

Nuclear Spin Polarization Transfer with a Single Radio-Frequency Field in Optically Pumped Indium Phosphide

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We describe a novel spin polarization transfer phenomenon observed in high-field, optically pumped NMR experiments on single-crystal indium phosphide. Polarization transfer from ^{115}In spins to ^{31}P spins occurs when a weak radio-frequency field is applied at the ^{31}P NMR frequency. Unlike other known high-field polarization transfer effects, no rf field near the ^{115}In frequency is required. We present evidence that the ^{31}P polarization arises from a state of optically pumped dipolar order in the ^{115}In spin system and propose two mechanisms that may contribute to the creation of this state. [S0031-9007(98)07539-5]

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Transfer of spin polarization between nuclei with different resonant frequencies is an essential component of many nuclear magnetic resonance (NMR) experiments. Polarization transfer from “sending” nuclei I to “receiving” nuclei S permits the indirect detection of NMR spectra of nuclei with low magnetogyric ratios, low concentrations, or long relaxation times [1–5], the enhancement of directly detected signals from such nuclei [6–8], and the measurement of correlations of NMR frequencies of I and S in multidimensional spectroscopy [9,10]. A variety of techniques for effecting spin polarization transfers have been developed, including techniques based on spin thermodynamics in resonant radio-frequency (rf) fields [1–4,6,7,11] and techniques based on the coherent evolution of coupled spins under rf pulse sequences [5,8–10]. As a rule, polarization transfers in high magnetic field, both in liquids and solids, are double-resonance experiments; i.e., they require at least two rf fields, one near the NMR frequencies of I , the other near the NMR frequencies of S . Double resonance is required to overcome the mismatch of spin-flip energies of I and S that otherwise prevents polarization transfer, or to prepare a nonequilibrium state of I in which significant population differences exist among nearly degenerate energy levels.

Here we report a novel *single-resonance* nuclear spin polarization transfer phenomenon (i.e., only one rf field is required) in high field. We have observed this phenomenon in NMR measurements on indium phosphide (InP) with optical pumping [12–26] at low temperatures. We attribute it to an optically pumped dipolar-ordered nuclear spin state [11,27–29], i.e., a state in which the spin angular momenta of dipole-coupled nuclei are correlated. The creation of such a state by optical pumping has not been reported previously. Our results suggest that similar effects may occur in optically pumped [13–18] and optically detected [19–26] NMR experiments on other semiconductors and perhaps other classes of materials, including quantum wells [14–16,22–25] and quantum dots [26]. Single-resonance polarization transfer may

have applications in optically pumped NMR studies of semiconductor heterostructures and in efforts to polarize nuclei in organic and biological overlayers deposited on optically pumped semiconductor substrates [30].

Figures 1a–1d are ^{31}P NMR spectra of a 10 mm \times 5 mm sample of a 350 μm thick, semi-insulating InP wafer [Fe-doped, (100) orientation, Showa Denko lot 60706], acquired with the timing sequence SAT- τ_L - τ_D - P_{exc} -FID, where SAT represents a train of 64 $\pi/2$

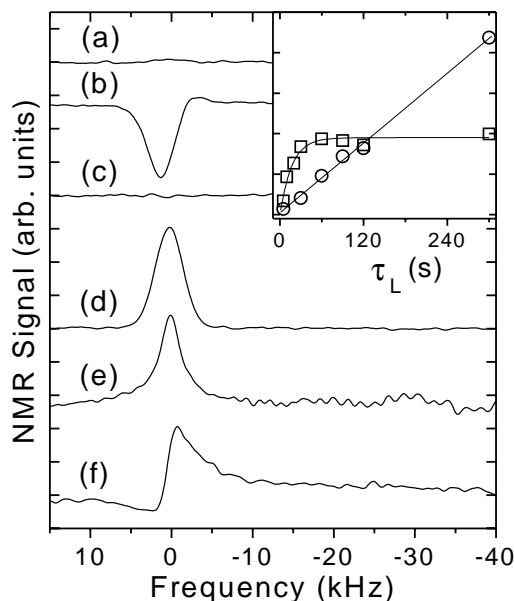


FIG. 1. ^{31}P (a)–(d) and ^{115}In (e),(f) NMR spectra of InP. (b), (d), and (f) obtained with optical pumping; (a), (c), and (e) without. Spectrum (b) is excited by a strong $\pi/2$ pulse while (d) is excited by a long weak pulse. Horizontal scale is the offset from rf carrier. Vertical scales in (a)–(d) are the same, as are (e),(f). Inset: Dependence of the ^{31}P NMR signal magnitude on optical pumping time, with strong $\pi/2$ pulse [circles, fit to straight line] or long weak pulse with $\tau_{\text{exc}} = 5$ ms and $\nu_{\text{exc}} = 3.4$ kHz [squares, fit to $f(\tau_L) = f_{\infty}(1 - e^{-\tau_L/\tau})$ with $\tau = 17$ s]. Laser wavelength is 835 nm.

pulses with 1 ms separations applied simultaneously at the ^{31}P (161.587 MHz, spin-1/2) and ^{115}In (87.552 MHz, spin-9/2) NMR frequencies to saturate (i.e., destroy) any initial ^{31}P and ^{115}In spin polarizations, τ_L is a period during which the sample is irradiated with near-infrared light, τ_D is a period during which the light is off, P_{exc} is an rf pulse at the ^{31}P NMR frequency of length τ_{exc} , and FID represents the detection of free-induction-decay signals with the light off. These spectra were obtained at 9.39 T and 8 K, using a spectrometer, cryostat, and optics arrangement described previously [14–16] and using a Ti:sapphire laser. Unless otherwise noted, the wavelength, power, and polarization of the light were 884 nm, 1300 mW/cm², and σ^+ . In Fig. 1a, $\tau_L = 0$, $\tau_D = 11$ s, and P_{exc} is a $\pi/2$ pulse with length $\tau_{\text{exc}} = 10$ μs and amplitude (i.e., Rabi frequency) $\nu_{\text{exc}} = 24$ kHz. In Fig. 1b, $\tau_L = 10$ s, $\tau_D = 1$ s, and P_{exc} is the same as in Fig. 1a. The difference in signal amplitudes in Figs. 1a and 1b demonstrates the standard optical pumping effect, in which the excitation of spin-polarized electron-hole pairs leads to the generation of nuclear spin polarization during τ_L through an Overhauser mechanism [12,13]. Figures 1c and 1d are ^{31}P NMR spectra under the same conditions as Figs. 1a and 1b, but with $\tau_{\text{exc}} = 8$ ms and $\nu_{\text{exc}} = 3.4$ kHz. Comparison of Figs. 1b and 1d shows that, under these conditions, *a long, weak rf pulse excites stronger NMR signals than a strong $\pi/2$ pulse*. This is surprising because a strong $\pi/2$ pulse should excite the maximum signal from optically pumped ^{31}P spin polarization.

Figures 1e and 1f are ^{115}In NMR spectra, obtained as in Figs. 1a and 1b but with P_{exc} applied at the ^{115}In NMR frequency, $\nu_{\text{exc}} = 22$ kHz, and 200 mW/cm² laser power. Phases of all spectra in Fig. 1, except Fig. 1d, are set so that equilibrium spin polarizations produce purely absorptive (i.e., purely positive) line shapes after a strong $\pi/2$ pulse. An additional phase adjustment of 90° is required to produce the absorptive line shape in Fig. 1d. The ^{31}P linewidth $\Delta_{31} \approx 4.5$ kHz (static field perpendicular to wafer surface) arises from a combination of ^{31}P - ^{31}P and ^{31}P - ^{115}In magnetic dipole-dipole and pseudodipole couplings [31]. The ^{115}In linewidth $\Delta_{115} \approx 2.6$ kHz arises from a combination of dipole-dipole couplings and small electric quadrupole couplings from strain that develops in the InP sample at low temperatures. At room temperature, $\Delta_{115} \approx 1.9$ kHz. The absence of detectable signals in Fig. 1a is due to the relatively long spin-lattice relaxation time (roughly 11 h) of ^{31}P in the dark at 8 K. The spin-lattice relaxation time of ^{115}In is roughly 2 h under the same conditions.

Figure 2a shows the dependence of the integrated ^{31}P NMR signal amplitude on ν_{exc} for fixed $\tau_{\text{exc}} = 8$ ms and on τ_{exc} for fixed $\nu_{\text{exc}} = 3.4$ kHz, with $\tau_L = 10$ s and $\tau_D = 1$ s. The signal amplitude is maximized when $\nu_{\text{exc}} = 3.4$ kHz and approaches an asymptotic maximum when $\tau_{\text{exc}} \geq 8$ ms. Figure 2b shows the dependence on the flip angle of P_{pre} in the modified

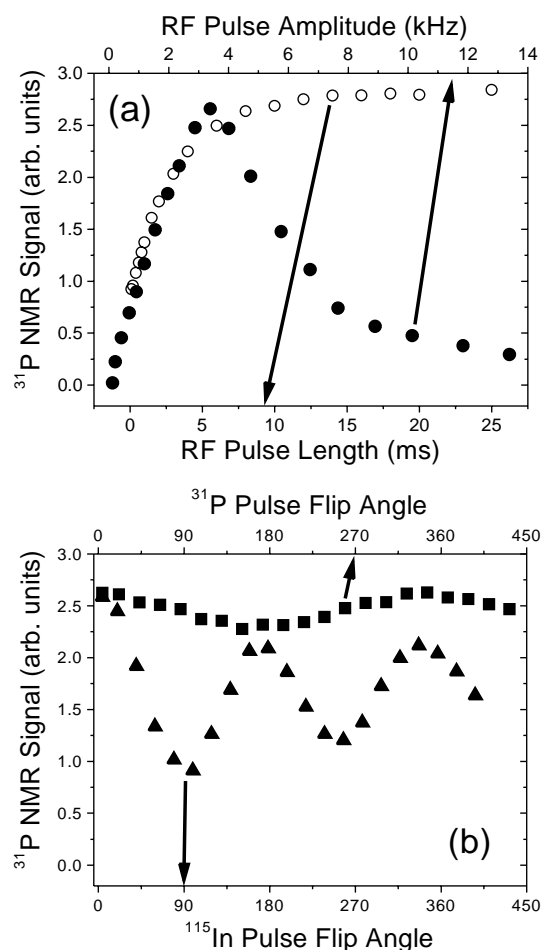


FIG. 2. (a) Dependence of the optically pumped ^{31}P NMR signal amplitude on the length (hollow circles) and amplitude (filled circles) of P_{exc} . (b) Dependence on the flip angle of a pulse P_{pre} that precedes P_{exc} when P_{pre} is applied at the ^{31}P frequency (squares) or the ^{115}In frequency (triangles).

sequence SAT- τ_L - τ_D - P_{pre} - P_{exc} -FID, where P_{pre} is an rf pulse of amplitude $\nu_{\text{pre}} = 22$ kHz (24 kHz) applied at the ^{115}In (^{31}P) NMR frequency, with $\nu_{\text{exc}} = 3.4$ kHz and $\tau_{\text{exc}} = 8$ ms. When P_{pre} is applied to ^{115}In nuclei, a strong oscillatory modulation of the ^{31}P signal is observed, with minima (maxima) at $\theta_{\text{pre}} \approx \pi/2$ and $\theta_{\text{pre}} \approx 3\pi/2$ ($\theta_{\text{pre}} \approx \pi$ and $\theta_{\text{pre}} \approx 2\pi$). When P_{pre} is applied to ^{31}P nuclei, a much weaker modulation is observed, with a minimum (maximum) at $\theta_{\text{pre}} \approx \pi$ ($\theta_{\text{pre}} \approx 2\pi$). In the latter case, FIDs in which the rf phase of P_{pre} relative to P_{exc} is 0°, 90°, 180°, and 270° are coadded.

The data in Figs. 1 and 2 indicate that new ^{31}P spin polarization develops in the dark during P_{exc} , independent of ^{31}P polarization that is generated during τ_L by optical pumping. The phase of the signal in Fig. 1d implies that the new polarization is aligned (i.e., spin locked) with the rf magnetic field of P_{exc} in the ^{31}P rotating frame. The source of this polarization appears to be the ^{115}In spin system. The polarization transfer process resembles Hartmann-Hahn cross polarization [1,2,7], in which spin-locked I polarization is transferred to

spin-locked S polarization when the two rf field amplitudes satisfy the matching condition $\nu_I^{\text{rf}} \approx \nu_S^{\text{rf}}$. In our experiments, the transfer occurs without any rf fields near the ^{115}In NMR frequency and is optimized at an apparent matching condition $\nu_{\text{exc}} \approx \Delta_{115}$, i.e., when the amplitude of the rf field applied to ^{31}P nuclei roughly equals the amplitude of dipole-dipole and quadrupole couplings of the ^{115}In nuclei. This matching condition and the dependence of the ^{31}P NMR signal amplitude on P_{pre} when P_{pre} is applied to ^{115}In nuclei suggest that the ^{31}P spin polarization evolves from dipolar order in the ^{115}In spin system [1,7,11,27–29]. The NMR line shapes in Figs. 1b and 1d, which exhibit a mixture of absorptive and emissive components, are also consistent with the presence of significant dipolar order [28,29]. In conventional high-field NMR experiments, dipolar order must be created from Zeeman order by rf irradiation [11,27] or pulse sequences [28,29]. In our experiments, dipolar order is created by the optical pumping process in the absence of rf fields.

To understand our observations, consider a system of many I spins coupled to one S spin, with interactions described by the following Hamiltonian terms:

$$H_I = \nu_I^0 \sum_i I_{zi} + \sum_{j>k} d_{jk} (3I_{zj}I_{zk} - \mathbf{I}_j \cdot \mathbf{I}_k) \quad (1a)$$

$$= H_{ZI} + H_{II}, \quad (1b)$$

$$H_{IS} = \sum_n b_n I_{zn} S_z, \quad (2)$$

$$H_S = \nu_{\text{exc}} S_x. \quad (3)$$

H_{ZI} and H_{II} represent the Zeeman and homonuclear dipole-dipole interactions of the I spins, with Larmor frequency ν_I^0 and dipole-dipole coupling constants d_{jk} . H_{IS} represents the heteronuclear I - S dipole-dipole interactions, with coupling constants b_n . H_S represents the interaction of the S spin with an on-resonance rf field, viewed in the S -spin rotating frame. \mathbf{I}_i and \mathbf{S} are the nuclear spin angular momentum operators. ν_I^0 is of order 10^8 Hz. d_{jk} and b_n are of order 10^4 Hz or less. The state of the spin system is described by a density operator $\rho(t)$, with $\rho(0)$ being the state prepared by optical pumping. Note that $[H_{ZI}, H_I + H_{IS} + H_S] = 0$. Therefore, if $\rho(0)$ is proportional to H_{ZI} or to any function of H_{ZI} such as $\exp(-H_{ZI}/kT_{ZI})$, which would correspond to I -spin Zeeman order with Zeeman spin temperature T_{ZI} , then $\rho(t) = \rho(0)$. In particular, $\rho(t)$ cannot develop a component proportional to S_x , which would represent spin-locked S -spin polarization [i.e., $\{S_x \rho(t)\} = 0$]. Thus, polarization of ^{115}In nuclei to a low Zeeman spin temperature by optical pumping, as described for other nuclei in other optical pumping studies [12–26], cannot account for our experimental results. Next, note that $[H_{II}, H_{IS}] \neq 0$ and $[H_S, H_{IS}] \neq 0$. According to the spin temperature hypothesis [32], optical pumping of the I spins will lead to

$$\rho(0) \propto \exp(-H_{ZI}/kT_{ZI}) \exp[-(H_{II} + H_{IS})/kT_D], \quad (4)$$

where T_D is the spin temperature describing dipolar order produced by optical pumping. After the rf field is applied to the S spins, the spin system will evolve to a quasiequilibrium state $\rho_{\text{eq}} \propto \exp(-H_{ZI}/kT_{ZI}) \times \exp[-(H_{II} + H_{IS} + H_S)/kT_{\text{eq}}]$. If $\nu_{\text{exc}} \sim d_{jk}$, ρ_{eq} will be reached rapidly and $T_{\text{eq}} \sim T_D$, so that a low dipolar temperature will lead to an appreciable spin-locked S -spin polarization. If the spin temperature formalism does not apply and $\rho(0)$ has a more general form, the condition $[\rho(0), H_{IS}] \neq 0$ must be satisfied for spin-locked S -spin polarization to develop. In this case, “dipolar order” is the component of $\rho(0)$ that does not commute with H_{IS} .

A more complete treatment would include the quadrupole interaction $H_{QI} = \sum_i \nu_{Qi} (3I_{zi}^2 - I_i^2)$ of the ^{115}In nuclei in Eq. (1). Since $[H_{QI}, H_{II}] \neq 0$, $\rho(0)$ in Eq. (4) would contain quadrupolar as well as dipolar order. We emphasize dipolar order because the quadrupole interactions in InP are very small and because ^{115}In quadrupolar order cannot evolve directly into ^{31}P polarization when an rf field is applied to ^{31}P spins, since $[H_{QI}, H_{IS}] = 0$. The H_{IS} term in $\rho(0)$ represents heteronuclear dipolar order. Because a rotation of S_z by π about the x axis changes the sign of H_{IS} , the presence of heteronuclear dipolar order accounts for the weak modulation of the ^{31}P NMR signals when P_{pre} is applied to ^{31}P nuclei in Fig. 2b. A rotation by θ about the x axis transforms H_{II} to $\tilde{H}_{II}(\theta)$, with $\text{Tr}\{\tilde{H}_{II}(\theta) \times H_{II}\} / \text{Tr}\{H_{II}^2\} = \frac{1}{2}(3 \cos^2 \theta - 1)$, which accounts for the periodicity of the strong modulation when P_{pre} is applied to ^{115}In nuclei.

At least two mechanisms may contribute to the creation of an initial state $\rho(0)$ containing dipolar order. One is the direct optical pumping of such a state. As a simplified model for this process, consider two spin-1/2 nuclei I_1 and I_2 , at positions \mathbf{r}_1 and \mathbf{r}_2 , that are coupled to one another by dipole-dipole coupling and to an electron spin by a dipolar hyperfine coupling. Let the electron be localized near position \mathbf{r}_3 , with small fluctuations $\delta\mathbf{r}(t)$, and maintained at spin temperature T_e by optical pumping. Assuming equal and uncorrelated amplitudes in the three components of $\delta\mathbf{r}(t)$, the rates $R_{\kappa m, \kappa' m'}$ of all possible transitions from nuclear spin state κ and electron spin state m to nuclear spin state κ' and electron spin state m' induced by these fluctuations are calculated in the short-correlation limit as

$$R_{\kappa m, \kappa' m'} = R_0 \sum_{u=x,y,z} | \langle \kappa' m' | V_u | \kappa m \rangle |^2 e^{-h\nu_e m / kT_e} \times \{ \eta(\delta E) + [1 - \eta(\delta E)] e^{-(\delta E)/kT} \}, \quad (5)$$

where R_0 is a constant, V_u is the operator coefficient of $\delta r_u(t)$ in the fluctuating dipolar hyperfine coupling, ν_e is the electron spin Larmor frequency, $\delta E = E_{\kappa'} - E_{\kappa} + h\nu_e m' - h\nu_e m$, E_{κ} is the nuclear spin energy in state κ , T is the lattice temperature, $m = \pm 1/2$, and $\eta(x)$ is the Heaviside step function. The steady-state populations of the nuclear spin states under optical pumping can then be obtained from Eq. (5). In high field,

the nuclear spin states are $|1\rangle = |++\rangle$, $|2\rangle = (|+-\rangle + | -+\rangle)/\sqrt{2}$, $|3\rangle = (|+-\rangle - | -+\rangle)/\sqrt{2}$, and $|4\rangle = |--\rangle$, with steady state populations p_1 , p_2 , p_3 , and p_4 . The component of $\rho(0)$ that does not commute with H_{IS} is $\rho_D = \frac{p_2 - p_3}{2}(|2\rangle\langle 2| - |3\rangle\langle 3|)$. In general, $\rho_D \neq 0$. For example, in numerical calculations assuming nuclear magnetogyric ratios of $2\pi \times 10^7$ rad/s T, nuclear Zeeman splittings of 100 MHz, an electron Zeeman splitting of 100 GHz, $|\mathbf{r}_1 - \mathbf{r}_3| = |\mathbf{r}_2 - \mathbf{r}_3| = 20 \text{ \AA}$, $|\mathbf{r}_1 - \mathbf{r}_2| = 4 \text{ \AA}$, $T = 5 \text{ K}$, and $T_e = -2 \text{ K}$, the maximum and average values of $|p_2 - p_3|$ (which depends on the field direction) are 0.087 and 0.031.

A second possible mechanism for the creation of dipolar order is based on the diffusion of optically pumped spin polarization in the presence of an NMR frequency gradient, following the analysis of Genack and Redfield [33]. The existence of NMR frequency gradients within the sample is suggested experimentally by the fact that ^{31}P NMR signals acquired in the dark after short periods of optical pumping (Fig. 1b) are shifted by about 1200 Hz from thermal equilibrium signals. The source of this shift is uncertain, but may be hyperfine interactions with trapped electrons at the optical pumping sites, which are believed to be associated with defects or impurities [12,20]. Based on measured hyperfine couplings in InP [34], we estimate that a trapped electron with a Bohr radius of 100 \AA produces a maximum contact hyperfine shift of $530 \text{ kHz} \times p_e$, where p_e is the electron spin polarization multiplied by the fractional occupancy of the trap site.

Genack and Redfield [33] derived coupled diffusion equations to describe the evolution of Zeeman and dipolar order in a homonuclear spin system with nonuniform magnetization $M(\mathbf{r}, t)$ and dipolar spin temperature $T_D(\mathbf{r}, t)$. Numerical solutions of these equations indicate that this mechanism can generate substantial dipolar order on the experimental time scale. The magnitude depends on the field gradient, the diffusion constants D_Z and D_D for Zeeman and dipolar order, the spin-lattice relaxation times T_{1Z} and T_{1D} , the rms dipolar field H_D , the distribution of optical pumping sites, and the maximum polarization produced at the pumping sites. For example, with $D_Z = D_D = 2 \times 10^{-14} \text{ cm}^2/\text{s}$, $T_{1Z} = 7000 \text{ s}$ and $T_{1D} = 30 \text{ s}$ (experimentally determined for ^{115}In), $T = 8 \text{ K}$, $T_{ZI} = 80 \text{ mK}$ (estimated from the magnitude of optically pumped NMR signals at large τ_L) at a 10 \AA cubic pumping site in the center of a 500 \AA cubic volume, $H_D = 69 \text{ \mu T}$, and an exponentially decaying NMR frequency gradient with a total frequency range of 2.0 kHz and a 50 \AA decay length, we find that the cubic volume reaches an average dipolar spin temperature $T_D = 0.01 \text{ mK}$ after 120 s. For comparison, an adiabatic demagnetization of the full thermal equilibrium polarization would be expected to lower T_D by a factor of $H/H_D \approx 140\,000$, corresponding to $T_D \approx 0.06 \text{ mK}$.

The ^{31}P NMR signal arising from ^{115}In dipolar order saturates with increasing τ_L , with a time constant of roughly 17 s (Fig. 1, inset). We attribute this saturation

to the short value of T_{1D} , which limits the diffusion of dipolar order from optical pumping sites to the bulk.

The heat capacity of the homonuclear dipolar reservoir, which is proportional to $\gamma^4 S^2(S+1)^2$, is 94 times smaller for ^{31}P than for ^{115}In . Thus, we expect relatively little ^{31}P dipolar spin order to be generated.

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