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# Optical detection of NMR in high-purity GaAs under optical pumping: Efficient spin-exchange averaging between electronic states

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In a semiconductor under light excitation, spin exchange between electronic states produces an extremely efficient spin averaging. This is shown theoretically, by a calculation of the corresponding cross section, and experimentally, using the optical detection of nuclear magnetic resonance (NMR) in high-purity gallium arsenide at liquid-helium temperature, excited by circularly polarized light (optical pumping). The feasibility of this detection comes from the large hyperfine nuclear field experienced by the spin-polarized photoelectrons. The change of the direction of this nuclear field in NMR conditions causes a precession of the electronic spins. The resulting electronic depolarization is detected from the polarization of the luminescence light. This holds for electrons trapped on donors. Free electrons experience a very small nuclear field, but are found to be depolarized at resonance, because of their spin-exchange coupling with trapped electrons. Furthermore, the spin exchange is responsible for an amplification and broadening of the optically detected NMR signal. This is shown by a calculation of the depolarization of this system of two electronic states, and is verified by a careful analysis of the observed resonance line. The study of this broadening indicates that the spin-exchange frequency is comparable with the precession frequency in the external field, in agreement with its theoretical estimate. The measured values of the ratios of the hyperfine nuclear fields of the various nuclear isotopic species yield the sharing of the electron between cation and anion sites. We point out that, due to the efficient spin exchange, the various electronic states behave as a single spin state. This basic feature, which has so far been overlooked in semiconductors under light excitation, allows a new insight at the various electronic spin properties, such as spin relaxation and optical detection of electronic resonance.

## I. INTRODUCTION

The basic principle of the optical detection of nuclear resonance is the following: in conditions of optical pumping in semiconductors that is, excitation by circularly polarized light,[1] the spin-polarized photoelectrons dynamically polarize the lattice nuclei, due to the existence of the hyperfine contact interaction.[2,3] In turn, these electrons experience an internal magnetic field $\vec{B}_n$ of nuclear origin, the effects of which have been shown in a variety of experiments.[3–7] The static external magnetic field $\vec{B}$ is parallel to the direction $z$ of the incident light, which will in the following be called the longitudinal direction. In off-resonance conditions, the nuclear field $\vec{B}_n$ is parallel to the mean electronic spin $\langle\vec{S}_0\rangle$, which lies along the $z$ direction, and has no effect on the direction and magnitude of $\langle\vec{S}_0\rangle$, apart from its possible influence via the electronic relaxation time.[4] If now a rotating field $B_1$ is applied near the resonance of one nuclear isotopic species, the magnetization of the corresponding nuclei is oblique, its value depending on the magnitude of the spin temperature of the nuclear-spin system.[8] The photoelectrons experience then a total oblique magnetic field and the subsequent precession of the electronic spins causes a decrease by Hanle effect of the longitudinal component of the mean electronic spin. This is detected from the corresponding decrease of the degree of circular polarization of the luminescence light.

The optically-detected nuclear resonance has first been observed by Berkovits, Ekimov, and Safarov in a ternary compound.[4] The case of high-purity gallium arsenide is presented in Fig. 1, which shows the resonance lines of the three nuclear isotopic species for positive and negative values of the external magnetic field. The various features of these resonances will be interpreted below. We point out here that the intensity of the signal is very large. For instance, in the case of arsenic, the luminescence degree of circular polarization is almost cancelled at resonance. This is due to the very strong value of the nuclear field $\vec{B}_n$ which, in agreement with theoretical estimates, is as high as several kilogauss. This work is a theoretical and experimental study of the optically-detected resonance in high-purity gallium arsenide at pumped-helium temperature. The main interest of this system lies in the fact that basically two kinds of electronic states are present, delocalized (conduction electrons), or localized (electrons trapped on impuri-

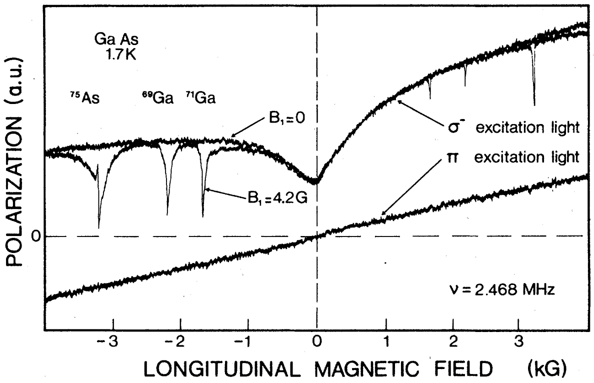

FIG. 1. General features of the optically detected NMR in high-purity GaAs. The luminescence degree of circular polarization is found to depend on the external longitudinal magnetic field, both for a circular and linear excitation light. This variation will not be discussed here. If now a rotating field $B_1$ is applied, one observes, for positive and negative signs of external field, the resonances of the three isotopic nuclear species.

ties), which correspond to distinct luminescence lines.[9–11] It has been shown previously[3] that the nuclei are polarized only in the vicinity of donors. In a pure compound, these nuclei represent a very small fraction of all the nuclear spins of the system. Consequently, in such a case, delocalized electrons experience a vanishingly small nuclear field and can only be depolarized, in conditions of NMR, through their possible coupling with trapped electrons. The study of the resonance signal, detected on luminescence lines corresponding to delocalized states, allows us to investigate the processes of exchange of magnetization between the two kinds of electronic states.

We show that the same signal is detected on all luminescence lines, thus evidencing a very efficient averaging between the various electronic states. A theoretical analysis indicates that the relevant mechanism is spin exchange[12] between free electrons and electrons trapped on donors. This mechanism is found to be fast as compared to relaxation and recombination in the different states, which explains satisfactorily the above experimental results. We analyze the resulting modification of the resonance line shape and we show that there also results an enhancement and broadening of the resonance signal. We have been able, after careful analysis of the experimental results, to find evidence of this enhancement, and we obtain an order of magnitude for the efficiency of spin exchange in our case. Furthermore, we evidence a strong Knight shift of the line, due to the hyperfine field of the optically oriented electrons.[3] The measured ratios of the nuclear fields of the three spin species present in GaAs are found to be in good agreement with their theoretical estimates.

In the following section, we describe the basic features of the optical detection of NMR, forgetting the effect of averaging between the different states. The theory of the line shape incorporating spin exchange is established in Sec. III. The experimental results are presented and analyzed in Sec. IV.

## II. PRINCIPLES

The possibility of optical detection of NMR comes from the fact that the nuclear field $\vec{B}_\alpha$ experienced by the electrons from a given nuclear isotopic species $\alpha$ is collinear with the magnetization of the corresponding nuclei. If, in conditions of NMR, this magnetization is driven away from the direction of excitation light, this field becomes oblique with respect to the mean electronic spin. The resulting precession of the electronic spins causes an electronic depolarization by Hanle effect, which is monitored from the corresponding decrease of the degree of circular polarization of the luminescence light. In the present section, we first calculate the value of the nuclear magnetization in conditions of NMR, and then we determine the resulting electronic depolarization.

We suppose here that we apply a static longitudinal field $B$. Since the nuclear magnetization obviously depends on the conditions of passage through resonance, we consider the case where the rotating field $B_1$, at frequency $\omega/2\pi$, is suddenly switched on at a given distance $\delta B$ from the center of the resonance of spins $\alpha$, given by

$$\delta B = B - \omega/\gamma_\alpha \ , \tag{2.1}$$

where $\gamma_\alpha$ is the gyromagnetic factor of nuclear isotopic species $\alpha$. The spins $\alpha$ experience an effective magnetic field in the rotating frame $\vec{B}_{\text{eff}}$, at angle $\phi_n$ with the longitudinal direction, where $\phi_n$ is given by

$$\tan\phi_n = B_1/\delta B \ . \tag{2.2}$$

Consequently, if the magnitude of the effective field $\vec{B}_{\text{eff}}$ is sufficiently strong, in a sense to be made clear below, one expects that there results a projection of the magnetization of the nuclear spins $\alpha$ on the direction of $\vec{B}_{\text{eff}}$. The field $B_\alpha^r$ of nuclei $\alpha$ is now oblique, its longitudinal and transverse components being given by

$$\begin{aligned} B_{\alpha z}^r &= B_\alpha \cos^2\phi_n \ , \\ B_{\alpha x}^r &= B_\alpha \sin\phi_n \cos\phi_n \ , \end{aligned} \tag{2.3}$$

and the following evolution of the magnetization of spins $\alpha$ is due to spin-lattice relaxation, in a time $T_1^\alpha$ of the order of seconds. We now discuss the value of the effective field $B_{\text{eff}}$, corresponding to saturation of the nuclear absorption signal, for which Eqs. (2.3) are valid. It is necessary to take into account the existence of interactions among the nuclear spins,[8] which are likely to modify the features of the nuclear-spin system. A study in the framework of the spin temperature theory[13] shows that the evolution of the system following application of $B_1$ involves the exchange of energy between the Zeeman and the secular and nonsecular spin-spin reservoirs. This is done in Appendix A and shows that Eqs. (2.3) are valid provided the rotating field $B_1$ is larger than the local field $B_{L\alpha}$, of the order of a fraction of a gauss, which characterizes the magnitude of the spin-spin interactions. The characteristic time of the motion of spins $\alpha$ is the spin-spin relaxation time $T_2^\alpha = (\gamma_\alpha B_{L\alpha})^{-1} \simeq 100$ $\mu$sec, so that the application of $B_1$ has to be done in a time shorter than $T_2^\alpha$.

In summary, to drive the magnetization of nuclear isotopic species $\alpha$ away from the longitudinal direction, we apply a rotating field $B_1$ of magnitude larger than the local field $B_{L\alpha}$, in a time shorter than the spin-spin relaxation time $T_2^\alpha \simeq 100$ $\mu$sec. Then after a time larger than $T_2^\alpha$, but shorter than the spin-lattice relaxation time $T_1^\alpha \simeq 3$ sec, the nuclear field $\vec{B}^{r}_{\alpha}$ of isotopic nuclear species $\alpha$ is given by Eqs. (2.3). This field is oblique and produces electronic depolarization by Hanle effect. We point out the interest of the present method which allows us to obtain a well-controlled value of the nuclear magnetization, whereas the other types of passage through resonance involve feedback effects between the electronic and nuclear-spin systems, in the case of slow passage, or produce irreversible losses of nuclear magnetization, in the case of adiabatic fast passage.[3,14]

We now calculate the electronic depolarization at resonance. The geometry of the electron-nuclear-spin system at resonance is shown in Fig. 2. The total field $\vec{B}_t$, experienced by the electrons, is given by

$$\vec{B}_t = \vec{B} + \sum_{\beta\neq\alpha} \vec{B}_\beta + \vec{B}^{r}_{\alpha} \ . \tag{2.4}$$

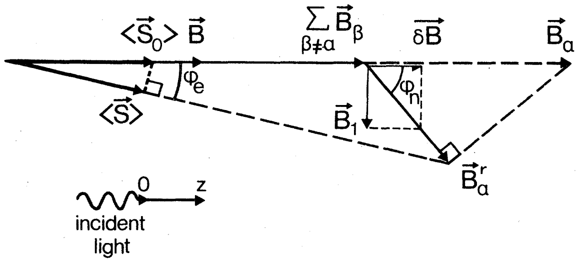

FIG. 2. Geometry of the electron-nuclear spin system: After application of the rotating field $B_1$ near the resonance of nuclear isotopic species $\alpha$, the field $\vec{B}^{r}_{\alpha}$ of the corresponding nuclei is oblique whereas the field $\sum_{\beta\neq\alpha}\vec{B}_\beta$ of the nuclei which do not resonate, is unchanged. There results an electronic depolarization by Hanle effect in the total field $\vec{B} + \sum_{\beta\neq\alpha}\vec{B}_\beta + \vec{B}^{r}_{\alpha}$. The mean electronic spin $\langle\vec{S}\rangle$ is the projection of the off-resonance mean spin $\langle\vec{S}_0\rangle$ on the direction of the total field.

It is the sum of the external field, of the unmodified longitudinal field of the nuclei $\alpha$ which do not resonate, and of the field $\vec{B}^{r}_{\alpha}$ given by Eqs. (2.3). This total field is oblique, at angle $\phi_e$ with the $z$ direction. The longitudinal component of the electronic mean spin is given by[5,14]

$$\langle S_z\rangle = \langle S_0\rangle \frac{\Delta B^2 + B_{tz}^2}{\Delta B^2 + B_t^2} \ , \tag{2.5}$$

where $\langle S_0\rangle$ is the off-resonance mean spin, lying along the $z$ direction. The field $\Delta B$ is the half-width of the Hanle depolarization curve in a purely transverse external field. It is related to the electronic relaxation time $T_1$ and lifetime $\tau$, by

$$\Delta B = \hbar(|g^*|\mu_B T_{1^*})^{-1} \tag{2.6}$$

and

$$1/T_{1^*} = 1/T_1 + 1/\tau \ . \tag{2.7}$$

The quantity $g^*$ is the effective $g$ factor at the bottom of the conduction band and $\mu_B$ is the Bohr magneton. In the simplified case where the magnitude of $B$ is much smaller than the field $B_t$ acting on the electrons, the electronic mean spin $\langle\vec{S}\rangle$ is the projection of the longitudinal off-resonance spin $\langle\vec{S}_0\rangle$ on the direction of $\vec{B}_t$. The decrease at resonance of the longitudinal component of the mean electronic spin is then

$$\Delta\langle S_z\rangle = \langle S_0\rangle \sin^2\phi_e \ . \tag{2.8}$$

Thus, in this case, the electronic relative depolarization at resonance $\Delta\langle S_z\rangle/\langle S_0\rangle$ is simply connected to the angle $\phi_e$ between the total field experienced by the electrons and the longitudinal direction.[15] This angle is related to the external and nuclear fields by the following relation

$$\cot\phi_e = \left| \frac{A_\alpha - \sin^2\phi_n}{\sin\phi_n \cos\phi_n} \right| \ , \tag{2.9}$$

which is obtained from Eqs. (2.3) and (2.4). The resonance signal depends on one parameter, the quantity $A_\alpha$, given by

$$A_\alpha = (B + \sum_\beta B_\beta)/B_\alpha \ , \tag{2.10}$$

which is the ratio of the total off-resonance field experienced by the electrons and of the field of the isotopic nuclear species $\alpha$ which resonates. The electronic relative depolarization at resonance is then completely defined by Eqs. (2.8) and (2.9), provided the value of the parameter $A_\alpha$ is known.[16] The experimental determination of $\Delta\langle S_z\rangle/\langle S_0\rangle$ is obtained from the measure of the degree of circular polarization $\mathcal{P}$ of the luminescence because, in low external fields, this degree is simply given by[17]

$$\mathcal{P} = -\langle S_z\rangle \ . \tag{2.11}$$

In fact, in external fields of the order of several kilogauss, there exists an extra contribution $\mathcal{P}_\infty$, due to the thermodynamically polarized holes, which is equal to the luminescence polarization for a linearly polarized excitation light.[14,18] These holes, of $p$-type orbital wave function, at least at $k=0$, do not experience the hyperfine contact interaction and the additional term $\mathcal{P}_\infty$ is not modified in conditions of resonance. Consequently, the longitudinal component of the electronic mean spin is in this case obtained from

$$\mathcal{P}-\mathcal{P}_\infty=-\langle S_z\rangle \ , \qquad (2.12)$$

by measuring the relative decrease at resonance of $\mathcal{P}-\mathcal{P}_\infty$.

To summarize, we have presented in this section a simple model which allows us quite generally to calculate the depolarization of electrons following application of the rotating field $B_1$ at a given distance $\delta B$ of resonance [Eqs. (2.8), (2.9), and (2.10)]. This is monitored by the subsequent decrease of the degree of circular polarization of the luminescence. The resonance line shape can be obtained by applying $B_1$ at different distances of the resonance. In the framework of the present model, this line shape is a symmetrical $W$ centered at resonance. The above model will in the following be called the geometrical model since all its predictions are derived from the geometry of the system described by Fig. 2.

## III. SPIN EXCHANGE BETWEEN THE VARIOUS ELECTRONIC STATES

In the preceding section, we have explained the principles of the optical detection of NMR. This has been done, supposing implicitly that there exists only one electronic state. We have calculated in this case the value of the NMR signal. We show in the present section that, before studying the experimental line shape, in the case of high-purity gallium arsenide, it is necessary to take into account (i) the presence of several electronic states, which experience different nuclear fields, and (ii) the existence of processes which average out the polarizations of these states, and to subsequently modify the theory of the resonance line shape.

Indeed, it is well known from luminescence studies[9-11] that there exist localized and delocalized electronic states. Due to the form of the hyperfine contact interaction with nuclear spins, this interaction is much stronger for localized than for delocalized electronic states.[3] Consequently, the only polarized nuclei are in the vicinity of the localization centers that is, within a distance of the donors approximately equal to the effective Bohr radius $a_0^* \simeq 100$ Å. This has been shown theoretically[3] and experimentally.[19] Then, in our pure samples, delocalized electrons experience a very small nuclear field and the variation of the mean spin of free electrons at resonance is, in the framework of the present model, expected to be very small so that the resonance signal should be optically detected on the only luminescence lines corresponding to localized electronic states. This is in contradiction with the experimental results, since the NMR signal can be observed on delocalized luminescence lines. Furthermore, as mentioned in a preliminary report,[20] the electronic relative depolarization is found to be exactly the same on all luminescence lines, as shown in Fig. 3, in the case of free excitons and electrons trapped on donors. This contradiction can be resolved if we assume the existence of averaging mechanisms between the various electronic states. In this case, free electrons, although experiencing a very small nuclear field, should be depolarized because of their strong coupling with electrons trapped on donors.

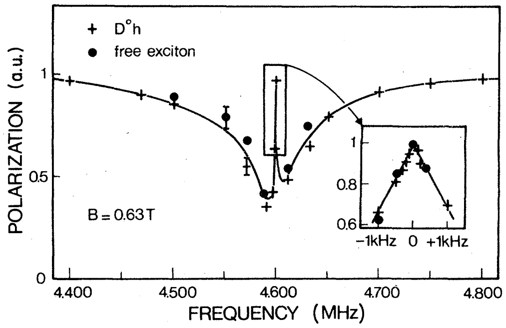

FIG. 3. Comparison of the relative depolarization of a delocalized state (free exciton) and a localized state (electron on donor) in conditions of NMR. This is the case of $^{75}$As nuclei, the nuclear field being antiparallel to the external field. Although free excitons experience a very small nuclear field, the results are exactly the same on the two luminescence lines, which demonstrates the fast averaging processes between the various electronic states.

### A. Discussion of the possible mechanisms of averaging

As shown by several experimental studies in silicon,[21] a possible mechanism of averaging is spin exchange between localized and delocalized states. When the spins of the two electronic states are antiparallel, their Coulomb interaction may result in a mutual flip-flop.[12] There results an equalization of the mean spins of the two states, in the case where the average time between two flip-flops is shorter than the lifetime of one of the two electronic states.

To evaluate the efficiency of this process, we have calculated the value of the spin-exchange cross section $\sigma_e$ for the scattering of a free electron by an occupied donor. This is done in Appendix B. This quantity is related to the zero-order phase shifts $\delta_{T0}(\delta_{S0})$ characteristic of the triplet (singlet) state of the system of two electrons, by

$$\sigma_e = \tfrac{1}{4}[\sigma_T + \sigma_s + 2(\sigma_T \sigma_S)^{1/2} \cos(\delta_{T0} - \delta_{S0})] \; , \quad (3.1)$$

where

$$\begin{aligned} \sigma_T &= 4\pi k^{-2} \sin^2 \delta_{T0} \; , \\ \sigma_S &= 4\pi k^{-2} \sin^2 \delta_{S0} \; , \end{aligned} \quad (3.2)$$

are the scattering cross sections in the two states. The quantity $k$ is the momentum of the delocalized electron. The values of the phase shifts have been numerically calculated by Schwartz[22] as a function of $p = ka_0$, for scattering of free electrons by hydrogen atoms. Here $a_0$ is the Bohr radius of the atom. Since the form of the interaction potential is essentially the same for a donor, the same calculations give the phase shifts in the case of gallium arsenide. We take for the parameter $p$, $k_T a_0^*$ where $k_T$ is the thermic momentum of the electron and $a_0^*$ is the donor effective Bohr radius. One obtains, taking a value of the temperature $T$ of the free-electron gas of the order of 10 K,[23]

$$\sigma_e \simeq 9 \times 10^{-12} \text{ cm}^2 \; . \quad (3.3)$$

This is probably valid within numerical factors of the order of unity.[24]

The evolution of the mean spin of the free and trapped electronic states is determined by writing the rate equations of the populations $n_f$ and $n_t$ of the two states, the quantization axis being the longitudinal direction. For free electrons, these equations can be written

$$\begin{aligned} \frac{\partial n_{f+}}{\partial t} &= -\sigma_e v n_{t-} n_{f+} + \sigma_e v n_{t+} n_{f-} \; , \\ \frac{\partial n_{f-}}{\partial t} &= -\sigma_e v n_{t+} n_{f-} + \sigma_e v n_{t-} n_{f+} \; , \end{aligned} \quad (3.4)$$

where $v$ is the electronic thermic velocity. Using the expressions of the mean spin of the two electronic states

$$\langle S_q \rangle = \frac{1}{2} \frac{n_{q+} - n_{q-}}{n_{q+} + n_{q-}} \; , \quad (3.5)$$

we obtain the contribution of exchange to the motion of the electronic spins

$$\begin{aligned} \left. \frac{\partial \langle S_f \rangle}{\partial t} \right|_e &= - \frac{n_t}{n_t + n_f} \frac{1}{\tau_e} (\langle \vec{S}_f \rangle - \langle \vec{S}_t \rangle) \; , \\ \left. \frac{\partial \langle S_t \rangle}{\partial t} \right|_e &= - \frac{n_f}{n_t + n_f} \frac{1}{\tau_e} (\langle \vec{S}_t \rangle - \langle \vec{S}_f \rangle) \; , \end{aligned} \quad (3.6)$$

where $n_t(n_f)$ is the total concentration of the trapped (free) electronic state. These equations have been established with the supposition that the magnetic field is parallel to the direction of excitation light. They are also valid in NMR conditions, for which the magnetic field experienced by trapped electrons is no longer longitudinal. Indeed, the electronic motion by precession in this field can be shown to be negligible during the spin-exchange process, so that this last process should not depend on the magnetic fields experienced by the two states. Thus, the two mean spins $\langle \vec{S}_t \rangle$ and $\langle \vec{S}_f \rangle$ tend to be equalized by spin exchange, the characteristic time of the decrease of $\langle \vec{S}_t \rangle - \langle \vec{S}_f \rangle$ being given by

$$\frac{1}{\tau_e} = (n_t + n_f) \sigma_e v \; . \quad (3.7)$$

This time should be compared to the lifetime of the free electrons, of the order of 10 nsec. The value of the electronic concentration which gives a comparable exchange time is found, from Eqs. (3.3) and (3.7) to be $10^{12}$ cm$^{-3}$, which is at least two orders of magnitude smaller than the actual concentration in our crystal.[11] This demonstrates that spin exchange is indeed very effective to equalize the populations of the two electronic states.

We examine now the possibility of other mechanisms of averaging. We recall that the thermal excitation to free electronic states, together with the impact ionization by energetic electrons, are ineffective due to the low values of both the lattice and free-electron-gas[23] temperatures. These other mechanisms can be the following.[25]

(a) Reexcitation to free electronic states by Auger processes[26] in the trapped excitonic states, or by dissociation of free excitons in the vicinity of impurities.[27] We have indeed observed, in agreement with the results of Shah *et al.*[28], a strong photoconductivity, only weakly dependent on energy, by exciting the localized electronic states with a tunable laser source.[29] The effectiveness of the reexcitation processes can be estimated from the calculation of the radiative lifetime of the complex $D_0X$, performed by Hwang and Dawson.[26] This time is approximately 2 nsec whereas the measured total lifetime of this complex is 1 nsec. This shows that the reexcitation processes are, at most, as effective as radiative recombination. They can thus be neglected as compared to spin exchange, which is at least two orders of magnitude more effective.

(b) Trapping of free electron in an excited state of the donor, followed by thermal excitation, according to the "giant trap" model of Lax.[30,31] In our case where the radius of spheres of polarized nuclei, around each donor, is comparable with the donor Bohr radius, this would result in a value of the average nuclear field experienced by the free electrons, smaller than that experienced by trapped electrons. This is not the case, which shows that spin exchange is more efficient than trapping in an excited state of the donor.

In summary, spin exchange is the dominant mechanism of averaging of the polarizations of the various electronic states. The resulting motions of the spins $\langle\vec{S}_t\rangle$ and $\langle\vec{S}_f\rangle$ are given by Eqs. (3.6). The spin exchange time is found to be at least two orders of magnitude shorter than the lifetime in the free electronic state so that the polarizations of the two states are equalized. Thus, although the various electronic states are characterized by distinct features (energy, kinetics of recombination,. . . ,), the spin properties of all these states are the same, due to the efficient averaging produced by spin exchange. This is the reason why the NMR line is also observed on the delocalized state.

### B. Theory of the resonance line shape including spin exchange

To calculate the resonance signal, taking into account the fast spin exchange, we consider for simplicity only two electronic states, free electrons and electrons trapped on donors. We thus forget the presence of excitons. Our image of the system is illustrated in Fig. 4: light excitation across the band gap creates free carriers which recombine via the trapped electronic state. As was discussed above, the nuclear field acts only in the trapped state, but the existence of averaging mechanisms causes depolarization of free electrons at resonance. The motion of the electronic spins is then due to three different processes: relaxation together with recombination, precession in the magnetic field experienced by the two states, and spin exchange. With the above form of the motion due to spin exchange, the coupled equations of evolution of the two states can be written

$$\frac{d\langle\vec{S}_f\rangle}{dt} = -\frac{1}{T_{1*}^f}\left[\langle\vec{S}_f\rangle - 0.25\theta\vec{u}\frac{T_{1*}^f}{\tau^f}\right] - \frac{g^*\mu_B}{\hbar}\langle\vec{S}_f\rangle\times\vec{B} - \frac{n_t}{n_t+n_f}\frac{1}{\tau_e}(\langle\vec{S}_f\rangle - \langle\vec{S}_t\rangle) \; , \tag{3.8}$$

$$\frac{d\langle\vec{S}_t\rangle}{dt} = -\frac{1}{T_{1*}^t}\left[\langle\vec{S}_t\rangle - \langle\vec{S}_f\rangle\frac{T_{1*}^t}{\tau^t}\right] - \frac{g^*\mu_B}{\hbar}\langle\vec{S}_t\rangle\times\vec{B}_t - \frac{n_f}{n_t+n_f}\frac{1}{\tau_e}(\langle\vec{S}_f\rangle - \langle\vec{S}_t\rangle) \; , \tag{3.9}$$

where $T_1^q$ and $\tau^q$ are the spin relaxation time and the lifetime of state $q$ and $T_{1*}^q = T_1^q\tau^q/(T_1^q+\tau^q)$. The quantity $\theta$ is the degree of circular polarization of the excitation light and $\vec{u}$ is the unit vector of the $z$ direction. The first term of these coupled equations describes the motion of the spins of the two states due to relaxation and recombination,[11] the initial mean spin being $-0.25\theta\vec{u}$ for the free state and, for the trapped state, the mean spin $\langle\vec{S}_f\rangle$ of free electrons which act as a source for the trapped state. The total field $\vec{B}_t$, acting on the trapped electrons, includes the oblique nuclear field and is given by Eqs. (2.3) and (2.4). The magnetic field acting on the free electrons is simply the external field $\vec{B}$. To solve the two above equations in steady-state regime, we make the simplifying assumption that spin exchange is fast as compared with relaxation and recombination, that is:

$$\frac{n_t}{n_t+n_f}\frac{1}{\tau_e}T_{1*}^f >> 1 \; ,$$
$$\frac{n_f}{n_t+n_f}\frac{1}{\tau_e}T_{1*}^t >> 1 \; . \tag{3.10}$$

Then, it can be seen, by considering the scalar product of Eq. (3.8) with $\vec{u}$, that the longitudinal components of $\langle\vec{S}_f\rangle$ and $\langle\vec{S}_t\rangle$ are equal. The common value of $\langle S_{fz}\rangle$ and $\langle S_{tz}\rangle$ is found to depend on the efficiencies of spin exchange on one hand, and of relaxation and recombination on the other hand, which are characterized by the two following magnetic fields.

(i) The field $\delta_e$, defined by

$$\delta_e = \frac{\hbar}{g^*\mu_B}\frac{n_t}{n_t+n_f}\frac{1}{\tau_e} = \frac{\hbar}{g^*\mu_B}\sigma_e n_t v \; , \tag{3.11}$$

which is, in units of magnetic field, the frequency of spin exchange for free electrons. Although the concentration $n_t$ of trapped electrons cannot be well characterized, this quantity can be assumed, at least for the high excitation intensities used in this work, to be of the order of the donor concentration which is several $10^{14}$ cm$^{-3}$ in our samples. Using Eq. (3.3)

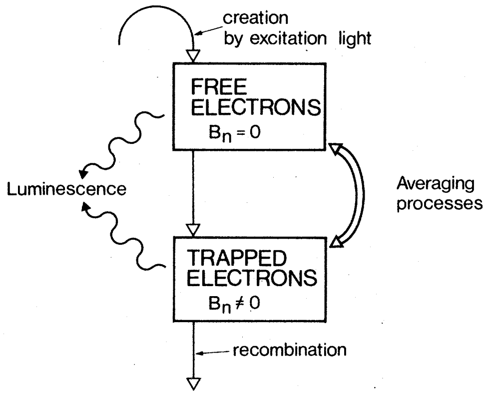

FIG. 4. Description of the system of localized and delocalized electronic states (see the text). The free electrons, although experiencing a very small nuclear field, are depolarized in conditions of NMR, through their contact with trapped electrons.

and taking $n_t = 10^{14}$ cm$^{-3}$, we find

$$\delta_e \simeq 1.8 \text{ kG} \ . \tag{3.12}$$

(ii) The width $\Delta B$ of the standard Hanle curve, in the absence of nuclear effects, which characterizes the efficiency of relaxation and recombination. This field can be experimentally determined and has been found to vary between 10 and 150 G, depending on excitation-light intensity. The field $\Delta B$ is quite generally of the form (2.6). In the presence of spin exchange, the total effective spin relaxation time $T_{1*}$ is however no longer given by Eq. (2.7), but by

$$\frac{1}{T_{1*}} = \frac{1}{T_{1*}^f} + \frac{n_t}{n_f}\frac{1}{T_1^t}\left(1 + \frac{n_t}{n_f}\right)^{-1} \ . \tag{3.13}$$

With the above definitions, the common value of $\langle S_{tz} \rangle$ and $\langle S_{fz} \rangle$ in conditions of NMR can be written

$$\langle S_{tz} \rangle = \langle S_{fz} \rangle = \langle S_0 \rangle \frac{\Delta' B^2 + B_{tz}'^2}{\Delta' B^2 + B_t'^2} \ . \tag{3.14}$$

This equation has the same form as the usual equation (2.5) of the Hanle effect in an oblique magnetic field. The off-resonance mean spin $\langle S_0 \rangle$ is

$$\langle S_0 \rangle = -0.25\theta \frac{T_{1*}}{\tau_f (1 + n_t/n_f)} \ . \tag{3.15}$$

The effective electronic relaxation time $T_{1*}$ being defined by Eq. (3.13).

The longitudinal and transverse components of the total effective magnetic field $B_t$ acting on the electronic spin system are defined, in the case of the resonance of isotopic nuclear species $\alpha$, by

$$\begin{aligned} B_{tx}' &= \mu^{1/2} B_{\alpha x}^{r\prime} \ , \\ B_{tz}' &= B + \sum_{\beta \neq \alpha} B_\beta' + B_{\alpha z}^{r\prime} \ , \end{aligned} \tag{3.16}$$

where the modified nuclear fields $B'$ are of the form

$$B_\beta' = (1 + \lambda)^{-1} B_\beta \tag{3.17}$$

and the nuclear fields $B_{\alpha x}^{r\prime}$ and $B_{\alpha z}^{r\prime}$ are obtained from Eq. (2.3) by replacing $B_\alpha$ by $B_\alpha'$, defined by the above equation. The coefficients $\lambda$ and $\mu$, given by

$$\lambda = \frac{n_f}{n_t} \frac{\delta_e^2}{\delta_e^2 + B^2} \ , \tag{3.18}$$

$$\mu = 1 + \frac{\delta_e}{\Delta B}\left(1 + \frac{n_t}{n_f}\right)^{-1} \frac{B^2}{\delta_e^2 + B^2} \ , \tag{3.19}$$

depend only on the magnetic field $B$ experienced by the free electronic state and are the same throughout the NMR line. The effective Hanle linewidth $\Delta' B$ is given by

$$\Delta' B = (1 + n_f/n_t) \Delta B \mu (1 + \lambda)^{-1} \ . \tag{3.20}$$

We now comment on the above results and discuss successively the value of the off-resonance electronic mean spin, of the effective magnetic field $B_t'$, and of the effective Hanle linewidth $\Delta' B$.

*a. Off-resonance mean spin.* The off-resonance mean spin $\langle S_0 \rangle$, as seen from Eqs. (3.13) and (3.15), depends on the concentrations $n_f$ and $n_t$ of free and trapped electrons. Two limiting cases can be distinguished. When the concentration $n_t$ of trapped electrons is very small, the off-resonance mean spin $\langle S_0 \rangle$ of the two electronic states is that of the free state, unmodified by the spin exchange with the trapped state. On the other hand, if the concentration of trapped electrons is large, the total loss of magnetization caused by electronic relaxation in the trapped state is large. Thus the magnetization loss of the free state, due to spin exchange with the trapped state, can be as large as to prevent the free electrons from being polarized by the excitation light. We have then $\langle S_t \rangle = \langle S_f \rangle = 0$.

*b. Effective magnetic field.* As seen from Eqs. (3.16), the introduction of spin exchange causes two modifications of the magnitude of the effective field acting on the electrons. Firstly, the fast spin exchange produces an averaging between the very small nuclear field experienced by the free electronic state and the nuclear field $B_n$ acting on the trapped electronic state. The mean nuclear field $B_\beta'$ of nuclear isotopic species $\beta$ is given by Eq. (3.17) and is smaller than $B_\beta$ by a factor $(1 + \lambda)$. The averaging factor $\lambda$, defined by Eq. (3.18), depends on the populations $n_t$ and $n_f$ of the two electronic states. Secondly, the electronic depolarization takes place as if the transverse component of the field $B_t$ acting on trapped electrons were multiplied by a factor $\mu^{1/2}$ larger than unity. The origin of this amplification is the following. At resonance, the two fields experienced by the free and trapped electrons are not parallel. Then, the modulation by spin exchange of the Zeeman interaction of a given electron causes an extra relaxation process, which does not exist in off-resonance conditions, and which results in an increase of the electronic depolarization at resonance. This enhancement of the resonance signal is obviously only present when precession is sufficiently fast to modify the electronic spin between two exchange processes, that is, if the external field $B$ is not too small. This last fact is indeed predicted by the theory which shows that for low external magnetic fields that is, if the following condition is verified:

$$B \ll (\delta_e \Delta B)^{1/2} \ , \tag{3.21}$$

the enhancement factor $\mu$ is very close to unity, so that the amplification of the signal is very small. On the other hand, if the following condition is satisfied:

$$B \gg \delta_e \ , \tag{3.22}$$

which indicates that, for the free electronic state, precession is faster than spin exchange, the enhancement factor $\mu$ has its maximum value, which is related with the ratio $\delta_e/\Delta B$ of the efficiencies of spin exchange and of recombination and relaxation. Taking the estimated value [Eq. (3.12)] of $\delta_e$ and the measured value of $\Delta B$, one sees that, in the case of high-purity gallium arsenide, the maximum value of the enhancement factor $\mu$ can be as large as 100. Consequently, the present theory predicts that the nuclear resonance signal should be strongly amplified due to the existence of spin exchange.

*c. Effective Hanle linewidth* $\Delta' B$. A standard approximation in the framework of the geometrical model is to neglect, in Eq. (3.14), the Hanle linewidth $\Delta B$ as compared with the magnetic field $B_t$ acting on trapped electrons. This approximation is justified if spin exchange is not considered, because $\Delta B$ is indeed small as compared with the value of the external and nuclear fields. This is no longer true if there exists an efficient spin exchange averaging because, as seen from Eq. (3.20), the effective Hanle linewidth $\Delta' B$ is in the general case different from $\Delta B$. The quantity $\Delta' B$ increases with the value of the external magnetic field. The effective Hanle linewidth is then likely to be much larger than $\Delta B$, so that the above approximation is not valid in all cases. Note that, in high magnetic fields, if for the two electronic states precession is faster than recombination and relaxation that is, if condition (3.22) and condition

$$B_t \gg (n_f/n_t)\delta_e \tag{3.23}$$

are fulfilled, the field $\Delta' B$ is equal to $\delta_e$. This high-field value of the effective Hanle linewidth $\Delta' B$ corresponds to a value of the effective electronic relaxation time $T_{1*}$, determined by an equation similar to Eq. (2.6), which is equal to the spin exchange time of the free electronic state. This comes basically from the existence, in the high-field case, of the extra electronic relaxation mechanism due to modulation by spin exchange of the electronic Zeeman interaction. Due to the strong value of the external field, the relaxing interaction is strong, and this case is analogous to the strong collision case in standard theory of relaxation. The relaxation time of the above mechanism is then of the order of the time of modulation of the relaxing interaction, which is in our case the spin exchange time. This time is much shorter than the electronic relaxation time and lifetime, and determines the value of the effective Hanle linewidth, which explains the high-field value of $\Delta' B$.

To summarize, we have calculated the value of the electronic mean spin in conditions of NMR, taking into account the fast spin exchange between free and localized electrons. The nuclear resonance signal is in the general case modified by three different effects: averaging of the magnetic fields experienced by the two states, which results in a decrease of the value of the nuclear fields; amplification of the transverse component of the field acting on the trapped electronic state; and consequently of the nuclear resonance signal, modification of the Hanle linewidth which is likely to be no longer negligible. The line shape is now determined by three parameters which are: (i) the quantity $A'_\alpha$ given by

$$A'_\alpha = \left| B_\alpha + \sum_\beta B'_\beta \right| \Big/ B'_\alpha \tag{3.24}$$

which is obtained by replacing in $A_\alpha$, given by Eq. (2.10), the nuclear fields $B_\beta$ by their averages $B'_\beta$

TABLE I. Effect of spin exchange on the resonance line shape. This table gives the values of the average nuclear fields $B'_\beta$, experienced by the system of two electronic states, of the enhancement factor $\mu$, and of the effective Hanle linewidth $\Delta' B$ in the low-field case and in the high-field case discussed in the text. One sees that in the low-field case, the resonance line shape can be interpreted in the framework of the geometrical model, with modified values of the nuclear fields. The high-field case is characterized by a strong amplification of the resonance signal.

| | General case | Low field Cond. (3.21) | High field Cond. (3.22) and (3.23) |
|---|---|---|---|
| Nuclear fields $B'_\beta$ | (3.17) | Smaller than $B_\beta$ | Unmodified by spin exchange, equal to $B_\beta$ |
| Enhancement factor $\mu$ | (3.19) | Negligible | Maximum value |
| Effective Hanle linewidth $\Delta' B$ | (3.20) | Negligible | Negligible |

over the two electronic states; (ii) the amplification parameter $\mu$, given by Eq. (3.19); and (iii) the effective Hanle linewidth $\Delta' B$, given by Eq. (3.20). It is possible to distinguish a low-field case and a high-field case, which are respectively defined by condition (3.21) and conditions (3.22) and (3.23), and basically correspond to fast precession or slow precession as compared to spin-lattice relaxation together with recombination. These two cases are analyzed in Table I, where the expressions of the three parameters of the system are given. One sees that in the low-field case, the amplification of the signal is negligible. This case can be interpreted in the framework of the geometrical model, simply taking into account the modified values $B'_\beta$ of the nuclear fields $B_\beta$. On the other hand, in the high-field case, there is no averaging of the nuclear fields ($B'_\beta = B_\beta$) but a strong amplification of the signal. The effective Hanle linewidth can be neglected in both the low-field limit and the high-field limit, but not in the intermediate case.

## IV. QUANTITATIVE STUDY OF THE LINE SHAPE

For the experimental study of the NMR line, we have used the method described in Sec. II, which consists of applying the rotating field at a given distance from exact resonance and of measuring the resulting electronic depolarization $\Delta \langle S_z \rangle$. This has been done in several *n*- and *p*-type high-purity samples at pumped-helium temperature. Since the results obtained do not depend strongly on impurity concentration, we present here only the case of an *n*-type sample of concentration of several $10^{14}$ cm$^{-3}$. The experimental setup and conditions, apart from the field configuration, are the same as discussed in Ref. 3. The external field, longitudinal with respect to the direction of light excitation, is as high as 12 kG. The magnet used is homogeneous enough for NMR detection (less than 50 mG in the illuminated volume of the sample) and at the same time allows laser excitation and luminescence detection along the magnetic field. The rotating field $B_1$, produced by a coil wound around the glass Dewar tail, can reach 5 G.

The general features of the observed nuclear resonances are shown in Fig. 5 for $^{75}$As in an external field of 11 kG, for the two cases where the nuclear field is parallel or antiparallel to $B$. In agreement with the above model, the two corresponding lines have a *W*-like shape. However: (i) The shape of the *W* is dissymmetric, and the center of the resonance is not situated at the same position for the two geometries; and (ii) the magnitude and width of the resonance lines are larger when the nuclear field is antiparallel to the external field than in the opposite case.

In this section, we show that these two effects cannot be interpreted by the above theory including spin exchange. They are due, respectively, to the existence of the Knight shift of the NMR line and to the inhomogeneities of the nuclear field. We find that we can sort out these effects to study the role played by spin exchange.

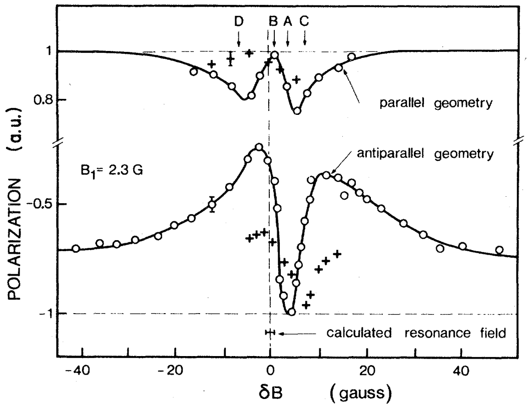

FIG. 5. Shape of the resonance of $^{75}$As nuclei at 8 MHz in the two cases where the nuclear field is antiparallel or parallel to the external field. The circles are the relative value of the electronic mean spin after application of $B_1$. The magnitudes of the two resonance signals are not the same, due to the geometry of the system (see Fig. 6). The centers of the two lines are not situated at the same position (points *A* and *B*), due to the existence of the Knight shift. The accurate value of this shift is best obtained from the center of the slow passage resonance curves (see the crosses on the figure) and, as predicted, has the same absolute value for the two geometries (points *C* and *D*).

### A. Knight shift of the line

The hyperfine field experienced by the nuclear spins $\alpha$ from the spin-polarized trapped electrons has been calculated in Ref. 3. This field, of the form $b_e^\alpha \langle \vec{S}_t \rangle$, where $\langle \vec{S}_t \rangle$ is the mean spin of trapped electrons, has been shown to be of the order of several gauss. In this case, the distance to resonance is no longer $\delta B$ given by Eq. (2.1), but now depends on the longitudinal component of $\langle \vec{S}_t \rangle$. It is given by

$$\delta' B = \delta B + b_e^\alpha \langle S_{tz} \rangle \quad , \tag{4.1}$$

so that the center of the observed resonance line, corresponding to $\delta' B = 0$ should be shifted from its calculated position.[32] Since the off-resonance mean electronic spin $\langle S_0 \rangle$ has opposite values for the parallel and antiparallel geometries, the sign of the resulting Knight shift is expected not to be the same for the two cases. This effect is directly evidenced from Fig. 5 which shows that indeed, the centers of the two resonance lines in the parallel and in the antiparallel geometries are not at the same position (points *A* and *B* of Fig. 5).

Let us point out however that: (i) the absolute values of the measured Knight shifts are found to be different for the two cases, although the mean electronic spin $\langle S_0 \rangle$ is exactly the same; and (ii) close to the center of the line, the resonance line shape is dissymmetric. We think that these two effects have the same origin and are due to the variation of the distance $\delta' B$, given by Eq. (4.1), due to the decrease at resonance of the longitudinal component $\langle S_{0z} \rangle$ of the electronic spin. This variation causes a change of the direction of the effective field $B_{\text{eff}}$ in the rotating frame, and there results a feedback between the nuclear and electronic spin systems which modifies the resonance signal. However, the coupled equations of evolution of the nuclear field $\vec{B}^r_\alpha$ and of $\vec{B}_{\text{eff}}$ after application of $B_1$ are intricate and will not be solved. Very schematically, one can explain the asymmetry of the resonance lines by noticing that the modification of the absolute value of $\delta' B$ due to the decrease of $\langle S_0 \rangle$ at resonance is an increase or a decrease depending on the side of the resonance line where $B_1$ is applied. Since in the geometrical model the magnitude of the signal only depends on $\delta' B / B_1$, this leads to a modification of the resonance signal which has an opposite sign for the two sides of the line and explains the asymmetry of the resonance line. To show that the above feedback also shifts the centers of the resonance lines, it is possible to analyze the slow-passage resonance curves. Indeed, close to the center of the line, in conditions of slow passage, the electronic spin has its off-resonance value $\langle S_0 \rangle$ and is constant, so that the feedback no longer exists. Then the values of the Knight shift, measured from the slow-passage resonance signals, are expected to be the same in the parallel and antiparallel geometries. This is indeed verified by the experimental results (points *C* and *D* of Fig. 5). The measure of the common value of the Knight shift yields the quantity $b_e^{\alpha}$. In the case of $^{75}$As, we find

$$b_e^{(^{75}\text{As})} = -50 \pm 10 \text{ G} \qquad (4.2)$$

which has the correct sign and is the value calculated from Ref. 3 for the arsenic nuclei situated at a distance from a donor equal to 80 Å.

### B. Inhomogeneities of the nuclear field

The existence of inhomogeneities of the nuclear field $B_n$ is revealed from the results of the optical detection of the electron spin resonance, obtained in the same sample.[33] Indeed, when the nuclear spins are dynamically polarized, one observes (see Fig. 1 of Ref. 33) a broadening of the electronic resonance signal, due to the inhomogeneities of the nuclear field which shifts the resonance. In the present section, we show that these inhomogeneities cause the width of the resonance line to be much larger in the case where the nuclear field $B_n$ is antiparallel to the external field than in the opposite case. This done in the framework of the geometrical model since the amplification parameter $\mu$ and the effective Hanle linewidth $\delta' B$, introduced by the theory including spin exchange, are the same for the two geometries, so that spin exchange plays no role in the interpretation of these effects.

To show the differences between the parallel and antiparallel geometries in the framework of the geometrical model, we compare the field configuration at resonance for the two cases, supposing first that $B_n$ is homogeneous. This is shown in Fig. 6. The only difference between the two cases represented on the figure is the sign of the nuclear fields, the other parameters of the system being exactly the same. We recall that the electronic relative depolarization is $\sin^2\phi_e$ where $\phi_e$ is the angle between the total field experienced by the nuclei and the longitudinal direction. One sees (i) that the resonance signal is quite generally larger in the antiparallel than in the parallel case, and (ii) that there exists a critical situation, for which the total nuclear field is equal to the external field. In this case the parallel resonance signal is basically unchanged whereas in the antiparallel geometry a very small rotation of the nuclear field $\vec{B}_\alpha$ produces an important change of $\phi_e$, and consequently, a large resonance signal. This means that, if the total off-resonance field $\vec{B} + \sum_{\beta \neq \alpha} \vec{B}_\beta + \vec{B}^r_\alpha$ is very small, the linewidth can be much larger in the antiparallel geometry than in the opposite case and should strongly decrease if the external field or the

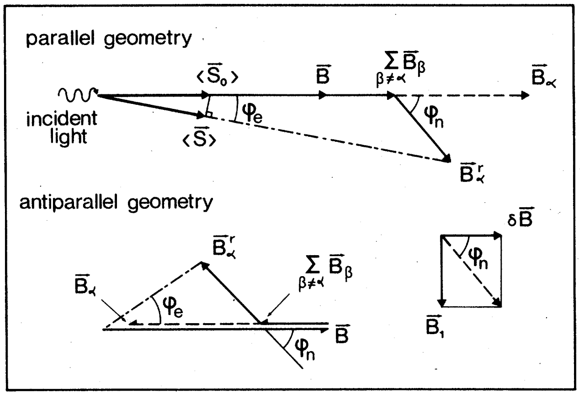

FIG. 6. The difference in the magnitudes of the resonance signals, in the two cases where the nuclear field is parallel or antiparallel to the external field, comes from the geometry of the system. For a given value of external and nuclear fields, and of the angle $\phi_n$, the angle $\phi_e$ of the total field experienced by the electrons with the direction of incident light is indeed larger in the antiparallel than in the parallel geometry. There results a stronger electronic depolarization in the former case.

nuclear field are slightly modified.

The above effect, which is predicted, with the supposition that $B_n$ is homogeneous, does not interpret the larger linewidth in the antiparallel geometry because the dissymmetry of the linewidths between the parallel and antiparallel geometries has been found experimentally to be independent of the relative values of external field and total nuclear field. If now we take into account the inhomogeneities of $B_n$, one sees that a broadening of the resonance line in the antiparallel geometry will be observed if there exists a fraction of electrons for which the nuclear field $B_n$ compensates the external field. This means that the resonance will be inhomogeneously broadened for a whole range of values of $B$, the extension of which is of the order of the inhomogeneities of $B_n$.

Consequently, we have shown that the inhomogeneities of $B_n$ are likely to explain the larger linewidth in the antiparallel geometry. Since the broadening is observed for a wide range of values of the external field $B$, we conclude that the width of the distribution of the nuclear fields is probably very large, comparable with the value of the average nuclear field. This is indeed verified from the conduction electron resonance results mentioned above. These are probably related to macroscopic fluctuations of impurity concentration which are not averaged out by the fast spin exchange.[34]

It is possible to illustrate more precisely the role played by the inhomogeneities of $B_n$. As stated before, the signal in the far wings of the line is due to the depolarization of the only trapped electrons for which the nuclear field $B_n$ compensates the external field. For the rest of the resonance line, all trapped electrons in principle contribute to the signal, but we shall only consider here the more numerous ones for which $B_n$ is equal to the average nuclear field $\bar{B}_n$. Consequently, if the external field $B$ compensates $\bar{B}_n$, the same electrons are dominant for the two parts of the resonance line and the effect of the inhomogeneities on the lineshape should be decreased. This is verified by the comparison, for several values of the nuclear field of the experimental electronic depolarization $\Delta\langle S_z\rangle^{\mathrm{expt}}$ and its theoretical value $\Delta\langle S_z\rangle^{\mathrm{theor}}$, obtained by an extrapolation from the far wings of the line in the framework of the geometrical model. This is shown by Fig. 7 which represents the variation with the distance $\delta B$ to resonance of $^{75}$As nuclei, of the error signal

$$e=\frac{\Delta\langle S_z\rangle^{\mathrm{expt}}-\Delta\langle S_z\rangle^{\mathrm{theor}}}{\Delta\langle S_z\rangle^{\mathrm{theor}}} . \tag{4.3}$$

Curve b of the figure corresponds to a nuclear field $\bar{B}_n$ larger than $B$, and curve c to $\bar{B}_n$ smaller than $B$. The case of compensation, shown in curve a, can be easily characterized because, as seen in Fig. 6, in the antiparallel geometry, it corresponds to a maximum electronic relative depolarization at least for small values of the angle $\phi_n$. Indeed, in this case, the error signal $e$ is found to be smaller than in the two other cases, which evidences the role of the inhomogeneities of the nuclear field. Of course, the quantitative understanding of the line is not perfect. This is mainly due to the crudeness of the above approximation with two types of trapped electrons, and also to the effects of spin exchange, which will be shown in the following section.

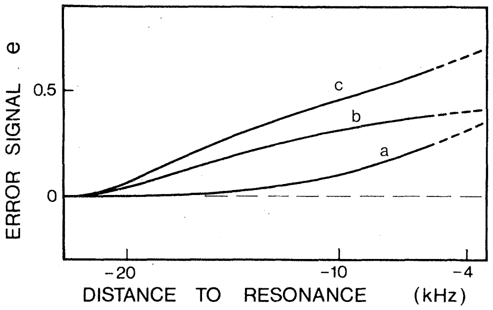

FIG. 7. Variation of the error signal given by Eq. (4.3) for three different values of the off-resonance electronic mean spin. This is the $^{75}$As resonance in the antiparallel geometry in an external field equal to 300 G. Curve a corresponds to the case where the nuclear field compensates the external field. In curve b(c) the nuclear field is larger (smaller) than the external field. In the geometrical model of Eqs. (2.8) and (2.9), the quantity $e$ should be zero. The better agreement for curve a is an evidence of the role of inhomogeneities of the nuclear field (see the text).

Note that if it is possible to characterize compensation of external and nuclear fields, it is in principle possible to estimate the ratio $b_\alpha=\bar{B}_\alpha/\langle \bar{I}_\alpha\rangle$ where $\bar{B}_\alpha$ is the average nuclear field of isotopic species $\alpha$ and $\langle \bar{I}_\alpha\rangle$ the corresponding mean spin. The nuclei $\beta\neq\alpha$ are resonantly saturated before application of $B_1$ on the resonance of nuclei $\alpha$. Then the compensation corresponds to $\bar{B}_\alpha+B=0$ so that $\bar{B}_\alpha$ is known. On the other hand, the measure of the luminescence polarization yields the mean electronic spin and from Eq. (2.17) of Ref. 3, allows us to estimate the average mean spin $\langle \bar{I}_\alpha\rangle$ of isotopic species $\alpha$. One obtains then for arsenic nuclei

$$b_{(^{75}\mathrm{As})}=6\pm 2\ \mathrm{kG} . \tag{4.4}$$

The large uncertainty of this value comes from the measurement of the luminescence polarization and of the possible imperfect saturation of gallium nuclei. The value obtained is three times smaller than a theoretical estimate [Eq. (2.19) of Ref. 3], supposing that all the nuclear spins situated in the region of localization of the trapped electrons are dynamically polarized. This difference probably comes from the decrease of the nuclear field caused by spin exchange [see Eq. (3.17)] and from the existence of other mechanisms of nuclear relaxation, apart from the hyperfine coupling with the trapped electrons.[3]

In conclusion, we have shown that there exist strong macroscopic inhomogeneities of the nuclear field $B_n$ experienced by the various trapped electrons. These inhomogeneities have qualitatively no effect on the resonance line in the parallel geometry, but drastically broaden the resonance line in the antiparallel geometry. Due to the strong width of the distribution of the nuclear fields, this is true almost independently of the value of the external field.

### C. Experimental study of the effect of spin exchange

In this section, we show the effects of spin exchange on the line shape which are predicted by the above theory, that is mainly the amplification of the resonance signal. We recall however that the existence of the Knight shift of the line and the inhomogeneities of the nuclear field are likely to produce uncontrolled modifications of the line shape which forbid an accurate analysis. To avoid these effects, we choose to study the only case where the nuclear field has the same sign as the external field, and for which it can be shown that the inhomogeneities of $B_n$ do not appreciably modify the line shape.[35] Furthermore we exclude from our analysis the center of the resonance line for which, as shown in Sec. IV A, the magnitude of the resonance signal is modified due to the existence of the electronic field.

It is at this point straightforward to show the enhancement produced by spin exchange in the parallel geometry because, as shown in Fig. 5, the width of the resonance line is in this case much larger than the magnitude of the rotating field $B_1$. This cannot come from usual inhomogeneous broadening of the line (quadrupolar effects, inhomogeneities of the Knight shift) since we have verified that the linewidth is indeed proportional to $B_1$. To show this enhancement more precisely, we point out that if no spin exchange is present, the theoretical value of the electronic depolarization $\Delta\langle S_z\rangle/\langle S_0\rangle$, given by Eq. (2.8), is in all cases smaller than $\sin^2\phi_n$, which is the value of $\Delta\langle S_z\rangle/\langle S_0\rangle$ if the total field experienced by the electrons is only composed of the field $\vec{B}'_\alpha$ of nuclei $\alpha$. Indeed Fig. 8 shows that, in the case where the external field is 10 kG, the experimental resonance line is broader and more intense than the above-defined theoretical signal. This demonstrates the enhancement produced by spin exchange.

Further investigation of the effects of spin exchange would in principle require us to determine the values of the three parameters of the system [$A'_\alpha$, given by Eq. (3.24), amplification parameter $\mu$, effective Hanle linewidth $\Delta' B$] and to study their variations as a function of the external magnetic field, keeping the nuclear field constant. However, due to the high number of adjustable parameters, we are not very confident in the reliability of such a study.

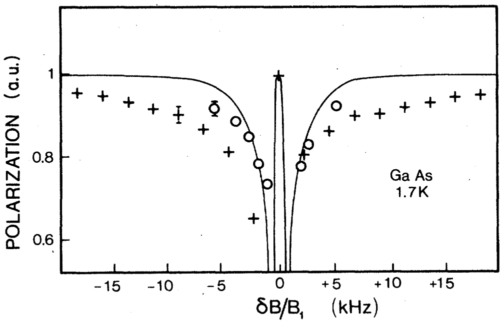

FIG. 8. Effect of spin exchange on the shape of the NMR line in the parallel geometry: The solid line is the calculated maximum electronic depolarization, in the absence of spin exchange. The experimental results obtained in a field of 10 kG (+) and in a low external field equal to 300 G (○), show the enhancement of the nuclear signal by spin exchange. In agreement with the theory this enhancement is found to increase with external magnetic field.

Furthermore, a change of the external field probably produces a change of the nuclear field $B_n$,[36] and consequently causes spurious modification of the parameter $A'_\alpha$. Therefore, we shall limit ourselves here to physical remarks which allow us to verify qualitatively the effect of spin exchange and its dependence as a function of external magnetic field.

The increase of the amplification parameter as a function of external field is first shown, at least qualitatively, in Fig. 8, which compares the shape of the resonance signal obtained in the above case where the external field is equal to 10 kG, and in a very low external field, equal to 300 G. One sees indeed that, in agreement with the theoretical predictions, the amplification parameter increases with the value of the external field. Furthermore, it is possible to analyze the experimental situation in the framework of the high-field case and of the low-field case discussed in the preceding section. The estimate of the quantity $\delta_e$ and the measure of the width $\Delta B$ of the Hanle curve show that the low-field case defined by condition (3.21) probably correspond to $B$ of the order of several hundred gauss, whereas the high-field case is likely to be obtained for a very strong external field, higher than 10 kG. Consequently, the total available range of the external field probably corresponds to the intermediate situation. This is seen, first by noticing that there still exists a small enhancement of the NMR signal in an external field of 300 G. Secondly, an analysis of the high-field results of Fig. 8 using Eqs. (3.14), (3.22), and (3.23), shows that the signal close to the center of the line is too small, as compared to the signal in the far wings, to be interpreted by the high-field case. This means that this case corresponds to the intermediate case, for which the effective Hanle linewidth is not negligible. Close to the center of the line, the effective field $B_t'$, defined by Eq. (3.16), is smaller than in the far wings, and is of the order of $\Delta' B$. The resulting incomplete Hanle effect causes the signal to be weaker than in the high-field limit. Consequently, in agreement with the theoretical predictions, the two resonance lines presented in Fig. 8 correspond to the intermediate case discussed in the preceding section.

Finally, we point out that quantitative study of the far wings of the resonance lines is possible, because these far wings can be shown to be described by the geometrical model, but with a value $A_\alpha''$ of the parameter $A_\alpha'$, given by

$$|A_\alpha''| = \mu^{-1}(\Delta' B^2/B^2 + A_\alpha'^2)^{1/2} , \tag{4.5}$$

which takes into account amplification parameter and Hanle linewidth. Thus, although the resonance signal is strongly modified by spin exchange, the ratio $B_\alpha / B_{\alpha'}$ should simply be obtained from the observation of the two resonances of nuclei $\alpha$ and $\alpha'$, by

$$B_\alpha / B_{\alpha'} = |A_{\alpha'}''| / |A_\alpha''| . \tag{4.6}$$

We measure[37]

$$\begin{aligned} B_{(^{75}\mathrm{As})}/B_{(^{71}\mathrm{Ga})} &= 2.5 \pm 0.2 , \\ B_{(^{75}\mathrm{As})}/B_{(^{69}\mathrm{Ga})} &= 2.0 \pm 0.2 . \end{aligned} \tag{4.7}$$

These values yield the ratios $d_\alpha / d_{\alpha'}$ of the electronic presence probabilities on the various nuclear isotopic species. These ratios are given by

$$\begin{aligned} d_{(^{75}\mathrm{As})}/d_{(^{69}\mathrm{Ga})} &= 1.68 \pm 0.15 , \\ d_{(^{75}\mathrm{As})}/d_{(^{71}\mathrm{Ga})} &= 1.78 \pm 0.15 . \end{aligned} \tag{4.8}$$

Thus, the experimental results are consistent with the equality of $d_{(^{69}\mathrm{Ga})}$ and $d_{(^{71}\mathrm{Ga})}$. The common value of the two above quantities is the ratio of electronic presence probabilities on cation and anion sites, which is a measure of the ionicity of the crystal. The theoretical value of this quantity, estimated from data in InSb, for which the ionicity is very close to that of GaAs,[3] is given by

$$d_{\mathrm{As}}/d_{\mathrm{Ga}} = 1.68 \tag{4.9}$$

and is in very good agreement with the experimental results.

## V. SUMMARY

The magnitude of the optically-detected nuclear-resonance signal in high-purity gallium arsenide has been calculated in the framework of a model with two electronic states, free electrons and electrons trapped on donors, taking into account the existence of the fast spin exchange between the two states. The free electronic state is supposed to be uncoupled to the nuclear-spin system. One predicts that the same NMR results are obtained on all electronic states, and that there occurs a strong enhancement of the resonance signal if the exchange time is smaller than the inverse precession frequency of the electronic spin in the magnetic fields experienced by the two states.

An analysis of the experimental results shows that: (i) the same NMR lines are indeed observed on all electronic states; (ii) the shape and position of the resonance line are modified by the existence of a strong Knight shift, the experimental value of which is of the same order as the theoretical estimate; and (iii) in the case where the nuclear field $B_n$ is antiparallel to the external field, there occurs an extra broadening of the resonance line, due to inhomogeneities of $B_n$. We show that the ratios $B_{\alpha'} / B_\alpha$ of the nuclear fields of the various isotopic species can be experimentally determined. These ratios are found to be in excellent agreement with theoretical calculations which involve the sharing of the electron between arsenic and gallium atoms. (iv) We give evidence of the amplification of the resonance signal due to spin exchange. In agreement with theoretical estimates, the spin exchange time is found to be comparable with the reciprocal precession frequency of the electronic spin in the magnetic field.

In conclusion, the overall agreement between theory and experiment shows that we understand the basic effects involved in optical detection of NMR in high-purity gallium arsenide. This work shows the remarkable efficiency of spin exchange under light excitation, which is found to be at least two orders of magnitude faster than recombination in the free electronic state and has so far been overlooked. In the following section, we discuss some consequences of this result.

## VI. CONCLUSION

The spin exchange between the various electronic states, which is present in high-purity gallium arsenide under light excitation is believed to be efficient in a wide range of III V and II VI compounds for which, although each electronic state is characterized by a distinct energy, wave function, lifetime , . . . , the whole electronic system behaves as a single state, as far as the spin properties are concerned. The purpose of this section is to discuss some consequences of this result.

### A. Intensity dependence of the nuclear effects

Due to the averaging produced by spin exchange, the effects of the nuclear field experienced by localized electronic states should strongly depend on the relative populations of the free and trapped states and consequently, on excitation light intensity. In particular, when the excitation light intensity is increased above the value corresponding to occupation of all donor states, the concentration $n_f$ of free electrons increases, whereas the concentration of trapped electrons stays the same. This should produce a decrease of the average of the nuclear fields experienced by the various electronic states. This is in agreement with the experimental results, which show that, for very strong excitation intensities, the observed NMR signal is very small.

### B. Optically-detected electron resonance

The conduction-electron spin resonance (CESR) has been optically detected in a variety of III V and II VI compounds.[7,33,38] The measured values of the $g$ factor have allowed detailed verifications of the $\vec{k}\cdot\vec{p}$ theory.[39] We point out however that the existence of spin exchange is likely to cause spurious modifications of the measured value of the $g$ factor, due to the resulting averaging between electronic states. This averaging is indeed present in CESR conditions since both free and trapped electrons seem to play an important role: On one hand, the resonance is observed whenever there exists a strong photoconductivity. On the other hand a strong Overhauser shift of the line is present in all cases. This shows that localized electrons, which experience the large nuclear field, play an important role. The spin exchange between free and trapped electrons does not in itself perturb the measurement of $g^*$, since these two states have the same $g$ factor. We point out however that this averaging should also include the free or trapped excitonic states, which have a different $g$ factor so that, in principle, the measured value of $g^*$ no longer corresponds to the $g$ factor at the bottom of the conduction band. We think however that, due to the short value of the excitonic lifetime, the concentration of excitons is much smaller than the concentration of electrons, so that the resulting modification of $g^*$ should be small. Further experiments are necessary to evaluate this modification precisely.

### C. Electron spin relaxation

We recall that the spin relaxation of free electrons in high-purity compounds such as GaAs and CdTe is so far not understood.[40] We point out that the modulation by spin exchange of the hyperfine interaction experienced by a given electron is found to be inefficient.[41] However, the free excitonic state is known experimentally to be fast relaxing,[11] which has been attributed to the existence of the exchange interaction between electrons and holes. Consequently the spin exchange of free electrons with free or trapped excitons could be an efficient relaxation mechanism for the free electronic state.

### D. Interpretation of standard optical pumping results

The measurement of the mean electronic spin $\langle S_0\rangle$ and of the characteristic width $\Delta B$ of its decrease by Hanle effect in a transverse magnetic field has proved a convenient way to determine electronic relaxation times and lifetimes in doped crystals of gallium arsenide and gallium antimonide. This has allowed detailed investigation of the mechanisms of electronic relaxation.[42–44] We point out here that this method cannot be applied to the case of pure crystals because several electronic states are present. Due to the fast spin exchange, the quantities $\langle S_0\rangle$ and $\Delta B$ are averages over all states present in the sample and no longer characterize an individual electronic state. This is in agreement with experimental results,[11] which show indeed that $\langle S_0\rangle$ and $\Delta B$ are the same for all electronic states.

We think that, for very low excitation intensities, the efficiency of this averaging should be greatly decreased, which might permit an independent study of each electronic state. This situation has not been achieved, in our samples, since the free electron depolarization at resonance is observed for the whole excitation light range which allows optical detection of NMR. However, purer samples, in the range $10^{13}$ donors per cubic centimeter, might show negligible spin exchange averaging. In this case, a wealth of information should be obtained on the electronic spin system. We point out finally that the nuclear effects described in this work are due to a very small fraction of nuclear spins, situated in the vicinity of the donor centers. Consequently, an investigation, from the optically detected NMR, of the relaxation of these nuclei,[19] should permit detailed study of the relevant mechanisms of nuclear polarization, including spin diffusion[45] between nuclear spins.

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## APPENDIX A: CALCULATION OF THE NUCLEAR MAGNETIZATION AFTER APPLICATION OF THE ROTATING FIELD (Ref. 13)

Before application of the rotating field, the Hamiltonian of the system of nuclear spins of isotopic species $\alpha$ is

$$\mathcal{H}_\alpha = -\gamma_\alpha \hbar B \sum_i I_{zi} + \mathcal{H}_{D\alpha} \ , \qquad \text{(A1)}$$

where $i$ designates an individual spin. This neglects the quadrupolar interactions. The interactions of spin $\alpha$ with the other isotopic species are much smaller than the difference of their Zeeman energies and play no role in the evolution of the system. Consequently, the spin-spin interactions are reduced to dipole-dipole interactions between spins $\alpha : \mathcal{H}_{D\alpha}$. Before application of the rotating field $B_1$, the system is in a state of internal equilibrium described by a density matrix

$$\underline{\sigma}_0 = (\underline{I} - \beta\mathcal{H}_\alpha)\cdot(\mathrm{Tr}\underline{I})^{-1} \tag{A2}$$

in the approximation where the nuclear spin temperature $1/k_B$, where $k_B$ is the Boltzmann constant, is sufficiently high to neglect higher-order terms. Immediately after application of $B_1$, the system is still described by the same density matrix, but the Hamiltonian, in the rotating frame, is now

$$\tilde{\mathcal{H}}_\alpha = -\gamma_\alpha\hbar\sum_i(\delta B\cdot I_{zi} + B_1\cdot I_{xi}) + \mathcal{H}'_{D\alpha} \ , \tag{A3}$$

where $\delta B$ is the distance to resonance and $\mathcal{H}'_{D\alpha}$ is the secular part of the dipole-dipole interactions, that is, the part which commutes with $I_z$. The density matrix $\underline{\sigma}_0$, given by Eq. (A2), no longer corresponds to an equilibrium. To study the evolution towards a new equilibrium, using perturbation theory, we write the Hamiltonian in the form of two commuting operators, and a perturbation which commutes with neither of them. This is done in the following way. The Hamiltonian $\tilde{\mathcal{H}}_\alpha$ can first be rewritten

$$\tilde{\mathcal{H}}_\alpha = -\gamma_\alpha\hbar B_{\mathrm{eff}}\sum_i I_{Zi} + \tfrac{1}{2}(3\cos^2\phi_n - 1)\mathcal{H}'_{D\alpha Z} + \mathcal{H}''_{D\alpha Z} \ , \tag{A4}$$

where the $Z$ direction is the direction of the effective field $\vec{B}_{\mathrm{eff}}$ in the rotating frame, at angle $\phi_n$ with $0z$. This field is equal to $(B_1^2 + \delta B^2)^{1/2}$. The Hamiltonians $\mathcal{H}'_{D\alpha Z}$ and $\mathcal{H}''_{D\alpha Z}$ are the parts of $\mathcal{H}'_{D\alpha}$ which commute or not with the Zeeman Hamiltonian. They are given by

$$\mathcal{H}'_{D\alpha Z} = \gamma_\alpha\hbar^2\sum_{i>j} r_{ij}^{-3}(3I_{iZ}I_{jZ} - \vec{I}_i\cdot\vec{I}_j) \ , \tag{A5}$$

$$\mathcal{H}''_{D\alpha Z} = \sin^2\phi_n(P_{\alpha Z} + P_{\alpha Z}^+) - \sin\phi_n\cos\phi_n(Q_{\alpha Z} + Q_{\alpha Z}^+) \ , \tag{A6}$$

where $r_{ij}$ is the vector joining spins $i$ and $j$. The operators $P_{\alpha Z}$ and $Q_{\alpha Z}$ are

$$P_{\alpha Z} = \tfrac{3}{4}\gamma_\alpha^2\hbar^2\sum_{i>j} r_{ij}^{-3}(I_{iX} + iI_{iy})(I_{jX} + iI_{jy}) \ , \tag{A7}$$

$$Q_{\alpha Z} = \tfrac{3}{2}\gamma_\alpha^2\hbar^2\sum_{i>j} r_{ij}^{-3}[I_{iZ}(I_{jX} + iI_{jy}) + I_{jZ}(I_{iX} + iI_{iy})] \ . \tag{A8}$$

We now use a unitary transformation of evolution operator $U$, given by

$$-\hbar\gamma_\alpha B_{\mathrm{eff}}\sum_i I_{Zi} + \mathcal{H}''_{D\alpha Z} = -\hbar\gamma_\alpha B_{\mathrm{eff}}\sum_i UI_{Zi}^+U \ .$$

The Hamiltonian $\tilde{\mathcal{H}}_\alpha$ is of the form

$$\tilde{\mathcal{H}}_\alpha = -\hbar\gamma_\alpha B_{\mathrm{eff}}\sum_i I_{Zi}^* + \tfrac{1}{2}(3\cos^2\phi_n - 1)\mathcal{H}'^*_{D\alpha Z} + \tfrac{1}{2}(3\cos^2\phi_n - 1)[R,\mathcal{H}'^*_{D\alpha Z}] \ , \tag{A10}$$

where

$$I_{Zi}^* = U^+I_{Zi}U \ , \tag{A11}$$

$$\mathcal{H}'^*_{D\alpha Z} = U^+\mathcal{H}'_{D\alpha Z}U \ , \tag{A12}$$

$$R = \frac{1}{\hbar\gamma_\alpha B_{\mathrm{eff}}}\sin\phi_n\cos\phi_n(Q_{\alpha Z} - Q_{\alpha Z}^+) + \frac{1}{2\hbar\gamma_\alpha B_{\mathrm{eff}}}\sin^2\phi_n(P_{\alpha Z}^+ - P_{\alpha Z}) \ . \tag{A13}$$

This Hamiltonian is the sum of two commuting operators, and of a third term, commuting with neither of them. If the field $B_{\mathrm{eff}}$ is larger than the local field $B''_{L\alpha}$ given by

$$B''^2_{L\alpha} = 3\,\mathrm{Tr}(\mathcal{H}''^2_{D\alpha Z})/(n\gamma_\alpha^2\hbar^2 I_\alpha^2) \ , \tag{A14}$$

where $n_\alpha$ is the total number of spins $\alpha$, the heat capacity of this term can be shown from Eqs. (A6) and (A13) to be very small, so that a perturbation treatment is possible. For a time scale of the order of $T_1^\alpha$, the effect of the perturbation can be neglected so that the two first terms are approximately constants of the motion. As a consequence of standard spin temperature theory,[46] the system is in this case described, after a time comparable with $T_2^\alpha$, by a density matrix

$$\underline{\sigma}_1 = \left[\underline{I} + \beta'\left(\hbar\gamma_\alpha B_{\mathrm{eff}}\sum_i I_{Zi}^*\right) - \beta(3\cos^2\phi_n - 1)\mathcal{H}'^*_{D\alpha Z}\right](\mathrm{Tr}\underline{I})^{-1} \tag{A15}$$

corresponding to the equilibrium, after the fast mixing between Zeeman and nonsecular dipolar energies. The inverse temperature of the secular dipolar energy is, on this time scale, a constant of the motion, and is equal to the initial inverse temperature, defined by Eq. (A2). The further evolution of the system includes the following. (i) Mixing of the Zeeman and nonsecular dipolar energies, together with the secular dipolar energy, under the influence of the perturbation, in a time which depends on the distance to resonance.[13] In the case where the effective magnetic field in the rotating frame is much larger than the local field $B'_{L\alpha}$, defined by

$$B'^2_{L\alpha} = 3\,\mathrm{Tr}(\mathcal{H}'^2_{D\alpha Z})/(n_\alpha\gamma_\alpha^2\hbar^2 I_\alpha^2) \ , \tag{A16}$$

this mixing does not modify appreciably the spin temperature of the Zeeman reservior and consequently, the magnetization of the isotopic species $\alpha$. (ii) Spin-lattice relaxation towards steady-state equilibrium, in a time $T_1^\alpha$ equal to several seconds. Consequently, the inverse temperature $\beta'$ of the Zeeman reservior does not vary appreciably during a time longer than $T_2^\alpha$ and shorter than $T_1^\alpha$. The value of $\beta'$ is calculated by expressing that the fast mixing of Zeeman and nonsecular dipolar interactions is done at constant total energy

$$\mathrm{Tr}(\underline{\sigma}_0\tilde{\mathcal{H}}_\alpha)=\mathrm{Tr}(\underline{\sigma}_1\tilde{\mathcal{H}}_\alpha) \ , \tag{A17}$$

where $\underline{\sigma}_0$ and $\underline{\sigma}_1$ are given by Eqs. (A2) and (A3). We obtain

$$\beta'=\beta\frac{B\delta B+B_{L\alpha}''^2}{B_{\mathrm{eff}}^2+B_{L\alpha}''^2} \ , \tag{A18}$$

where the local field $B_{L\alpha}''$ is given by Eq. (A14). If the effective field $B_{\mathrm{eff}}$ in the rotating frame is much larger than this value, Eq. (A18) becomes

$$\beta'=\beta(B\delta B/B_{\mathrm{eff}}^2) \ . \tag{A19}$$

The total magnetization of the system of spins $\alpha$, given by

$$\langle\vec{I}_\alpha\rangle=\mathrm{Tr}\left[\underline{\sigma}_1\sum_i\vec{I}_{i\alpha}\right] \tag{A20}$$

is then found to be the projection of the off-resonance magnetization on the direction of the effective field $\vec{B}_{\mathrm{eff}}$ in the rotating frame.

We recall that this result is valid after a time following application of $B_1$, larger than the spin-spin relaxation time $T_2^\alpha$, but smaller than the spin-lattice relaxation time $T_1^\alpha$. This also requires that the magnitude of $\vec{B}_{\mathrm{eff}}$ should be large as compared to the sum of the two fields $B_{L\alpha}'$ and $B_{L\alpha}''$, defined by Eqs. (A16) and (A14). This sum is of the order of the dipolar local field $B_{L\alpha}$, given by

$$B_{L\alpha}^2=3\,\mathrm{Tr}(\mathcal{H}_{D\alpha}^2)/(n_\alpha\gamma_\alpha^2\hbar^2I_\alpha^2) \ , \tag{A21}$$

which has been calculated in Ref. 3 to be equal to 0.3 G for $^{75}$As nuclei.

## APPENDIX B: CALCULATION OF THE SPIN EXCHANGE CROSS SECTION (Ref. 47)

The scattering of a free electron by an occupied donor state in a direct-bandgap compound can be treated in the same way as the scattering of a free electron by a hydrogen atom, which has been extensively studied.[12] The basic set of wave functions of the two-electron system is composed of the singlet state and of the three triplet states:

$$S=\tfrac{1}{2}[\psi_t(1)\psi_f(2)+\psi_t(2)\psi_f(1)](1\uparrow2\downarrow-1\downarrow2\uparrow) \ , \tag{B1}$$

$$T_0=\tfrac{1}{2}[\psi_t(1)\psi_f(2)-\psi_t(2)\psi_f(1)](1\uparrow2\downarrow-1\downarrow2\uparrow) \ , \tag{B2}$$

$$T_\uparrow=(1/\sqrt{2})[\psi_t(1)\psi_f(2)-\psi_t(2)\psi_f(1)]1\uparrow2\uparrow \ , \tag{B3}$$

$$T_\downarrow=(1/\sqrt{2})[\psi_t(1)\psi_f(2)-\psi_t(2)\psi_f(1)]1\downarrow2\downarrow \ , \tag{B4}$$

with the usual shorthand notations for the spin and orbital wave functions. The function $\psi_t$ describes the orbital state of the electron trapped on the donor. The function $\psi_f(r)$ is the free-electron wave function, given by

$$\psi_f(r)=e^{ikr}\psi_{f0}(r) \ , \tag{B5}$$

where $\psi_{f0}(r)$ is the electron wave function at the bottom of the conduction band. The incident state $\Psi(1,2)$ of the system is quite generally a linear combination of the four above states. The corresponding outgoing state $\Psi^*(1,2)$, in the limit where the distance of the scattered electron to the donor center is large as compared with the donor effective Bohr radius, is given by standard diffusion theory. Indeed, if $A$ denotes one of the four basic states, the state $A^*$ is given by

$$A^*=f_\mu(\theta)\tilde{A} \ , \tag{B6}$$

where $\tilde{A}$ is obtained by replacing in $A$ the function $\psi_f(r)$ by a spherical wave defined by

$$\psi_f(r)=(e^{ikr}/r)\psi_{f0}(r) \ . \tag{B7}$$

The function $f_\mu(\theta)$, where $\mu$ is $S$ or $T$ depending on the singlet or triplet character of $A$, is given by

$$f_\mu(\theta)=k^{-1}\sum_{l=0}^{\infty}(2l+1)\sin\delta_{\mu l}e^{i\delta_{\mu l}}P_l(\cos\theta) \ , \tag{B8}$$

where $P_l(\cos\theta)$ is the $l$th-order Legendre polynomial and $\delta_l$ are the scattering phase shifts. The triplet and singlet total cross sections, defined by

$$\sigma_\mu=2\pi\int_0^\pi|f_\mu(\theta)|^2\sin\theta d\theta \tag{B9}$$

are then given by

$$\sigma_\mu=4k^{-2}\sum_{l=0}^{\infty}(2l+1)\sin^2\delta_{\mu l} \ . \tag{B10}$$

A simplified expression for the scattering cross sections is obtained by considering only the term corresponding to $l=0$ in Eq. (B10). This holds provided the binding energy of the trapped electron is large as compared with the kinetic energy of the free electron, that is, if the quantity $k_Ta_0^*$ where $k_T$ is the thermic electronic momentum and $a_0^*$ is the effective donor

Bohr radius, is small as compared to unity.[48] This is not too bad an approximation in the case of gallium arsenide, for which the calculated value of $k_T a_0^*$ is 0.46. The functions $f_{\mu 0}(\theta)$ are independent of $\theta$ and are simply given by

$$f_{\mu 0} = k^{-1} \sin\delta_{\mu 0} e^{i\delta_{\mu 0}} \tag{B11}$$

and the approximate values of the scattering cross sections in the singlet and triplet states are

$$\sigma_\mu \simeq 4\pi k^{-2} \sin^2\delta_{\mu 0} \ . \tag{B12}$$

Note that the zero-order scattering phase shifts $\delta_{S0}$ and $\delta_{T0}$ have been computed numerically by Schwartz in the analogous case of the hydrogen atom.[22] Consequently, the treatment of the scattering of a free electron by an occupied donor state can be performed completely.

The calculation of the spin-exchange cross section is a slightly different problem because the spin state of the incident electron is fixed. Therefore it is convenient to describe the state of the two-electron system by the basis composed of $T_\uparrow$ and $T_\downarrow$, defined by Eqs. (B3) and (B4), and the two following wave functions:

$$L_\downarrow = (1/\sqrt{2})[\psi_t(1)\uparrow\psi_f(2)\downarrow - \psi_t(2)\uparrow\psi_f(1)\downarrow]$$
$$= (1/\sqrt{2})(S+T_0) \ , \tag{B13}$$

$$L_\uparrow = (1/\sqrt{2})[\psi_t(1)\downarrow\psi_f(2)\uparrow - \psi_t(2)\downarrow\psi_f(1)\uparrow]$$
$$= (1/\sqrt{2})(-S+T_0) \ . \tag{B14}$$

The wave functions $T_\uparrow$ and $L_\uparrow$ (respectively, $T_\downarrow$ and $L_\downarrow$) constitute the basic subset of functions for the case where the spin of the incident electron is $\uparrow$ (respectively, $\downarrow$). We consider now the particular case where the spin of the incident electron is $\uparrow$. The state of the two-electron system is in this case of the form

$$\Psi(1,2) = \alpha T_\uparrow + \beta L_\uparrow \tag{B15}$$

and the spin exchange process corresponds to the transtion from $\Psi(1,2)$ to the state $\alpha T_\uparrow^* + L_\downarrow^*$, as can be seen from the form of the functions $T_\uparrow^*, L_\uparrow^*$, and $L_\downarrow^*$.

The state $\Psi^*(1,2)$ is then obtained from Eqs. (B6), (B11), and (B15). It is given by

$$\Psi^*(1,2) = (2k)^{-1}(\sin\delta_{T0} e^{i\delta_{T0}} + \sin\delta_{S0} e^{i\delta_{S0}})(\alpha\tilde{T}_\uparrow + \beta\tilde{L}_\uparrow) + (2k)^{-1}(\sin\delta_{T0} e^{i\delta_{T0}} - \sin\delta_{S0} e^{i\delta_{S0}})(\alpha\tilde{T}_\uparrow + \beta\tilde{L}_\downarrow) \ . \tag{B16}$$

As seen from the form of the functions between parentheses, the first term corresponds to scattering without spin exchange and the second term to scattering with spin exchange. Then, in analogy with Eqs. (B6) and (B9), we obtain the expressions of the cross sections $\sigma_e$ and $\sigma_{ne}$ of these two processes:

$$\sigma_{ne} = \pi k^{-2} |\sin\delta_{T0} e^{i\delta_{T0}} + \sin\delta_{S0} e^{i\delta_{S0}}|^2 = \tfrac{1}{4}[\sigma_S + \sigma_T + 2(\sigma_T\sigma_S)^{1/2}\cos(\delta_{S0} - \delta_{T0})] \ , \tag{B17}$$

$$\sigma_e = \pi k^{-2} |\sin\delta_{T0} e^{i\delta_{T0}} - \sin\delta_{S0} e^{i\delta_{S0}}|^2 = \tfrac{1}{4}[\sigma_S + \sigma_T - 2(\sigma_T\sigma_S)^{1/2}\cos(\delta_{S0} - \delta_{T0})] \ . \tag{B18}$$

Consequently, the exchange scattering cross section can be calculated, in the *s*-wave approximation, since the phase shifts $\delta_{S0}$ and $\delta_{T0}$ are known. Note that in the case where $\delta_{T0} = \delta_{S0}$, this cross section is zero, so that the spin-exchange process is only possible when the two phase shifts are different.

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[*] Groupe de Recherche du Centre National de la Recherche Scientifique.

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shown that this is not true in all cases (see Refs. 4 and 42). As seen from Eq. (2.8), the magnitude of the NMR signal is, in such a case, no longer proportional to $\sin^2\phi_e$, but can be more complicated. However, in high-purity GaAs, no dependence of $\langle S_0 \rangle$ on the nuclear field can be observed, at least for the strong excitation intensities used in this work (higher than 100 $W/cm^2$) so that the present analysis is correct. The above-mentioned dependence, evidenced in less pure crystals, is due to the variation of the electronic spin relaxation time with the magnetic field experienced by the electrons, which includes the nuclear field. The absence of this effect in high-purity GaAs indicates that the electronic relaxation is most efficient in the delocalized state, for which the nuclear field is small. However, a detailed interpretation is beyond the scope of this work, since the relevant mechanism of electronic spin relaxation in high-purity gallium arsenide is not known (see Ref. 40).

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[31] Reexcitation after trapping in an excited state of the donor is quite possible, since the transition time between the continuum and the 2*s* state has been found by R. Ulbrich [in *Proceedings of the Twelfth International Conference on the Physics of Semiconductors, Stuttgart, 1974,* edited by M. H. Pilkuhn (Teubner, Stuttgart, 1974), p. 376] to be anomalously long.

[32] To calculate the unshifted resonance position, it is necessary to know the value of the chemical shift. This value is found in R. L. Mieher, in *Semiconductors and Semimetals,* edited by R. K. Willardson and A. C. Beer (Academic, New York, 1966), Vol. 2, p. 141.

[33] C. Weisbuch and C. Hermann, Phys. Rev. B 15, 816 (1977)

[34] This comes from the small value of the electron mean-free path, of the order of several microns, as compared to the diameter of the excitation light spot.

[35] In principle, the inhomogeneities of $B_n$ evidenced in the antiparallel geometry are also likely to alter the line shape in the parallel geometry. This is however much less important than in the former case. A numerical calculation in the framework of the geometrical model shows that in the case of Fig. 7, the corresponding modification is indeed negligible.

[36] This can come from the field dependence of the electronic mean spin, or of the speed of nuclear relaxation.

[37] This has been done in the antiparallel geometry, because of the larger resonance signal. The inhomogeneities of $B_n$ which play a role in this case, can be shown not to modify the value of $B_\alpha/B_{\alpha'}$. This comes from the fact that, in the antiparallel geometry, the far wings of the different resonance lines are due to the same donor centers, for which the total nuclear field $B_n$ compensates the external field, and for which the ratios are obviously unmodified by the inhomogeneities.

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