the variation ΔI_+ and ΔI_- of the σ^+ and σ^- components of the luminescence light. These two quantities are measured by placing a fixed quarter-wave plate and linear polarizer on the luminescence. The absolute value of the polarization *p* of the photoelectrons, which is created by circularly polarized excitation, is given by

$$p = (\Delta I_+ - \Delta I_-) / I. \quad (4.1)$$

A comparison of the results of Figs. 6(a) and 6(c) for the D - A , e - A , and D lines gives $p = 9\%$ for the D - A and e - A lines and 17% for the D line.⁴⁷

We now comment on the results of Fig. 6(c) in the case of manganese emission, for which Eq. (4.1) does not hold since the exact symmetry of the manganese state is not known in detail. We first point out that, as for the other luminescence lines, one has $\Delta I_+ \neq \Delta I_-$, which shows that the recombination of the spin-polarized electrons on the manganese level produces circularly polarized light. This constitutes the first observation of optical pumping on a recombination involving a deep state.⁴⁸ The second point we now explain is the dissymmetry of the two curves ΔI_+ and ΔI_- . The quantity $\Delta I_+ + \Delta I_-$ is not zero because this quantity is the above-described variation of the luminescence intensity due to SDR. This variation is, in the case of the manganese emission, of the same order as the optical-pumping signal $\Delta I_+ - \Delta I_-$ that explains the above dissymmetry.

B. Quantitative analysis of the SDR effects

In order to analyze the effects shown in Fig. 6, we first show that we are in the weak-SDR case discussed in Sec. II, where the concentration of both free electrons and electrons trapped on shallow donors is constant when the excitation-light polarization is modulated. For the case of free electrons, we have studied the luminescence emission between 1.495 and 1.500 eV, which we have shown from photoluminescence excitation spectra to be entirely due to e - A emission, with a negligible contribution from the nearby D - A .⁴⁹ The SDR signal at this energy is found to be very small, as shown by the pluses in Fig. 6(a). The explanation of this effect, as seen from Eqs. (2.13) and (2.14), can be either that the photoelectron concentration n is constant and that the relative variation $\Delta\tau/\tau$ due to the SDR effect of the e - A emission is weak, or that the e - A emission is the dominant recombination process for free electrons, so that one has $\Delta n/n + \Delta\tau/\tau = 0$. However, the second hypothesis is not reasonable, since the recombination of electrons on shallow acceptors is not the dominant recombination path for free electrons. Indeed, the luminescence spectrum shows that the high-energy side of the manganese emission, which will be shown in the following subsection to be due to the recombination of free electrons, has an intensity larger than that of the e - A line. Thus, we conclude that the first above hypothesis is correct, so that the free-electron concentration is not affected by modulation of excitation-light polarization. This can be explained by assuming that the dominant recombination mechanisms for free electrons which determine the value of n are very likely through deep centers other than manganese impurities, and are not spin dependent.⁵⁰ The case of electrons trapped on shallow donors can be treated exactly in the same way as for free electrons, since the SDR signal on the D line, which is due to the recombination of electrons trapped on shallow donors with valence holes,⁵¹ is very small. An upper limit of the signal at $\lambda = 8180 \text{ \AA}$ is 0.5% , which is much smaller than the value of 1.5% obtained for the donor-acceptor line

that arises from the same initial state. We conclude that in our case, both the free-electron concentration and the concentration of electrons trapped on shallow donors are constant. In the same way, we find that the polarization of the photoelectrons does not depend on the magnetic field, which indicates that the existence of SDR processes does not modify the electronic polarization. This means that, unlike the case in the preceding section, the characteristics of the photoelectron reservoir are completely unmodified by SDR so that the present situation corresponds to the weak-SDR limit discussed in Sec. II. Thus, the results obtained can be analyzed conveniently, since on each luminescence line, the SDR signal is only dependent on the features of the corresponding recombination process, and is quite simply given by Eq. (2.16). This allows us to conclude that the SDR signals observed on the D - A line and on the manganese line are due to distinct SDR processes, which are, respectively, the recombination on shallow acceptors and on the deeper manganese acceptors. We now perform a more detailed study of the SDR effects. Since the centers have been shown to be thermodynamically polarized by the magnetic field, one has

$$p_c = \xi \tanh(g^* \mu_B B / 2kT), \quad (4.2)$$

where g^* is the effective Landé factor of the centers, and ξ is a numerical coefficient of order unity, that accounts for possible incomplete relaxation of the centers. This last equation supposes that the centers have a spin of one-half. In agreement with Eqs. (2.16) and (4.2), we have observed that the SDR signals are proportional to the magnetic field up to the maximum available value of 11.4 kG , so that even at 1.7 K , it was not possible to completely polarize the centers. This last result is indeed expected since, for a center of spin $\frac{1}{2}$ and supposing that the effective g factor is equal to 2, the thermodynamic polarization is found in these conditions to be 50% , and the departure of p_c from a behavior proportional to the magnetic field is very small. Let us also mention that we have studied, for a given magnetic field, the variation of p_c as a function of temperature T , and that we have verified that p_c decreases with increasing lattice temperature.⁵²

Thus, the magnetic field and the temperature dependence of the SDR effects are in agreement with our simple model. Precise analysis of the magnitude of the signal on the various lines is intricate, since this magnitude depends on several parameters which are not known. These parameters are the effective Landé factor g^* of the centers,⁵³ the coefficient ξ of Eq. (4.2),⁵⁴ and a possible multiplicative factor due to the fact that the spin of the center can be larger than $\frac{1}{2}$.^{55,56} It is, however, possible to make an order-of-magnitude estimate for $\Delta I/I$ by taking $g^* = 2$, $\xi = 1$, and $p = 17\%$. We find $\Delta I/I = 2\%$, which has to be compared with the value of 1.5% for the D - A line and of 10% for the manganese line. We consider that the agreement between the above prediction and the measured value of $\Delta I/I$ is satisfactory, with respect to the very crude approximations made.⁵⁷⁻⁵⁹ The possible reasons for the dependence of the magnitude and also of the sign of the signal on the various lines will be discussed below.

C. Analysis of the SDR signal on the manganese emission

The manganese zero-phonon emission line shown in Fig. 6(a) has a position which is very close to that observed in Mn-diffused GaAs samples by Lee and Anderson.⁴³ On the other hand, luminescence studies using epitaxial samples report a luminescence composed of two distinct lines, at an energy 2 meV lower than the energy of the present line.^{41,42} These two lines are due, respectively, to the recombination with manganese of free electrons and of electrons trapped on shallow donors. In this subsection, we show that the zero-phonon line shown in Fig. 6(a) exhibits the same structure. A luminescence study at very low excitation levels has not allowed us to reveal this structure. On the other hand, SDR results shown in Fig. 6(b) clearly show such a structure since the SDR signal is much larger on the high-energy side than on the low-energy side of the line. More precise analysis of this effect is shown in Fig. 7, which is done at 1.7 K at low excitation intensity. One clearly sees the appearance of two distinct lines from the SDR results, situated, respectively, at 1.407 and 1.409 eV, the latter line showing a larger SDR signal. In the case of Fig. 7, the SDR signal on the line at 1.409 eV is found to be approximately constant and equal to 5%. The SDR signal at 1.406 eV, for which the luminescence is entirely due to the lower-energy line, is equal to 1.7%. Note also that the SDR signal increases again at energies below 1.405 eV, which is very likely due to the onset of the TA phonon replica of the manganese emission, shown in Fig. 6(a). Thus, our SDR results reveal that the zero-phonon manganese emission has the same structure as that observed in epitaxial samples. We

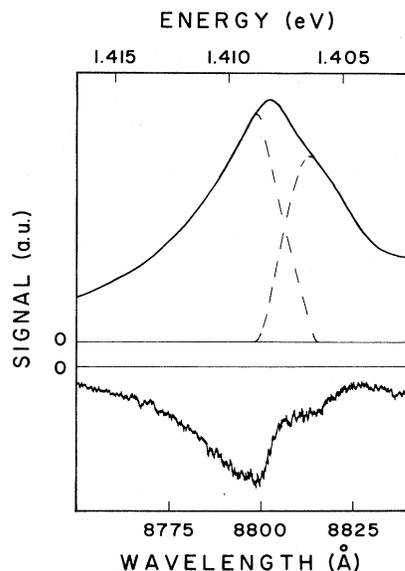


FIG. 7. Detailed analysis of the SDR effects on the zero-phonon manganese emission. The top curve is the luminescence spectrum. The bottom curve is the σ^+/σ^- effect similar to that of curve (b) of Fig. 6. The SDR results allow us to resolve the line into two distinct lines. The sign of the magnetic field was opposite to that of Fig. 1(b), which changes the sign of the effects.

conclude that the manganese impurities give rise to the same recombination process in the two cases. The shift of 2 meV between the two cases could be due to Coulomb interactions with defects of unknown origin or to uncontrolled local stress present in the sample.

In summary, we have demonstrated in the present case of GaAs:Mn, the spin-dependent character of the recombination of photoelectrons on deep manganese acceptors, as well as on shallow acceptors. The acceptors are found to be thermodynamically polarized by the external field. This has been done by using a simple nonresonant method that involves the modulation of excitation-light polarization. The results can be straightforwardly interpreted since the above spin-dependent processes are not the dominant recombination processes, so that the photoelectron concentration is not affected by the above modulation.

D. DISCUSSION

The results presented in the present section show that, in the case where electron concentration is not modified by SDR, the magnitude of the SDR signal strongly depends on the luminescence line under observation. Indeed, in the case of the shallow-acceptor emission, the SDR signal on the e - A line is much smaller than that on the D - A line. The situation for the manganese emission is opposite, since the signal for the e -Mn line is much larger than that for the D -Mn line. We have obtained this type of result in many different samples. For example, in the same sample prior to manganese diffusion, the situation is reversed, since SDR effects are obtained on the e - A line but not on the D - A line. Owing to these effects, the present method can be used fruitfully in order to resolve the structure of complex luminescence lines, such as the zero-phonon manganese emission in the present case. Thus, this method provides the same spectroscopic tool as ODMR, but does not require the observation of any resonance.

We do not understand in detail the origin of the large difference in the SDR signals between the various lines that we observe. Indeed, the main difference between the D -Mn and the D - A lines on one hand, and the e -Mn and the e - A lines on the other hand, is that the first lines arise from a pair recombination. However, it has been shown in Sec. II B that, in the case of thermodynamically polarized centers, the SDR signal for pair recombination is the same as that for recombination of free electrons. Indeed, the only possible difference between the two cases, which lies in the initial polarization of the electrons [Eq. (2.19)], does not play a role here since the polarization on the e - A and e -Mn lines is the same as that of the D - A and D -Mn lines, respectively. A possible explanation for the observed effect could involve the modification of the wave functions of the hole trapped on the acceptor, due to the electric field of the nearby donor. Another interpretation, for the case of the D -Mn line, comes from the fact that the corresponding recombination is probably the dominant recombination mechanism for donors situated close to manganese impurities. Then, the population of these particular donors could be affected by SDR, which might decrease the value of the SDR signal. Further experi-

ments are necessary to provide an unambiguous interpretation for the difference in the magnitudes of the SDR signals observed on the various luminescence lines.

We now comment on the fact that, as shown by the SDR results, the relevant manganese level at 114 meV above the top of the valence band is found to be paramagnetic, and we discuss the possible nature of this level. We have performed ODMR experiments by observing the above SDR signal in resonant conditions in the X band. These experiments were done at Centre National d'Etudes des Télécommunications (Lannion, France). We have not observed the usual resonance of the manganese d^5 state.^{60,61} Since the SDR signal is directly proportional to the polarization p_c of the relevant centers, we can estimate that the relative decrease at resonance of p_c is less than 5%. Unless the effective relaxation time of this center is strongly modified by light excitation, it is difficult to believe in the relevance of the manganese d^5 state since, at the microwave powers (5W) that we used, the resonance of this state is known to be completely saturated. In the same way, we think that the $Mn^{3+}(d^4)$ state is not relevant, since this state is neutral with respect to the lattice and could not explain that the donor-manganese emission has been found to have the usual donor-acceptor line shape.^{41,45}

This seems to favor the model that the relevant manganese level is constituted by a $Mn^{2+}(d^5)$ on which a valence hole is loosely bound, as already formulated by Kaufmann and Schneider on the basis of the stability of the half-filled d shell.⁶² The fact that the same manganese level is found in the absence of excitation light by transport studies⁴² can be explained by stating that the origin of the hole is probably the manganese impurity itself, which only contributes two s electrons to satisfy its bonds with its neighbors. Another fact which supports this hypothesis is that the excited states of the manganese level can be adequately described by effective-mass theory.⁶³ Note, however, that the SDR results reveal an important difference between the manganese level and the shallow-acceptor level, since the SDR signals of the two lines have opposite signs. The difference of the sign of $\Delta I/I$ for shallow acceptors and for manganese acceptors does not originate in a possible multiplicative coefficient, which could appear in Eq. (4.2), to take into account the symmetry of the acceptor state, since as shown above, these two states are believed to have the same symmetry. We believe that this difference arises from the difference of the sign of the effective g factor of the two states. This originates quite simply from the fact that the g factor of shallow acceptors depends more strongly on the valence-band parameters than the deeper manganese level. An independent way to verify this hypothesis is to measure the sign of the degree of circular polarization induced by a magnetic field in conditions where the sample is irradiated by linearly polarized light.⁶⁴ We have done this experiment, and have indeed found signals of opposite signs for the $D-A$ line and for the manganese line. This result is in agreement with recent studies of the hot luminescence of GaAs:Mn, which indicate a value of g^* of 3.2 for manganese acceptors and of -1.15 for shallow acceptors.⁶⁵ Note furthermore that the hot luminescence has been

found to exhibit SDR effects which are similar to those presented here.

V. CONCLUSION

In this work we have developed the basis for optical-pumping studies of SDR in semiconductors, and we have shown from two distinct experimental situations, which are semi-insulating GaAs and GaAs:Mn, that (i) the existence of SDR quite generally introduces a reciprocal coupling between the photoelectron centers, which results in a modification of both the photoelectronic polarization and concentration. (ii) The centers can be either thermodynamically polarized by the magnetic field, or dynamically polarized due to the spin-dependent character of the recombination. It is possible to distinguish between these two cases by performing controlled changes of excitation-light polarization. (iii) The application of a magnetic field parallel to the direction of light excitation is crucial for the appearance of SDR effects. In the case of dynamic polarization of the centers, this may originate from the nondiagonal elements of the hyperfine interaction or from a possible field dependence of the center spin-lattice relaxation time.

The simple model we have suggested allows us to interpret the experimental results. There are, however, two experimental observations which are not understood in detail and which require further studies. The first one is that the magnitude of the effects is larger than predicted. The interpretation of this effect involving pair recombination does not hold in the present case. We propose an alternative explanation involving capture through an excited state of the center, which could quite generally produce enhancement of SDR effects. The second experimental fact is that SDR effects seem to be very different for free-to-bound and for donor-acceptor transitions. This allows SDR studies to resolve the structure of complex luminescence lines, as shown for the case of the zero-phonon manganese emission in GaAs.

We recall that the method presented here is very general, at least in the case of gallium arsenide. Indeed, we have studied a wide range of samples and have, in all cases, been able to produce photoelectronic spin polarizations of a few percent by circularly polarized excitation, and have been able to observe SDR effects under application of a magnetic field. Owing to its nonresonant nature, this technique can be used fruitfully as a preliminary step for ODMR studies.³ Indeed, such a detection requires, quite generally (i) that the recombination be spin dependent, and (ii) that it is possible to saturate appreciably the magnetization of this center in resonance conditions. The present method can then be used as an independent test of SDR, and allows us to find the most appropriate conditions for ODMR such as the value of wavelength. We think that a critical parameter for ODMR observation is the value of the external field, since the SDR signal strongly increases with magnetic field. In this work we have shown the paramagnetic nature of the acceptor level introduced by manganese in GaAs, as well as of the state responsible for the broad luminescence around 0.65 eV, which is identified with the EL2 center. It is beyond the

scope of the present study to interpret these effects unambiguously from the only SDR results alone, since this requires ODMR experiments. We think that the use of the present technique should allow, in the future, successful ODMR studies of these two levels.

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