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Effect of holes on the dynamic polarization of nuclei in semiconductors

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In semiconductors optically enhanced polarization of nuclei is known to be primarily due to photoexcited electrons. We show that holes play a role in this process via the spin-dependent recombination of the carriers. Our results are obtained in *n*-type InP where spin-dependent recombination leads to the inversion of the nuclear field direction due to the donor spins cooling under optical excitation.

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Manipulation and control of nuclear spins in semiconductors is a major challenge for new applications such as signal enhancement in biological solid-state NMR,[1] and quantum computation.[2,3] Promising methods for the manipulation of nuclear states rely on the dynamic nuclear polarization (DNP) by electron spin.[2–6] The DNP originates from cross relaxation between electrons and nuclei coupled by the hyperfine Fermi interaction. On the other hand, the dipole-dipole hyperfine interaction between nuclei and holes is much weaker.[7] Therefore, the effect of holes on the DNP is usually neglected.

In this Rapid Communication we show that the photocreated holes strongly influence the DNP via the spin-dependent recombination (SDR) of the photoexcited carriers. Depending on the semiconductor band structure, the SDR may increase (GaAs, CdTe) or decrease (InP) the electron spin temperature and thus may affect the nuclear spin polarization via hyperfine coupling. The relevance of the SDR to the DNP has been evoked,[8] but is not fully recognized so far. To reveal the importance of the SDR we study the DNP in *n*-doped InP. In this semiconductor the SDR reverses the nuclear spin-polarization direction. Therefore, a nuclear field antiparallel with an external magnetic field is expected and observed in our experiments. Our results suggest that taking the SDR into account is mandatory when precise control of the nuclear spin by optical fields is required.

To measure nuclear spin polarization the shift of the electron spin resonance (ESR), the so-called Overhauser shift, is routinely used. The ESR and Overhauser shift are detected in the time domain using a time-resolved magneto-optical Kerr rotation technique[4,5] in a pump-probe geometry where pump and probe pulses are used to enhance and monitor the polarization of the nuclei, respectively, (see Fig. 1). In such experiments a circularly polarized pump pulse creates an electronic spin polarization in the direction of light z' normal to the surface of the sample. This spin polarization starts to precess in the external field $B \| z$ which makes an angle α with z'. The angle θ_K, by which the probe beam polarization is rotated after reflection from the sample, is proportional to the projection of this polarization along the probe beam direction (nearly normal to the surface). The angle θ_K measured as a function of the pump-probe delay Δt oscillates at the Larmor frequency $\omega_L = g_e \mu_B B_{\text{tot}}/\hbar$. g_e is the electron g factor, μ_B is the Bohr magneton, and $B_{\text{tot}} = B + B_N$, where B_N is the nuclear field, collinear with the external field.[7] Therefore, the value and the direction of B_N can be deduced precisely from the variation of ω_L as the nuclear spins get polarized (Overhauser shift).

In order to separate the contribution of the SDR from the other factors driving the DNP two different experimental configurations are used. In the first configuration (Voigt configuration, Fig. 1) the magnetic field (strong) is applied parallel to the sample surface ($\alpha = 90°$), and circular polarization of the pump is modulated at 50 kHz, so that the average electron spin polarization created by the pump is zero. But the photocreated holes get rapidly polarized in the magnetic field, which enables the SDR process. In the second configuration the field (low) is oblique to the sample surface (Fig. 3), and the circular pump polarization is fixed, so that a nonzero electron spin polarization is photoexcited along the magnetic field. The field is kept low enough so that the polarization of the holes is negligible, and therefore the SDR is disabled.

The sample used in the experiments discussed below is a 3.5 μm thick InP *n*-doped layer ($n = 3 \times 10^{16}$ cm^{-3}) deposited on a semi-insulating Fe-doped InP substrate oriented [001]. The donor concentration in the epitaxial layer is close to, but still below the critical concentration of the Mott transition. Reflectivity reveals the presence of the free exciton transition at 1.4165 eV redshifted by 2 meV as compared to the high purity sample.[9]

We begin with the results obtained in the Voigt configuration. Figure 1 shows the color map of the Kerr rotation measured at temperature $T = 2$ K, magnetic field $B = 5$ T, and Δt from 950 to 1000 ps (y axis).[10] The titanium-sapphire laser light (~100 fs pulse duration) at $E = 1.417$ eV is switched on just before acquisition, and successive scans are repeated with a 20 s time interval during 5 min (x axis). One can see that the oscillations of the Kerr rotation angle shifts significantly with illumination time. This phase shift results from the variation of ω_L on a time scale of a few minutes, typical

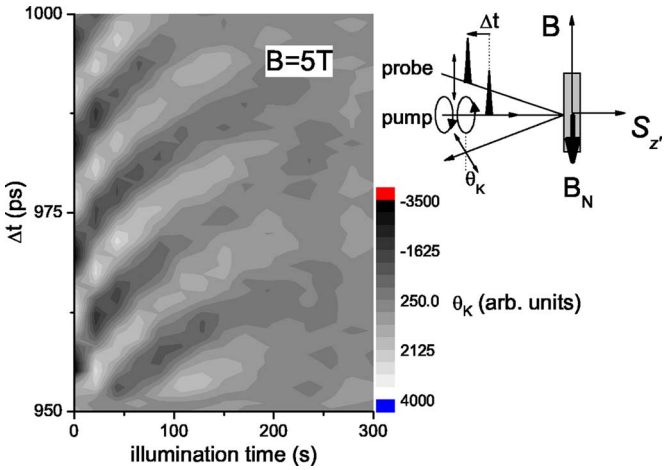

FIG. 1. (Color online) Gray-scale map of the time-resolved Kerr rotation exhibiting the slowing down and fading of the electron spin precession with illumination time (left). Schematics of the pump-probe configuration (right).

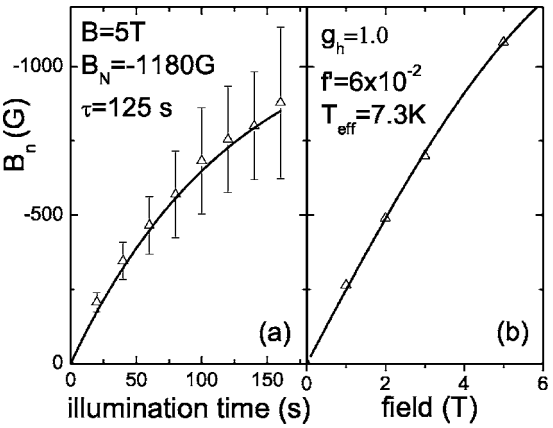

FIG. 2. Buildup of the nuclear field as a function of illumination time. The error bars indicate the width of the nuclear field distribution and the solid line is an exponential fit of the data (a), and its dependence on the applied magnetic field (b).

for the nuclear field buildup. Another characteristic of the nuclear field is that it disappears rapidly with temperature in our sample at temperature above 25 K. The direction of the nuclear field is given by the sign of the Overhauser shift. Since ω_L decreases, the nuclear field develops in the direction opposite to that of the external field. This result contradicts previous measurements on n-doped GaAs.[5]

Another striking feature apparent in Fig. 1 is that the oscillations are fading away with increasing illumination time, and are no longer visible at $\Delta t > 950$ ps before the nuclear field reaches its steady-state value. We have checked that the Kerr rotation angle at $\Delta t = 0$ does not change and therefore this is not due to some long-term variation of the pump-probe signal, but rather to a spin dephasing, which increases in concert with the nuclear field. This spin dephasing originates from a spatially inhomogeneous distribution of nuclear fields, each electron precessing at a different Larmor frequency in the local nuclear field. Indeed, one can show that for a Gaussian distribution of nuclear fields, at a given external magnetic field the transverse electron spin dephasing time T_2 is given by

$$\frac{1}{T_2(\Delta B_N)} = \frac{1}{T_2(0)} + \frac{g_e \mu_B \Delta B_N}{\hbar\sqrt{2}}, \qquad (1)$$

where $T_2(0)$ is the dephasing time in the absence of a nuclear field and ΔB_N is the Gaussian standard deviation of the nuclear field distribution. Thus, from the phase shift of the oscillations of θ_K we deduce B_N, and from T_2 we deduce ΔB_N using Eq. (1). Figure 2 shows the onset of the nuclear field antiparallel to the external field at 5 T as a function of the illumination time (a) as well as the steady-state values of B_N as a function of the external field (b). The error bars represent the width of the nuclear field distribution.

The large distribution of nuclear fields is due to spatial inhomogeneity. Indeed the electrons localized at donor sites are known to be more efficient for the DNP than for delocalized electrons.[11] Besides, the Kerr rotation signal that we measure at long pump-probe delays, and from which the nuclear field is deduced, is due to donor bound electrons. Therefore, the observed distribution means that B_N varies from one donor site to another.

Let us now address the central point of this Rapid Communication. We will argue that the observed direction of the nuclear field in the Voigt configuration evidences the major role of SDR in DNP. It is well established that the nuclei acquire a polarization $\langle I_z \rangle$ due to cross relaxation with photoexcited electrons, which is proportional to the difference $\langle S_z \rangle - S_0$ between the time-averaged electron spin in the direction of the magnetic field $\langle S_z \rangle$ and its thermal equilibrium value S_0.[7,12] This property may be used to deduce the sign of $\langle S_z \rangle - S_0$ from the measured nuclear field, and elucidate the role of the SDR. Prior to that one must check whether nuclei are predominantly polarized via scalar Fermi interaction, in which case $\langle I_z \rangle$ and $\langle S_z \rangle - S_0$ have the same sign, or via dipolar interactions, which give opposite signs.[12,13]

For that purpose we resort to the configuration shown in Fig. 3, i.e., fixed helicity σ^- of the pump polarization and the oblique field low enough to suppose $S_0 = 0$ and to neglect the SDR. The optical selection rules set the initial electron spin $\langle S_{z'} \rangle = +1/4$, and therefore define the sign of $\langle S_z \rangle$ along the field for its two different orientations, B_1 and B_2 (see Fig. 3). For B_1 ($\alpha = 144°$) $S_z < 0$, for B_2 ($\alpha = 36°$) $S_z > 0$, while $S_0 = -2.5 \times 10^{-3}$ is negligible. In Fig. 3, the Kerr rotation angle oscillates at largely different frequencies for these two configurations, indicating that the nuclear field changes its direction with respect to the external field. The larger precession frequency is obtained for the field B_2, which means that $B_{N2} > 0$. Since the nuclear field depends on $\langle I_z \rangle$ according to $B_N = A\langle I_z \rangle / g_e \mu_B$, with the hyperfine coupling constant $A > 0$, and $g_e = +1.2$ in InP,[17] B_N and $\langle I_z \rangle$ have the same sign. Therefore, both $\langle I_z \rangle$ and $\langle S_z \rangle$ are positive, which means that cross relaxation is dominated by the Fermi interaction. The same conclusion is drawn from the other field direction, where both $\langle I_z \rangle$ and $\langle S_z \rangle$ are negative.

In the Voigt configuration we found $B_N < 0$, i.e., $\langle I_z \rangle < 0$, hence we deduce $\langle S_z \rangle - S_0 < 0$. Because

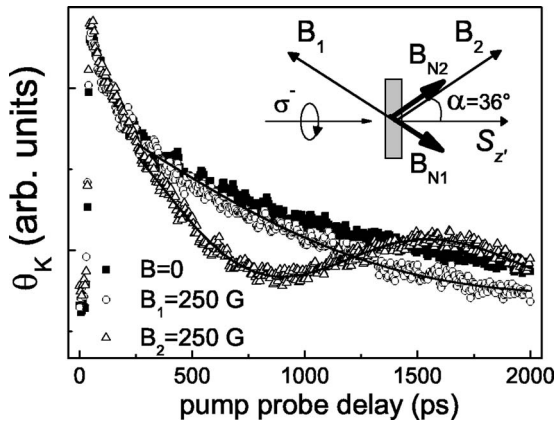

FIG. 3. Kerr rotation for σ^- pump helicity at the zero field and for two directions $\mathbf{B}_1$ and $\mathbf{B}_2$ of the magnetic field. Solid lines are fits of the data with a damped cosine, taking into account the asymmetry of the oscillations in the oblique field. The Larmor frequency is the only fitting parameter, the other parameters being obtained from the zero-field curve. We deduce $B_{N1}=-110$ and $B_{N2}=+123$ G for the two directions of the external field B_1 and B_2, respectively.

$S_0=-1/2\tanh(g_e\mu_B B/2k_B T)$ is negative, we conclude $|\langle S_z\rangle|>|S_0|$, which amounts to saying that the electron spin is cooled below the lattice temperature.

This can be explained only if the SDR of electrons with polarized holes is introduced. Due to conservation of total angular momentum during optical transitions, the recombination probability of a given electron spin depends on the occupation factor of hole Zeeman levels, the ordering of which is determined by the Luttinger parameter κ. For InP κ is positive,[14] corresponding to the hole ground state with total angular momentum $J_z=-3/2$. This state will be the most populated, bearing in mind the very fast hole spin relaxation in bulk cubic semiconductors, and may only recombine with an electron of spin $+1/2$, corresponding to the upper spin level, because $g_e>0$. Therefore, the SDR tends to deplete the excited electron spin levels and accordingly to cool the electron spins.

In order to establish the conditions for electron spin cooling let us calculate the steady-state polarization of neutral donors under cw illumination.[15] We assume that a neutral donor can bind an optically created exciton only if their relative electron spins are antiparallel, thus forming a $D^\circ X$ exciton complex in a singlet electron spin state. Because the hole spin is polarized in the external magnetic field, the SDR of the $D^\circ X$ leaves the neutral donors with a net spin polarization. In fact, whether the electrons are localized on donors or not appears to be irrelevant for the calculation of the steady-state electron spin polarization. It is given by[16]

$$\langle S_z\rangle=\frac{nS_0+\rho G\tau_s J_0/3}{n+G\tau_s}, \tag{2}$$

where ρ is the radiative yield, G is the carrier excitation rate, τ_s is the electron spin (longitudinal) relaxation time, and J_0 is the thermodynamic value of the hole angular momentum. The sign of the nuclear field is determined by

$$\langle S_z\rangle-S_0=\frac{G\tau_s}{n+G\tau_s}(\rho J_0/3-S_0), \tag{3}$$

which is negative if $|J_0|>3|S_0|/\rho$. In the linear regime [a rather good approximation in our case, see Fig. 2(b)], the expansion of the Brillouin functions describing J_0 and S_0 shows that this condition is equivalent to $g_h>3g_e/5\rho$, where g_h stands for the effective g factor of the hole bound to the $D^\circ X$ complex. Assuming purely radiative recombination of exciton bound to neutral donors ($\rho=1$), one gets the condition to achieve a negative nuclear field $g_h>0.72$. This condition seems compatible with most of the published values of the Luttinger parameter κ despite their large spreading.[14] However, the exact relationship between g_h and κ is not known to the best of our knowledge.

When the DNP is mainly due to Fermi interaction the nuclear field can be expressed as

$$B_N=\tfrac{4}{3}(I+1)fB_S(\langle S_z\rangle-S_0) \tag{4}$$

provided the applied magnetic field is much larger than the local nuclear field.[7] f is the leakage factor taking into account the nuclear spin-lattice relaxation, I is the nuclear spin, and $B_S\approx 2.4$ T is the nuclear field at complete nuclear polarization estimated from the value of the hyperfine constant.[17]

Inserting Eq. (3) in Eq. (4) we get

$$B_N=\tfrac{4}{3}(I+1)f'B_S(\rho J_0/3-S_0), \tag{5}$$

where we have introduced $f'=fG\tau_s/(n+G\tau_s)$. The fit of the data using this expression and assuming $\rho=1$, $g_h=1$ (the product of these two quantities must be larger than 0.72 anyway in order to get the electron spin cooling) is shown in Fig. 2(b). The factor $f'=0.05$ is found to be comparable with f, which is estimated independently from the measurements at low field (Fig. 3) and the average electron spin deduced from the circular degree of photoluminescence. It is also in agreement with a previous work.[18] Two other parameters deduced from the fit are $\tau_s\sim n/G\sim 10$ ns and the effective temperature $T_{\text{eff}}=7.3$ K. Increasing the pump power by nearly a factor 2 increases B_N by only 10%. This indicates that at this excitation level (70 W/cm^2) B_N saturates, as predicted by Eq. (5).

The observed distribution of B_N indicates that the localized centers (probably donors) responsible for the DNP are not all equivalent. This could be due either to different local environments, such as the distance from a nearby acceptor,[19] or to a systematic dependence on the distance to the sample surface related to the existence of a depletion layer. In both cases, without excitation some donors are neutral while others are ionized. The SDR will have a different impact on the DNP in both cases, leading to the observed broad distribution of B_N.

To get a deeper insight into the donor spin polarization, it is instructive to look at the degree of circular polarization of the DAP emission P_C. At low field a linear approximation gives $P_C=(J_0-S_0)-(\langle S_z\rangle-S_0)$, where the first term is the thermal equilibrium value of P_C at the actual temperature of the lattice, and the second term is the electron spin deviation from thermal equilibrium responsible for the DNP. Experi-

mentally P_C is always negative and decreases in absolute value when excitation density increases (data not shown). It means $J_0 - S_0 < 0$, in this case both heating of the lattice and donor spin cooling tend to decrease $|P_C|$ when the excitation density increases. Therefore, distinction between lattice heating and spin cooling effects is difficult. Nevertheless, a fit of P_C vs B up to 6 T, at low excitation density, gives an estimate of $g_h = 0.85$ for the hole bound to an acceptor. This value is consistent with the spin cooling model if $\rho > 0.85$.[20]

The existing experimental results, obtained either by purely optical methods, or by the NMR and the ESR are consistent with our model. In particular, in the ESR experiments the ESR saturation corresponds to donor spin heating, and in this case the nuclear field is restored parallel to the external field.[17] In the case of GaAs, g_e and g_h have opposite signs and the SDR contribute to electron spin heating. Nevertheless it must be also considered for a quantitative analysis of the DNP. Finally, the phase inversion of the ^{115}In NMR signal observed in InP (with *n*-type conductivity) under optical pumping could possibly be explained by the SDR mechanism, rather than dipole-type hyperfine coupling.[13] On the other hand, Fe-doped InP exhibits a similar phase inversion effect on the ^{31}P NMR signal, but not on the ^{115}In NMR signal.[21]

In conclusion, it is demonstrated that in semiconductors, the photoexcited holes may strongly influence the DNP via the SDR. This is shown experimentally in *n*-InP, a semiconductor with the band parameters such that the SDR reverses the nuclear field. The SDR may provide additional means for nuclear spin control in particular in systems of reduced dimensionality. In quantum wells, due to the large heavy-hole spin anisotropy, the hole spin polarization is controlled by varying the orientation of the magnetic field with respect to the quantum well plane, thus changing the spin balance in the SDR. Finally, because the SDR is particularly important at a high magnetic field, it must be properly handled in quantum computing protocols, in which optical fields are used to manipulate the nuclear spins.[3]

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