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Optical dynamic nuclear polarization in InP single crystal: Wavelength and field dependence of NMR enhancement

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The magnetic field and optical excitation wavelength dependence of the In-115 nuclear spin polarization enhancement due to optical pumping in undoped, *n*-type InP single crystal, is reported. In the optical wavelength dependence, the enhancement drops sharply when the excitation energy exceeds the luminescence energy due to impurities near the band edge, but remains roughly constant as the energy is increased above the band gap. The 0–25-T magnetic field dependence exhibits a maximum In-115 NMR enhancement at 1.7 T, while negligible enhancement is observed at >15 T. In comparison with the previously reported field dependence of the NMR enhancement in GaAs, the maximum NMR signal enhancement in InP is found at lower magnetic field. According to hyperfine relaxation theory, this observation is consistent with the larger g factor of InP. Furthermore, the enhanced In-115 NMR signal using unpolarized optical excitation is emissive in phase with respect to the thermal equilibrium absorptive signal. This observation is consistent with a hyperfine cross-relaxation mechanism that is dipolar, rather than scalar in nature. [S0163-1829(99)50332-9]

Nuclear magnetic resonance signals in bulk III-V semiconductors such as GaAs and InP can be enhanced by near band gap optical excitation at low temperature, a phenomenon discovered by Lampel[1] and studied extensively by numerous other groups.[2] Dynamic nuclear polarization occurs when free excitons in a nonequilibrium spin state become trapped at shallow donor sites. The spin polarization of the electron is dictated by the selection rules for optical interband transitions in the material. According to the widely accepted mechanism of this dynamic nuclear polarization effect, trapping at the shallow donor impurities results in a localization of the electron wave function, thereby enhancing the electron-nuclear cross-relaxation rate for nuclei in close proximity to the impurity. The resulting optical enhancement of nuclear polarization (i.e., hyperpolarization) can be observed by various methods, including direct radio-wave detection of NMR,[1,3–8] optically detected NMR,[2,9–18] or by electrical magnetoconductance detection.[19] Diverse physical properties of bulk, quantum-well, and quantum-dot semiconductor systems have been studied by these magnetic resonance methods.

Recent reports on the enhancement of the NMR intensity by optical pumping in single crystal InP have made note of the unexpected and remarkable creation of a homonuclear dipolar order among the In spins.[8] The potential application of InP as a polarized substrate for nuclear spin polarization transfer NMR enhancement of surface adsorbed molecular species has also been suggested.[7] Polarization transfer enhancement across a semiconductor/adsorbate interface will be most effective under experimental conditions that maximize the nuclear polarization in the semiconductor. Here we explore the magnetic field and optical excitation wavelength parameter space in search of the conditions yielding maximum optical pumping NMR enhancement in InP. We will also compare the results for InP with the corresponding data obtained for GaAs.[5,6] The experimental findings will be interpreted within the context of hyperfine cross-relaxation theory.

At a temperature of 4.2 K, the band gap of InP occurs at 877 nm.[20] The accepted value $g_e = +1.26$ of the electron g factor was originally determined from the Zeeman effect in the photoluminescence spectrum of excitons bound to doped bismuth centers[21] and has recently been confirmed (in magnitude and sign) both theoretically[22] and experimentally.[23,24] The measurements described in this paper were all performed on an undoped InP single crystal sample (Showa Denko, Lot No. 3161) of *n*-type conductivity with a $100 \pm 0.1°$ surface orientation, (300 K) carrier concentration of $5-10\times10^{15}$ cm^{-3}, and (300 K) mobility of 3800 cm^2/Vs.

Figure 1 presents the wavelength dependence of the optically pumped ^{115}In NMR signal amplitude in a static field $B_0 = 3$ T applied parallel to the optical pumping beam. The optical power density in this experiment was approximately 500 ± 100 mW/cm^2 (over a 3–4 mm-diameter circular area). In contrast to GaAs at 4.2 K, where a sharp peak in the optically enhanced NMR intensity is observed at wavelengths just below the free exciton band gap,[5] the optical pumping NMR enhancement in InP at 4.2 K is more closely described as a step function at 4.2 K. The enhancement remains constant between 875–840 nm, and then decreases slowly upon further reduction of the wavelength down to 773 nm. On the same wavelength scale in Fig. 1, we present the photoluminescence spectrum obtained by low power (≈ 10 μW) excitation at 488 nm. The photoluminescence band centered near 877 nm exhibits several resolved peaks which can be assigned to the recombination luminescence due to free excitons and excitons bound to neutral or ionized donors.[23,25] The wavelength of the donor-trapped exciton recombination light coincides with the sudden drop in the optically pumped NMR enhancement.

Representative ^{115}In NMR spectra obtained with unpolarized optical excitation and without excitation are provided in the inset of Fig. 1. Note that the phase of the NMR transition due to optical pumping is emissive with respect to the absorption phase signal obtained at thermal equilibrium, a find-

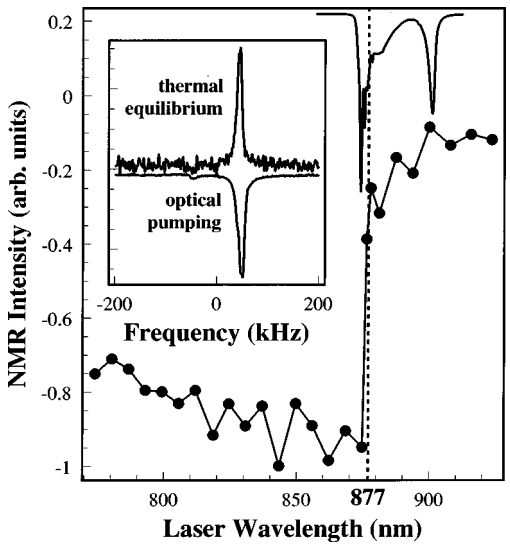

FIG. 1. Wavelength dependence of optically enhanced ^{115}In NMR signal integral in InP. At the top of the figure is the photoluminescence spectrum of the same sample, excited at 488 nm with 10-μW power over a 4-mm-diameter circular region. The peak near 900 nm corresponds to the acceptor bound excitons and appears not to be associated with dynamic nuclear polarization. Inset: representative ^{115}In NMR spectra recorded with and without optical excitation using unpolarized light, as indicated. The same phase correction was applied to both spectra. The vertical axis of the optical pumping signal is scaled down by a factor of 100.

ing we will discuss in detail below. Furthermore, we have observed a phase inversion in the ^{31}P optically pumped NMR, in agreement with a previous InP study.[7,8] The phase inversion has also been observed in the optically pumped NMR of ^{71}Ga, ^{69}Ga, and ^{75}As, in high-purity GaAs[5] with unpolarized light. Under experimental conditions similar to those above, no optical pumping NMR enhancement was observed in a Sn-doped InP sample (Showa Denko, Lot No. 40472) with a carrier concentration of 3×10^{18} cm^{-3}.

The magnetic field dependence of the ^{115}In NMR enhancement due to excitation with unpolarized light was measured at a temperature corresponding to a ^{4}He vapor pressure of 6 mBarr ($\approx$1.5 K). The $4\times6\times0.2$-mm^3 sample was in direct contact with the liquid ^{4}He bath. The experiments were conducted using a 25-T powered magnet at the National High Magnetic Field Laboratory, Tallahassee. The light was transmitted through a 600-μm-diameter optical fiber terminating about 5 mm from the surface of the sample. The optical power density was comparable to that used for the wavelength dependence of optical pumping, as described above. The field dependence experiments employed the field cycling procedure described in a previous study of optical NMR enhancement in GaAs.[5,6] Following the presaturation of the nuclear spins by a multiple-pulse train, the magnetic field is quickly ramped to the ''pumping field.'' After a controlled optical exposure time of 15 s, the magnetic field is cycled back to the initial value for NMR detection using a hard (3 μs) $\pi/2$ rf pulse. A field ramp rate of 0.75 T/s enables the field cycle to be performed without appreciable spin-lattice relaxation during the ramp. The entire field cycling procedure is repeated for different values of the pumping field, but the presaturation and detection field of 8.07 T remain constant. Using the same field cycling sequence, the ''dark'' signal arising from spin relaxation without optical excitation was also recorded.

Although dipolar order in the ^{115}In spin system is known to be created under the experimental conditions employed in this work,[8] the application of a hard $\pi/2$ pulse produces an NMR response proportional to the Zeeman order only. In density operator language, this is because the homonuclear dipolar order commutes with the ^{115}In spin Hamiltonian, as discussed in Ref. 8.

To model the buildup of the nuclear spin Zeeman order $\langle I_z\rangle$ under optical pumping conditions, we use the equation for cross relaxation between coupled electron and nuclear spins induced by fluctuations in the dipolar or scalar hyperfine interaction:[5,26]

$$\frac{d\langle I_z\rangle}{dt}=D\nabla^2\langle I_z\rangle-\left(\frac{1}{T_1}+\frac{1}{T_1^{II}}\right)(\langle I_z\rangle-I_0)-\frac{1}{T_1^{IS}}(\langle S_z\rangle-S_0), \tag{1}$$

where T_1 is the nuclear spin relaxation time in the absence of light, and I_0, S_0 are the expectation values of the nuclear and electron spin at thermal equilibrium. For example, $I_0=\mathrm{Tr}\{I_z\rho_{\mathrm{eq}}\}$, where ρ_{eq} is the density operator at thermal equilibrium. For scalar relaxation,

$$\frac{1}{T_1^{II}}=\frac{S(S+1)}{3}J^{(0)}(\omega_I-\omega_S), \tag{2}$$

where

$$J^{(0)}(\omega_I-\omega_S)=\frac{2A^2\tau_e}{1+(\omega_I-\omega_S)^2\tau_e^2}. \tag{3}$$

τ_e is the correlation time of the fluctuation in the hyperfine interaction, A is the time-averaged scalar hyperfine coupling constant, and ω_S,ω_I are the electron and nuclear Larmor frequencies, respectively. Within the scalar mechanism, it can be shown that[26]

$$\frac{T_1^{II}}{T_1^{IS}}=-\frac{I(I+1)}{S(S+1)}. \tag{4}$$

In the case of dipolar relaxation,[26]

$$\frac{1}{T_1^{II}}=S(S+1)\left\{\frac{1}{12}J^{(0)}(\omega_I-\omega_S)+\frac{3}{2}J^{(1)}(\omega_I)+\frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right\}, \tag{5}$$

$$\frac{1}{T_1^{IS}}=I(I+1)\left\{-\frac{1}{12}J^{(0)}(\omega_I-\omega_S)+\frac{3}{4}J^{(2)}(\omega_I+\omega_S)\right\}. \tag{6}$$

Equation (1) is a partial differential equation in time and displacement with exact solutions that require numerical computation, but an appropriate analytical solution containing the essential physics can be obtained for short pumping times where the nuclear spin diffusion term $D\nabla^2\langle I_z\rangle$ can be ignored. Neglecting the dark relaxation term ($T_1^{II}\ll T_1$),

$$\langle I_z\rangle(t)=\left(I_0-\frac{T_1^{II}}{T_1^{IS}}[\langle S_z\rangle-S_0]\right)(1-e^{-t/T_1^{II}}). \quad (7)$$

Note that when the electron spin-lattice relaxation time T_{1s} substantially exceeds the excited state lifetime τ, the steady state $\langle S_z\rangle=S_z'$ is determined by the interband dipole transition intensities, but more generally, $\langle S_z\rangle=(S_z'T_{1s}+S_0\tau)/(\tau+T_{1s})$. When $\tau\gg T_{1s}$, $\langle S_z\rangle-S_0$ cannot be driven away from zero. With $T_1\gg T_1^{II}$, the thermal equilibrium nuclear spin polarization, while not enhanced, can recover from saturation more quickly than without optical excitation. This situation may occur in samples with high impurity densities.

To investigate the field dependence and phase inversion of the ^{115}In NMR signal induced by optical pumping with unpolarized light, whereby $\langle S_z\rangle$ is driven toward zero, it is convenient to express Eq. (7) as an NMR enhancement factor, $\mathcal{E}$. We make use of the high temperature approximation of the nuclear and electron spins, where $I_0=I(I+1)\gamma_I\hbar B_0/3kT$ and $S_0=S(S+1)g_e\gamma_S\hbar B_0/3kT$. Hence,

$$\mathcal{E}=\frac{\langle I_z\rangle}{I_0}=\left\{1+\frac{S(S+1)}{I(I+1)}\frac{T_1^{II}}{T_1^{IS}}\frac{g_e\gamma_S}{\gamma_I}\right\}(1-e^{-t/T_1^{II}}). \quad (8)$$

Since γ_S is negative for the electron, Eq. (7) demonstrates that the sign of the NMR signal enhancement with respect to I_0 depends on the product of the signs of g_e, T_1^{IS}, T_1^{II}, and γ_I. For unpolarized light, this conclusion is valid even if partial electron spin relaxation occurs in the excited state ($T_{1s}<\tau$). In GaAs and InP, $g_e=-0.44$ and $g_e=+1.26$, respectively. The sign of γ_I and hence the sign of I_0 is positive for all of the naturally abundant nonzero spin isotopes of GaAs and InP: ^{69}Ga, ^{71}Ga, ^{75}As, ^{113}In, and ^{115}In. The relative signs of T_1^{IS} and T_1^{II} depend on what type of hyperfine relaxation mechanism dominates. For scalar hyperfine relaxation, Eq. (4) shows that the signs oppose. For dipolar relaxation, the signs are alike; the expression

$$\frac{T_1^{II}}{T_1^{IS}}\approx\frac{I(I+1)}{S(S+1)}\times\frac{5}{7+3(1+\tau_e^2\omega_S^2)}, \quad (9)$$

can be derived from Eqs. (5) and (6) under the conditions $\tau_e\ll\omega_I^{-1}$ and $\omega_S\gg\omega_I$[26].

Figure 2 presents the experimental field dependence of the optically enhanced and thermal equilibrium ^{115}In NMR signal integrals obtained by the field cycling procedure. The signal obtained without optical exposure was assigned a positive phase, as shown in the inset of Fig. 1. The occurrence of a maximum in the dark signal reflects the increased nuclear spin-lattice relaxation rate at low field. At very high field, the dark signal again increases due to the increased total elapsed time required to complete the field cycle. The dark signal was subtracted from the optically enhanced NMR signal, after applying the same phase correction, yielding the signal due to optical pumping alone. In summary, the maximum enhancement occurs at a magnetic field of 1.7 T, while negligible signal is observed at >15 T. Also shown in Fig. 2, for comparison, is the field dependence of the optically enhanced NMR intensity for ^{69}Ga in bulk GaAs, where optimum enhancement occurs at 3.4 T. While the overall field dependence has the same general features, it is evident that the GaAs enhancement maximum occurs at slightly higher magnetic field and decreases more slowly with increasing field than does the InP signal.

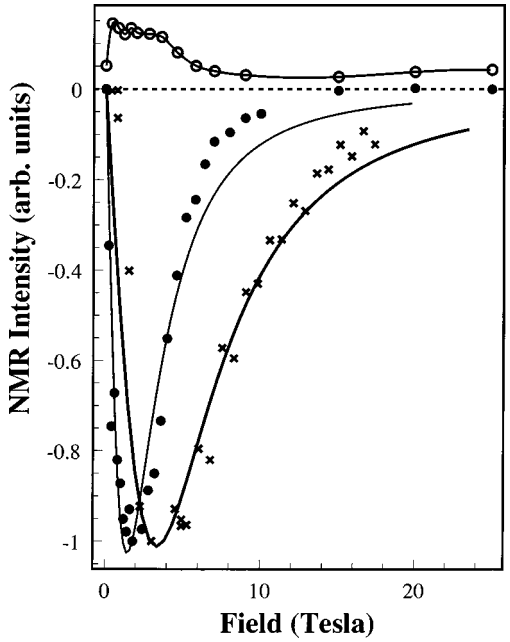

FIG. 2. Magnetic field dependence of optically enhanced ^{115}In (filled circles) and ^{69}Ga (crosses) NMR signal amplitudes in InP and GaAs using unpolarized light of $\lambda_{exc}=835$-nm and 820-nm excitation wavelengths, respectively, and intensity $I\approx 500\pm 100$ mW/cm^2. The background ^{115}In signal (open circles) obtained in the absence of light was subtracted away from the optically enhanced signals. The solid curves represent the best least-squares fits to the numerical solutions of Eq. (1) for which the correlation time and vertical scaling factor were taken as fitted parameters.

As noted above, the optically pumped ^{115}In NMR signals were found to be inverted in phase with respect to the thermal equilibrium signals at all magnetic fields, wavelengths, and at all pumping times. According to Eqs. (4) and (8), the inversion of the ^{115}In signal with respect to the thermal equilibrium signal is inconsistent with the scalar hyperfine relaxation mechanism. On the other hand, the negative enhancement is consistent with Eqs. (5), (6), and (8) pertaining to dipolar hyperfine relaxation.

The dipolar mechanism could become dominant if the hyperfine dipolar coupling is much greater than the hyperfine contact coupling. Alternatively, it could be that τ_e for fluctuations in the dipolar interaction is substantially longer than for scalar interaction. These factors depend on the electron spin density distribution, trapping-recombination dynamics, and spin-exchange processes, none of which are well characterized in InP. If both scalar and dipolar couplings are present, their contributions to the relaxation times can be added independently.[26]

The solid curves shown in Fig. 2 represent least squares fits of the solutions to Eq. (1), assuming dipolar hyperfine relaxation for InP and scalar relaxation for GaAs. For InP, $g_e=+1.26$ and $D=3000$ Å^2/s have been used. Due to the relatively short experimental pumping time of 15 s, the simulations are not highly sensitive to the value of D since the spin diffusion is restricted to a distance of about $\sqrt{Dt}$

$\approx$200 Å. The localization radius of $\approx$100 Å determines the volume of directly pumped nuclei. For short pumping times the overall amplitude $\langle I_z \rangle$ calculated from Eq. (1) is proportional to A^2, but the shape of the curve is independent of this parameter. Since there is an arbitrary scaling factor relating the experimental and simulated field dependence, it suffices to use a rough estimate of $A=1$ MHz for shallow donors in GaAs[11]. Given these fixed parameters, a fitted value of $\tau_e = 6.0\times10^{-12}$ s is obtained for InP. Using $g_e = -0.44$ for GaAs yields $\tau_e = 1.5\times10^{-11}$ s.

A simple expression for $B_0^{\max}$ can be derived from Eq. (7) to predict the magnetic field $B_0^{\max}$ yielding optimum NMR enhancement. Setting $\partial\langle I_z\rangle/\partial B_0 = 0$, we have $B_0^{\max} = |g_e \gamma_S \tau_e|^{-1}$. Since g_e is known, $B_0^{\max}$ can be used to determine the correlation time τ_e. Conversely, if the correlation time τ_e is similar in two materials, then the observed change in $B_0^{\max}$ should occur in proportion to the ratio of the g factors. In comparing the field dependence of the optical enhancement in InP with that of GaAs, this is qualitatively what is observed. Finally, it should be noted that the optimal pumping field should be *independent of temperature* (all other factors remaining constant). This finding, while not intuitive, is also borne out by the experimental field dependence in InP and GaAs obtained at 1.5 and 4.2 K.[5]

In conclusion, the excitation wavelength and magnetic field dependence of the optically pumped NMR signal enhancement in InP has been presented. The sharp drop in the NMR enhancement at approximately 877 nm coincides with the wavelength of the recombination luminescence of the donor-trapped excitons. The phase of the optically pumped ^{115}In and ^{31}P NMR signals are found to be inverted with respect to the thermal equilibrium signal. Within the framework of hyperfine relaxation theory, this signal inversion can only be explained by a dipolar mechanism. Although further investigation of the dynamic nuclear polarization mechanism is warranted to confirm this explanation, the experimental features of the magnetic field and optical polarization dependence in undoped GaAs and InP can be accounted for by Eq. (1). Finally, we have derived a simple expression for the magnetic field yielding maximum NMR signal enhancement. The optimal field is inversely proportional to the product of the g factor and the correlation time of the hyperfine coupling, and is temperature independent. The expression correctly predicts the down-field shift of the optimum pumping field upon increasing the magnitude of the g factor.

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