Helicity asymmetry of optically-pumped NMR spectra in GaAs

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The origin of σ± asymmetries in the optically-pumped NMR signal and hyperfine shift in GaAs is derived analytically and tested experimentally. The ratio of the optically-pumped to the equilibrium electron spin polarization is a key parameter in determining both asymmetries. Variations in asymmetry with photon energy and laser power reflect variations in the local temperature and the electron spin polarization, and these two quantities are extracted from the asymmetry through a simple methodology. Other contributions to the asymmetry are considered.

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Optical polarization of nuclear spins in semiconductors has sparked high sensitivity NMR studies of the quantum Hall regime[1], spatial mapping[2] of lattice strain[2] and proposals for biological polymers. In the optically-enhanced or optically-pumped NMR (OPNMR) spectrum, σ± asymmetry has been noted in both the hyperfine-induced frequency shift[3,4] and the NMR signal magnitude[5,6,7,8] as shown in Fig. 1A. Variations in the asymmetry with photon energy[9] and laser power (shown herein) have not yet been explained, even for the most well-studied semiconductor, GaAs. Varying values of τ/T₁e, where τ and T₁e are the electron recombination and spin-relaxation times, were recently invoked to explain variations in signal magnitude asymmetry in GaAs[5]. It is shown herein that the standard OPNMR model for GaAs predicts that τ/T₁e only affects the hyperfine shift asymmetry.

It is often assumed that the initially-excited electron spin polarization ⟨Sz⟩₀≡S₀ with σ± light in bulk semiconductors is constant (±50% for cubic crystals) for photon energies E in the range E_g < E < E_g + Δ (where E_g is the band-gap energy and Δ is the spin-orbit splitting) and there is very little literature on optical electron spin orientation with E ≤ E_g. By dropping the assumption that S₀ is a constant, we find an explanation for the varying asymmetry of OPNMR spectra. It furthermore follows that this asymmetry is related so simply to electron spin parameters that it can be used to measure the electron spin polarization. Thus, this article outlines a “spinometry” method that, because the hole spin-nuclear spin interaction is very weak, probes the electron spin polarization under optical pumping.

It was shown previously that the OPNMR signal in GaAs strongly correlates with the phot conductivity, and that the excitation spectrum of OPNMR signals can be largely understood from a simple picture in which optical absorption generates free electrons which then bind to shallow donors, analogous to the way that a gas adsorbs to a solid surface with a fixed number of sites. Rapid spin exchange[11] maintains the steady-state polarizations of the free and donor-bound electron reservoirs to be equal and thus given by a single equation[12,13,14,15] for the Boltzmann electron polarization. Once bound to shallow donors, the electrons experience a strong hyperfine interaction and can undergo mutual spin flips with nearby nuclear spins. The dimensionless nuclear polarization, C = ⟨Iz⟩/I, near the shallow donors then evolves over space and time according to a generation-diffusion-loss equation[11,16]

\[ \frac{\partial C}{\partial t} = D \nabla^2 C + \frac{1}{T_{1H}(\vec{x})} (1 - C) - \frac{1}{T_{1L}(\vec{x})} C \]  

where \( I_s \) is the theoretical maximum nuclear polarization achievable through cross relaxation, D is the nuclear spin diffusivity, T₁H is the hyperfine cross-relaxation time, T₁L is the nuclear spin-lattice relaxation time by all other mechanisms, and the Boltzmann nuclear polarization is neglected. During this microscopic evolution, the bulk NMR signal I(t) grows in proportion to the total nuclear z-angular momentum, found by integrating ⟨Iz⟩ over all space: \( I(t) = \int \langle I_z \rangle(\vec{x}, t)dV = \int I_s C(\vec{x}, t)dV \). In the high lattice temperature approximation, \( I_s \) is given by[17] \( I_s = \frac{\Gamma(I + 1)}{S(S + 1)} \kappa(S_e - S_q) \equiv \frac{\Gamma(I + 1)}{S(S + 1)} \kappa \). Here, I and S are the nuclear and electron spin quantum numbers and \( \kappa = (w_0 - w_2)/(w_0 + w_0 + w_2) \), where w₀, w₂, and w₁ are the transition probabilities per time for electron-nuclear flip-flops, flip-flips, and independent nuclear flips. Thus, the NMR signal follows a complicated equation:

\[ I(t) = (S_0 - S_{eq}) \int \frac{\Gamma(I + 1)}{S(S + 1)} \kappa C(\vec{x}, t) dV + \tau/T_{1e}dV. \]  

This expression can be reduced to something simple through a transformation. Consider that S₀ varies sinusoidally with the angle θ of the quarter-wave retarder, through which the laser light passes, according to S₀ = A sin 2θ. (A is treated as an experimentally determined quantity in this paper.) Ignoring any dependence of S_{eq}, τ, T₁e, and C(\vec{x}, t) on the light helicity, Eq. 6 gives A ≡ (I_{σ⁺} - I_{σ⁻}) = k(t)A and B ≡ (I_{σ⁺} + I_{σ⁻}) = k(t)S_{eq}, where I_{σ±} denotes the NMR signal induced by σ± light.
All the time dependence and all the nuclear spin parameters are contained in $k(t)=-2\int \frac{I(t+1)}{S(t+1)} \kappa CdV$. So the ratio of the two equations cancels out everything but the electron spin polarizations:

$$R_I \equiv \frac{I_{\sigma+} - I_{\sigma-}}{I_{\sigma+} + I_{\sigma-}} = \frac{\Lambda}{S_{eq}}.$$  \hspace{1cm} (4)

This simple relationship provides an interpretation for the asymmetry of OPNMR signals, and forms the basis for extracting $S_0$ from the signal asymmetry:

$$S_0 = S_{eq} R_I \sin 2\theta.$$  \hspace{1cm} (5)

A similar procedure can be followed for the hyperfine shift of the OPNMR line. This shift is given by:

$$\Delta \nu(t) = \Delta \nu_m \int S_s F e^{-r/\kappa_0} (I_z) dV/ \int (I_z) dV,$$

where $\Delta \nu_m$ is a constant specific to the nuclear isotope, $r$ is the distance to the nearest shallow donor, $F$ is the occupation probability of that donor, and $\kappa_0$ is its Bohr radius. Using Eq. (1) and assuming that $\tau/T_{1e}$ (and thus, $S_s$) is spatially uniform:

$$\Delta \nu(t) = \Delta \nu_m (S_0 + \frac{\tau}{T_{1e}} S_{eq}) \int \frac{F e^{-r/\kappa_0} C dV}{(1 + \tau/T_{1e})} \int C dV.$$  \hspace{1cm} (6)

Denoting the hyperfine shift with a light as $\Delta \nu_\pm$ and making the same approximations as those made in deriving $R_I$, we obtain $(\Delta \nu_- - \Delta \nu_+) = m(t) \Lambda$ and $(\Delta \nu_- + \Delta \nu_+) = n(t) \frac{\tau}{T_{1e}} S_{eq}$. All the time dependence is contained in $m(t) = 2 \Delta \nu_m \int F e^{-r/\kappa_0} C dV$. Again, taking the ratio of the two equations gives an interpretation for the asymmetry of hyperfine shifts:

$$R_\nu \equiv \frac{\Delta \nu_- - \Delta \nu_+}{\Delta \nu_- + \Delta \nu_+} = \frac{\Lambda}{\frac{\tau}{T_{1e}} S_{eq}}.$$  \hspace{1cm} (7)

Just like Eq. (1), this is a simple relationship between measurable NMR quantities and time-independent electronic parameters. Equations (1), (4), and (7) may be combined to solve for $S_s$:

$$S_s = S_{eq} \frac{R_I \sin 2\theta + R_I/R_\nu}{1 + R_I/R_\nu}.$$  \hspace{1cm} (8)

The above derivation shows that $\Lambda/S_{eq}$ is a key parameter in determining the asymmetry of OPNMR spectra. Other contributions to the asymmetry may result from effects such as inhomogeneous Knight fields, large Overhauser nuclear fields, and spin-dependent recombination. Respectively, these effects would impart a helicity dependence to $S_{eq}$ (through the magnetic field), and $\tau$. The helicity dependence of $\tau$ can be measured by the helicity dependence of the photoconductivity. Figure (B) plots the photoconductivity asymmetry: $\Delta c/c = (c_{\sigma+} - c_{\sigma-})/(c_{\sigma+} + c_{\sigma-})$, which is attributed to SDR, observed for laser power $P \approx 200$ mW at the $B_0$, $T$, and $E$-range under which our OPNMR measurements were performed. The data indicate that SDR is present in semi-insulating (SI) GaAs and is larger for $E > E_g$, but overall it appears to be small: $\Delta c/c$ is $\lesssim 5\%$ over this photon energy range. So the helicity dependence of $\tau$ appears not to be the dominant contribution to the OPNMR asymmetry. SDR may also alter the form of Eq. (1), although this would go beyond the standard model for OPNMR in GaAs.

Through a laser heating model and a procedure to extract all three parameters: $\Lambda$, $T$, and $S_s$, from the OPNMR spectrum.

For an irradiated volume with heat capacity $C_p$ and surface area $2\sigma$, where $\sigma$ is the laser spot area, absorbing a net power of $fP$ and losing heat to the surroundings.
Figure 2: (A) Power dependence of $\Lambda$ and $B$, defined in text, for $E=1.509$ eV and $T_0=5$ K. (B) Extracted $T$ versus power. Inset: Extracted $\Lambda$ over this temperature range.

(temperature $T_0$), an energy balance gives:

$$C_p \frac{dT}{dt} = fP - 2h\sigma(T - T_0). \quad (9)$$

The steady-state temperature $T_s$ grows linearly with $P$:

$$T_s = T_0 + fP/(2h\sigma). \quad (10)$$

This model further suggests that $T$ rises extremely fast after laser exposure due to the low $C_p$ at low $T$: the initial rise rate being $fP/C_p \sim 1$ K/10 $\mu$s at 5 K and $P=200$ mW. Steady-state is reached typically within the first millisecond, which is very rapid compared to optical nuclear polarization, so $T$ can be assumed constant during the nuclear polarization process.

A procedure for extracting the parameters is: (1) Measure $R_I$ at very low $P$ where $T \approx T_0$ and calculate $\Lambda = -\frac{\sigma}{4k_B T_0} [R_I|_{P=0}]$. In other words, extract $\Lambda$ from the y-intercept of the $R_I$ vs. $P$ plot. (2) Go to the $P$ of interest and extract $T$ using $S_{eq} = \Lambda/R_I$. (3) Extract $S_s$ at this $P$ from Eq. (8). Thus, the OPNMR signal serves as a spinometer and a thermometer. This thermometry method requires no sample preparation and is an in situ measurement of the irradiated volume’s temperature. Figure 2B shows a thermometry curve obtained with this method, the linear dependence on $P$ being consistent with the model’s prediction. Also obtained with this method, the inset shows that $\Lambda$ at 1.509 eV is $\sim 0.3$ and is practically $T$-independent from 4.5 K-14 K.

Laser heating is major concern in OPNMR. In previous studies of the $P$-dependence of OPNMR signals from a single light polarization were plotted vs. $P$, which had the disadvantage that the signal depended on $S_{eq}$, and thus was vulnerable to laser heating effects. The quantity $A$ is independent of $S_{eq}$, more robust to laser heating, easier to model, and better for studying nonlinear effects like 2nd order carrier recombination and shallow-donor filling. Figure 2A plots $A$ and $B$ vs. $P$. While $B$ saturates at some $P$ value, $A$ keeps on growing. Previously, saturation of OPNMR signals with linear polarized light at high $P$ was attributed to complete filling of shallow donors but the data in Fig. 2 show that it was actually due to laser heating, and we can no longer say that we obtained proof of shallow-donor filling from the $P$-dependence of OPNMR. (This does not eliminate the possibility that shallow-donor filling is important at these powers.) So this thermometry method has had immediate impact on our understanding of OPNMR data.

$S_0$ and $S_s$ were also measured for SI GaAs with the above method. The NMR lineshapes were Gaussian for all $t$, so the hyperfine shift extracted from a Gaussian fit was equivalent to the first moment as defined above. For $E=1.509$ eV, $T_0=5K$, and $P=123$ mW, the calculated parameters are: $T=9.5K$, $\tau/T_{1e}=R_I/R_0=1.2$, $\Lambda=0.294\pm0.02$, $S_{s,\sigma^-}=-0.184\pm0.03$, and $S_{s,\sigma^+}=-0.088\pm0.02$. The extracted $\Lambda$ is slightly
greater than the theoretically predicted value of 0.25.

It has been derived analytically and demonstrated experimentally that the asymmetry of optically pumped NMR spectra in GaAs is a measure of $T$ and $\langle S_z \rangle$. This method is now applied to literature data to map out the $E$-dependence of $\langle S_z \rangle$. Figure 3A shows the spectrum of $S_0$ and $S_x$ excited by $\sigma^\pm$ light, for Si GaAs at $B_0=4.7$ T, $T=6$ K, $P=2.5$ W/cm$^2$. There are several peaks and valleys, indicating that the $E$-dependence of $\langle S_z \rangle$ should be taken into account when modeling OPNMR $\sigma^\pm$ data. Similar oscillations have been observed in GaAs quantum wells so the strong magnetic field may provide the analogous confinement potential that breaks the degeneracy between heavy-hole and light-hole excitations and gives rise to oscillations in optical orientation.

$S_0$ gradually increases over a 30 meV region just below the band edge, a feature that was reproduced in all 8 OPNMR data sets that we inspected, including those for different nuclear isotopes and magnetic fields. A reasonable explanation is an increasing proportion of shallow defect-to-band relative to deep defect-to-band absorption as $E$ approaches $E_g$. Only the former transitions have the same selection rules (thus the same spin-selectivity) as band-to-band transitions. Shallow acceptors in GaAs sit $\sim 26$ meV above the valence band so onset of band-to-band-like optical electron spin orientation likely coincides with onset of shallow acceptor absorption. The lower value of $\Delta/S_{xx}$ at low $E$ shown here may explain the observed inversion of $\sigma^-$ OPNMR signal at low $E$.

Fig. 3B plots the ratio of the two asymmetries $R_1/R_\nu = \tau/T_{1x}$, which decreases by $\sim 1$ order of magnitude as $E$ increases from below to above $E_g$. Overlaid is a theoretical spectrum ($\times 3.6$ for comparison) predicted by our previous OPNMR model without adjusting any fitting parameters. It accounts only for the variation of $\tau$ (assumes constant $T_{1x}$) and likewise predicts the decrease by 1 order of magnitude. So the main feature in the $E$-dependence of $\tau/T_{1x}$ may be explained by the $E$-dependence of $\tau$: the shorter penetration depth at higher $E$ confines the electron-hole gas to a smaller volume, increasing the recombination rate. The lower $\tau/T_{1x}$ at higher $E$ pulls $S_x$ closer to $S_0$, as seen in Fig. 3A. This implies that super-gap irradiation leads to a better retention of the injected polarization in the steady state.

The asymmetry of literature Ga OPNMR signals was different for strained and unstrained GaAs, as shown in the inset of Fig. 3B. The asymmetry difference is consistent with the strain enhancing the initially-excited electron spin polarization by about a factor of 2, which is precisely what is predicted for a compressive strain perpendicular to the magnetic field. This enhancement of optical electron spin orientation with strain was not considered in previous OPNMR data interpretation.

In conclusion, an interpretation was given for the asymmetry of OPNMR signals and hyperfine shifts in GaAs in terms of the local temperature and the electron spin polarization. This provided a methodology for extracting the latter two quantities from OPNMR asymmetries. This method may be used to investigate effects of quantum confinement, strain, and applied magnetic field on optical pumping, to probe spin-selective excitation of defects, and to study electron recombination and spin-lattice relaxation. The author thanks Jeff Reimer for helpful suggestions and support, and acknowledges support from the NSF under project ECS-0608763.

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25. Also note that a non-negligible Boltzmann nuclear polarization in Eq. (2) could affect the asymmetry at high magnetic fields and conditions that favor short $T_{1L}$.
26. This method also requires that any dark NMR signals be
phase-cycled away from the OPNMR spectrum, say, with a spectrometer-controlled laser shutter.

It is unclear whether temperatures in the literature are corrected for laser heating. Thus, uncertainties on spin polarizations extracted from the literature cannot be provided. Not accounting for laser heating would overestimate $\langle S_z \rangle$. 