Modelling of OPNMR Phenomena Using Photon Energy-Dependent $\langle S_z \rangle$ in GaAs and InP

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Abstract

We have modified the model for optically-pumped NMR (OPNMR) to incorporate a revised expression for the expectation value of the z -projection of the electron spin, $\langle S_z \rangle$ and apply this model to both bulk GaAs and a new material, InP. This expression includes the photon energy dependence of the electron polarization when optically pumping direct-gap semiconductors in excess of the bandgap energy, E_g . Rather than using a fixed value arising from coefficients (the matrix elements) for the optical transitions at the $\mathbf{k} = 0$ bandedge, we define a new parameter, $S_{\text{opt}}(E_{\text{ph}})$. Incorporating this revised element into the expression for $\langle S_z \rangle$, we have simulated the photon energy dependence of the OPNMR signals from bulk semi-insulating GaAs and semi-insulating InP. In earlier work, we matched calculations of electron spin polarization (alone) to features in a plot of OPNMR signal intensity versus photon energy for optical pumping [K. Ramaswamy et al. Phys Rev. B 82 (2010) 085209]. By incorporating an electron spin polarization which varies with pump wavelength into the penetration depth model of OPNMR signal, we are able to model features in both III-V semiconductors. The agreement between the OPNMR data and the corresponding model demonstrates that fluctuations in the OPNMR intensity have particular sensitivity to light hole-to-conduction band transitions in bulk

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systems. We provide detailed plots of the theoretical predictions for optical pumping transition probabilities with circularly-polarized light for both helicities of light, broken down into illustrative plots of optical magnetoabsorption and spin polarization, shown separately for heavy-hole and light-hole transitions. These plots serve as an effective roadmap of transitions, which are helpful to other researchers investigating optical pumping effects.

Keywords: Optically-pumped NMR (OPNMR), electron polarization, optical pumping, GaAs, InP, ^{69}Ga NMR, ^{31}P NMR, semiconductor

1. Introduction

In GaAs, InP, CdTe, and other *direct-gap* III-V and II-VI semiconductors, optical excitation by circularly polarized light at photon energies above the bandgap energy (E_g) results in a net polarization of electrons in the conduc-
5 tion band of the material [1]. Spin-polarized electrons can become trapped at “optically relevant defects” (ORDs) [2] where they are able to strongly couple with nearby nuclear spins which can be observed via NMR. While OPNMR has been demonstrated in indirect-gap semiconductors such as Si [3], excitation must occur with the assistance of a phonon to populate the band edge states.

10 Dynamic polarization of nuclei by means of coupling to optically oriented electron spins was first demonstrated by Lampel in 1968 [3]. Since then, numerous investigations in II-VI [4, 5], III-V [6–16], and Group IV [17] semiconductors have been conducted with the primary objective of creating and detecting nuclear spin orientation. Under the broad definition of “optically pumped NMR”
15 (OPNMR) or “laser-enhanced NMR,” many investigations have been done that study the dependence of nuclear spin polarization on a number of variables, including laser wavelength and polarization [18–20], sample temperature [12], and magnetic field strength [9, 11, 21]. Applications of this research on the field of spin-based electronic devices (or spintronics) have been of interest due to the
20 potential for manipulation of long-lived nuclear spin states [22–26]. In order to fully realize these applications, it is of paramount importance to understand

the origin and dependence of the nuclear polarization on various experimental parameters.

The dependence of the OPNMR signal from semiconductors with respect to
 25 photon energy and polarization of the incident laser light has been an ongoing
 area of investigation in the field [5–9, 11–14]. In past work, the effects of photon-
 energy-dependent optical absorption, $\alpha(E_{\text{ph}})$, were used to scale the occupation
 probability, Γ , of the ORDs, a quantity originally introduced by Paget to model
 a fast spin exchange between free electrons and localized electrons coupled to
 30 the nuclei [27]. In a magnetic field, the absorption coefficient is modulated,
 leading to the fine structure above the bandedge due to the formation of Lan-
 dau levels [19]. The modulation is also reflected in the OPNMR signals, and it
 has been demonstrated that the phase-sensitive nature of radio-frequency (RF)
 NMR detection is sensitive to the population *difference* between spin-up and
 35 spin-down conduction electron states which we modeled, simply, for an ideal-
 ized example at the near-surface of GaAs [7, 21, 28]. These states are evident in
 conventional optical magnetoabsorption measurements, but are observed (opti-
 cally) as the sum of (rather than the difference between) these populations [28].
 Consequently, our earlier efforts scaling $\langle S_z \rangle$ by $\alpha(E_{\text{ph}})$ can be further improved
 40 upon. It is a well-known phenomenon that the OPNMR resonances obtained
 with σ^+ and σ^- light are generally unequal in intensity for a given excitation
 energy. The physical origin of this NMR signal intensity difference and its de-
 pendence on light helicity can be calculated using a *revised* expression for $\langle S_z \rangle$,
 the subject of the work reported here.

45 In the present study, we have simulated the OPNMR signal dependence on
 the photon energy and helicity of the optical pumping source for both helici-
 ties of light, using calculations of $S_{\text{opt}}(E_{\text{ph}})$ in the expression for $\langle S_z \rangle$ (see Eq.
 2). We will extend our previous “penetration depth” model of the OPNMR
 data which we used previously to address subgap irradiation and the resulting
 50 asymmetry between OPNMR signals with σ^+ and σ^- light by using $\alpha(E_{\text{ph}})$ as
 a means for scaling Γ . This new expression for $\langle S_z \rangle$ addresses the effects of
 magnetoabsorption arising from a spin-split bandstructure to explain the po-

sitions of maxima and minima of ^{69}Ga OPNMR signals in GaAs with respect to the optical irradiation photon energy and helicity, as demonstrated in Ramaswamy, *et al.* (which did not account for the effects of nuclear polarization away from the near surface). Here, we now propose to replace the constant ± 0.25 term for the optically generated form of $\langle S_z \rangle$ with a more physically relevant variable $S_{\text{opt}}(E_{\text{ph}})$, and we demonstrate that the model can predict features in both GaAs and InP, including penetration depth effects from optical absorption, making $\langle I_z \rangle$ both depth- and photon energy- dependent. While previous models have assumed a simple model of constant polarization for photoexcited electrons (and hence $\langle S_z \rangle$), we show that it is more physically meaningful to introduce a variable photogenerated electron polarization as a function of excitation energy, E_{ph} , to provide a match with experimental data.

2. Experimental Data

Samples were studied experimentally by OPNMR through well established procedures and two prior publications provided the data used here – see Ref. [28] for GaAs and Ref. [10] for InP. OPNMR data were collected on semi-insulating GaAs (si-GaAs) obtained from ITME, Warszawa, Poland (sample characteristics: growth direction [100], thickness 400 μm , mobility 5630 $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$). We also model the OPNMR data from Michal and Tycko [10] on an Fe-doped semi-insulating InP bulk single crystal wafer obtained from Showa Denko (lot 60706) (sample characteristics: growth direction [100], thickness 348 μm).

3. Results and Discussion

3.1. Optical Polarization

The quantity $\langle S_z \rangle$ is the projection of the average electron spin on the z -axis. It depends upon two terms. The first results from the optically polarized electron spins (at steady-state optical pumping), S_{opt} . The second term arises from the *spin-relaxation* of the conduction electrons, S_0 [29].

80 An expression for the optically induced electron spin polarization is readily obtained at the band edge (where $\mathbf{k} = 0$). Using the wavefunctions provided in the Supplementary Materials (Eq. 4), we readily find that the ratio of transition probabilities from the heavy-hole and light-hole states is 3:1 for circularly polarized light. Since, for a given circular polarization of light, the light-hole
85 transitions produce electrons with the *opposite* spin polarization as the heavy-hole transitions, the expected instantaneous polarization in the conduction band would be:

$$\mathcal{P}_{\text{opt}} = \frac{\pm(3-1)}{3+1} = \pm 0.5. \quad (1)$$

One might think that away from (but *near*) the band edge, and hence $\mathbf{k} \neq 0$, the optical polarization would be approximately constant and still equal to ± 0.5 .
90 This is not the case, and there are many possible effects that must be taken into account which will be described below. The net result is that the optical polarization is *a varying function of the energy above the band gap* and not a constant. It depends critically on the material under study.

The details of optical polarization, especially the optical transition matrix
95 elements and the resulting electronic polarization, are described in the Supplementary Materials.

The total expectation value for $\langle S_z \rangle$ is the sum of the optically generated component, S_{opt} , and the thermal equilibrium component, S_0 , weighted according to the respective relaxation rates [30]:

$$\langle S_z \rangle = \frac{T_{1e}}{T_{1e} + \tau_e} S_{\text{opt}}(E_{\text{ph}}) + \frac{\tau_e}{T_{1e} + \tau_e} S_0, \quad (2)$$

100 where T_{1e} is the longitudinal spin relaxation time of the photoexcited electrons and τ_e is the electron-hole recombination time for conduction electrons. The first term in $\langle S_z \rangle$ is the spin orientation of the photogenerated carriers, and the second term is the contribution from carriers occupying the states at or just below the bottom of the conduction band which have spin-relaxed between the
105 conduction band states, but not yet relaxed back to the valence band.

Effects that influence the optical polarization fall into two main categories: 1) effects away from $\mathbf{k} = 0$ and 2) effects which break the degeneracy of the

heavy- and light-hole states even at $\mathbf{k} = 0$.

Some of the effects away from $\mathbf{k} = 0$, include:

110 **Density of States Effects.** Away from $\mathbf{k} = 0$, owing to differences in the effective masses of the heavy and light holes, the bands are no longer degenerate. As a result, for a given laser wavelength, transitions occur at different hole wave vectors. This is illustrated in Fig. 1. The number of $\mathbf{k}$ states within a given energy range depends upon the joint density
115 of states for the optical transition. Different masses in the valence bands lead to different joint density of states. In three dimensions, the density of states, $D(\epsilon)$, is proportional to the reduced mass (μ) to the 3/2 power, $D(\epsilon) \propto (\mu)^{3/2}$ leading to a factor of 2–3 enhancement for the heavy-hole transitions.

120 **Band Mixing away from $\mathbf{k} = 0$.** Away from $\mathbf{k} = 0$, the conduction and valence bands are no longer given by the simple $\mathbf{k} = 0$ expressions given in the Supplementary Materials (Eq. 4). Instead, $\mathbf{k} \cdot \mathbf{P}$ theory tells us that the wavefunctions are now linear combinations of the $\mathbf{k} = 0$ wavefunctions, and result in a mixing of the $\mathbf{k} = 0$ states [31]. The matrix elements for the various transitions will also change with $\mathbf{k}$, leading in turn
125 to a *photon-energy-dependent* optical polarization. As a result, oscillator strength will not be increased for transitions which were normally forbidden. This is illustrated in Tables 1 and 2 for the transition states which are labeled in Fig. 3.¹ The value for p corresponds to the Pidgeon-Brown manifold number and we show the mixing up to the $p = 4$ manifold. The
130 superscripts correspond the Landau level number n (*i.e.*, the harmonic oscillator state). Note that as the degree of mixing increases, the transition probability splits between the two transitions, leading to a lower intensity for each individual transition (most prominent for the peaks marked (C,

¹A full list of wavefunctions for the first six manifolds can be found in Table 1 in the Supplementary Materials.

Figure 1: Transitions away from $\mathbf{k} = 0$. Differences in effective masses between the light and heavy holes means that for a given photon energy, there will be a different number of $\mathbf{k}$ -state transitions that are allowed. The strength of the transitions will depend on the *joint density of states* for the transition. In three dimensions, this is proportional to $\mu^{3/2}$ where μ is the reduced mass, $1/\mu = 1/m_e + 1/m_h$.

135 D) and (E, F) in Fig. 3). It is also important to note that, though the
bands are mixed, the standard selection rules still apply (*i.e.*, there will
be no $|\text{HH}\uparrow\rangle$ transitions under σ^+ , etc.). The lowest Landau levels are
pure states, but higher Landau levels are strongly mixed which signifi-
cantly changes the strength of the transition. This results in an optical
140 polarization that is strongly energy dependent.

Effects which split the degeneracy of the light and heavy hole even at $\mathbf{k} = 0$
include:

Magnetic Fields. Magnetic fields can split not only the degeneracy between
light and heavy holes, but also the degeneracy between the $\pm m_J$ states
145 within either the heavy-hole or the light-hole bands. As a result, we ex-
pect that the conduction-band spin polarization will become highly energy
dependent in the presence of a strong magnetic field. The change in the
energy levels of GaAs due to these effects are calculated by diagonaliz-
ing an 8×8 $\mathbf{k} \cdot \mathbf{P}$ effective mass Hamiltonian based on the Pidgeon-
Brown model [32, 33]. The model includes conduction electrons, heavy-,
150 light-, and split-off holes. This model has been described in detail pre-
viously [34, 35], and has been used to accurately model ultrahigh-field
cyclotron resonance [34, 36, 37].

Quantum Confinement. The effects of quantum confinement can split the
155 degeneracy of the heavy and light holes even at $\mathbf{k} = 0$ resulting in a
change in the conduction band spin-polarization.

Strain. Strain at an interface, such as between a quantum well and the barrier
or even between a sample and the substrate, can also split the degener-
acy of the heavy and light holes resulting in a strong change in the spin
160 polarization.

3.2. OPNMR of GaAs

In Fig. 2, the OPNMR data have been plotted as a function of photon
energy used for optical pumping of si-GaAs (data adapted from Ref. [28]).

Manifold	Label	Start (p, ν)	End (p, ν)	Mixing of start state ($ \text{LH} \downarrow\rangle, \text{HH} \uparrow\rangle$)	
$p = 0$	A	4 (0, 3)	11 (1, 6)	100.0% $ \text{LH}^0 \downarrow\rangle$	–
$p = 1$	B	9 (1, 4)	19 (2, 7)	99.9% $ \text{LH}^1 \downarrow\rangle$	–
$p = 2$	C	18 (2, 6)	27 (3, 7)	30.2% $ \text{LH}^2 \downarrow\rangle$	69.8% $ \text{HH}^0 \uparrow\rangle$
	D	16 (2, 4)	27 (3, 7)	69.6% $ \text{LH}^2 \downarrow\rangle$	29.9% $ \text{HH}^0 \uparrow\rangle$
$p = 3$	E	26 (3, 6)	35 (4, 7)	46.3% $ \text{LH}^3 \downarrow\rangle$	52.7% $ \text{HH}^1 \uparrow\rangle$
	F	24 (3, 4)	35 (4, 7)	53.0% $ \text{LH}^3 \downarrow\rangle$	47.0% $ \text{HH}^1 \uparrow\rangle$

Table 1: Band mixing showing the dominant $|\text{HH} \downarrow\rangle$ and the $|\text{LH} \uparrow\rangle$ states for the first few σ^+ transitions in bulk GaAs for a field of $B_0 = 4.7$ T. The numbers indicate the percentage of the $\mathbf{k} = 0$ wavefunctions in each state. Here p is the Pidgeon-Brown manifold number and superscripts in the states refer to the Landau level number, n . The ID number identifies the state in Table 1 in the Supplementary Materials. While the lowest Landau levels are almost pure states, higher Landau levels are heavily mixed, substantially changing the strengths of the transitions. The net result is that the optical polarization becomes strongly energy dependent.

Manifold	Label	Start (p, ν)	End (p, ν)	Mixing of start state ($ \text{LH} \uparrow\rangle, \text{HH} \downarrow\rangle$)	
$p = 0$	A	5 (0, 4)	10 (1, 5)	99.7% $ \text{LH}^0 \uparrow\rangle$	0.3% $ \text{HH}^2 \downarrow\rangle$
$p = 2$	B	17 (2, 5)	12 (1, 7)	85.7% $ \text{LH}^1 \uparrow\rangle$	14.3% $ \text{HH}^3 \downarrow\rangle$
$p = 3$	C	25 (3, 5)	20 (2, 8)	82.6% $ \text{LH}^2 \uparrow\rangle$	17.4% $ \text{HH}^4 \downarrow\rangle$
$p = 4$	D	33 (4, 5)	28 (3, 8)	80.5% $ \text{LH}^3 \uparrow\rangle$	19.5% $ \text{HH}^5 \downarrow\rangle$

Table 2: The same data as in Table 1, but for σ^- transitions.

Figure 2: Experimental ^{69}Ga OPNMR signal intensities from si-GaAs (circles: open, σ^- irradiation and filled, σ^+) are plotted as a function of the photon energy used for optical pumping. The lines are the simulations of the OPNMR data using the revised expression for $\langle S_z \rangle$ in Eq. (4), the dashed line for σ^- and solid line, σ^+ . The following light hole-to-conduction band Landau level transitions are labeled: $\text{LH}^0\text{-CB}^0$ (A), $\text{LH}^1\text{-CB}^1$ (B), $\text{LH}^2\text{-CB}^2$ (C), $\text{LH}^3\text{-CB}^3$ (D), $\text{LH}^4\text{-CB}^4$ (E), $\text{LH}^5\text{-CB}^5$ (F).

Each experimental data point (shown by symbols) represents the integrated
 165 area of the recorded ^{69}Ga OPNMR signal at 4.7 T. The open circles depict
 the absorptively-phased data recorded with σ^- irradiation, and the filled circles
 show the emissively-phased data recorded with σ^+ irradiation, similar to those
 described previously [28]. Included in the figure is the simulation of the photon
 energy dependence based on a model (detailed below) incorporating a redefined
 170 $\langle S_z \rangle$ for these phenomena (shown as a dashed line for σ^- irradiation and a solid
 line for σ^+ irradiation).

Landau levels are known to modulate the absorption coefficient observed in
 magnetoabsorption experiments on GaAs and other semiconductors. In a similar
 manner, the OPNMR signal is strongly affected by the splitting of the bands
 175 into Landau levels, and fine structure is observed as a function of photon energy,
 as expected [19, 28]. However, as we will discuss, optical magnetoabsorption
 provides insights regarding energies, while OPNMR is distinctly sensitive to
 light hole(LH)–to–conduction band (CB) transitions.

There is asymmetry in the ^{69}Ga OPNMR signal intensity with respect to
 180 the helicity of light at a given photon energy. The emissively-phased OP-
 NMR signals (from σ^+ irradiation) are generally larger than the corresponding
 absorptively-phased OPNMR signals (from σ^- irradiation). Similar observa-
 tions have been made via OPNMR in the past [6, 7, 9, 12, 13, 38], and a
 model for the below-gap optical-pumping asymmetries arising from the thermal
 185 contributions of S_0 to $\langle S_z \rangle$ was proposed in a previous publication [18]. The
 asymmetry in the signal intensity with respect to the helicity of light is also
 captured in our simulations, but it requires a detailed examination of the pre-
 dicted value for $\langle S_z \rangle$ at each photon energy (ultimately leading to nuclear spin
 polarization, which is the measured quantity).

190 While below-gap ($E_{\text{ph}} < E_g$) irradiation could be addressed by the previously-
 used expression for $\langle S_z \rangle$,

$$\langle S_z \rangle_{\sigma^\mp} = \frac{T_{1e}}{T_{1e} + \tau_e} \cdot (\pm 0.25) + \frac{\tau_e}{T_{1e} + \tau_e} S_0 \quad (3)$$

(where the fixed value of ± 0.25 is present in lieu of the newly-introduced S_{opt})

term), the data shown in Fig. 2 with excitation energy in excess of E_g are not well represented by this expression with a constant (fixed) value for S_{opt} (discussed below, and depicted in Fig. 4).

To further refine the model, we have adopted a calculated optical absorption coefficient $\alpha(E_{\text{ph}}, B_0)$ generated by including the spin-split band structure for GaAs in the presence of a magnetic field. We incorporate this quantity into the optically-generated electron polarization, $S_{\text{opt}}(E_{\text{ph}})$, calculated from a model of heavy-hole (HH) and light-hole (LH) transition probabilities between Landau levels in the valence and conduction bands. In this model, electron polarization is a variable quantity dependent on the photon energy.

Results, using known band parameters for GaAs [39], are displayed for the spin-split valence and conduction bands at 4.7 T in Fig. 3. The absorption spectrum (Fig. 3, solid purple line) is the *sum* of the light-hole and heavy-hole transitions shown on the bottom as dashed blue and dotted red lines. The absorption spectrum is expressed as the sum of the light-hole and heavy-hole transitions since the absorption of an incident photon does not depend on whether the transition originated from the light or heavy hole – the spin orientation of the CB state is not conventionally recorded in optical magnetoabsorption. The *difference* between light-hole and heavy-hole transitions (shown as the dot-dashed orange line) is relevant to OPNMR because the positive/negative phase arising from the population difference between $|\text{CB}\uparrow\rangle$ and $|\text{CB}\downarrow\rangle$ is shown in this curve and can be used to determine the polarization of the electrons upon excitation at a given E_{ph} . The steady-state electron polarization can then be calculated using Eq. (2) with the optically-generated electron polarization as $S_{\text{opt}}(E_{\text{ph}})$.

4. Simulations of OPNMR Signals

As we have demonstrated previously in a model to address polarization in a near-surface layer of GaAs, OPNMR signals arise from nuclear polarization, $\langle I_z \rangle$ [28]. Assuming an initial condition of saturation for the nuclear spins, the average z -component of nuclear spin, $\langle I_z \rangle$, evolves under optical pumping time,

(a) Calculated transition probabilities for absorption of σ^- light (b) Calculated transition probabilities for absorption of σ^+ light

Figure 3: Calculated transition probabilities for a pure GaAs crystal above E_g under (a) σ^- and (b) σ^+ irradiation. The solid curve (purple) shows the sum of LH and HH contributions, the physical measurement of which is optical magnetoabsorption. The dotted (red) curves show the LH transitions while the dashed (blue) curves show the HH transitions. The most informative curve is the depiction of the *difference* “spectrum” between the HH and LH absorptions shown by the dot-dashed curve (orange), where the light-hole transitions subtract from the upper curve, causing regions where these two diverge, making them distinctly visible. (marked with vertical bars). Further description of the states assigned to these transitions are given in Tables 1 and 2. Features in this difference spectrum coincide with experimental OPNMR features. (Color online.)

τ_L , according to Eq. (4) [21],

$$\begin{aligned} \frac{\partial \langle I_z \rangle}{\partial \tau_L} = & D \nabla^2 \langle I_z \rangle - \frac{1}{T_1^{II}} \left[\langle I_z \rangle - I_0 \right. \\ & \left. - \frac{I(I+1)}{S(S+1)} (\langle S_z \rangle - S_0) \right] \\ & - \frac{\langle I_z \rangle - I_0}{T_{1n}}, \end{aligned} \quad (4)$$

where D is the isotropic nuclear spin diffusion coefficient, T_1^{II} is the electron-nuclear cross-relaxation time [40], and I_0 is the thermal equilibrium nuclear polarization which is typically on the order of 10^{-4} at these conditions [41].
 225 Under optical pumping conditions, $\langle S_z \rangle - S_0 \gg I_0$ and $T_{1n}^{-1} \approx 0$.

The first term on the right-hand side of Eq. (4) accounts for the diffusion of nuclear polarization away from the ORD, and the second term accounts for the buildup of nuclear polarization due to the Fermi-contact interaction [42]. It
 230 is worthwhile to note that optical pumping in InP has been found to generate dipolar order, populating a coupled nuclear spin system (manifested by ^{31}P lineshapes)[10, 43]. In this work, the ^{31}P data appears to be modeled well using a Fermi-contact hyperfine interaction, as the data were not from such distorted lineshapes. The relaxation rate in Eq. (4) is given by [2, 18],

$$\begin{aligned} \frac{1}{T_1^{II}(r, z, E_{\text{ph}})} \approx & \left[\frac{-8\pi}{3} \frac{\mu_0}{4\pi} g_0 \mu_B \gamma_\delta d_\delta \frac{v_0}{\pi a_B^3} \right]^2 \\ & \times \frac{2\tau_c \cdot \Gamma(z, E_{\text{ph}})}{1 + (\omega_I - \omega_S)^2 \tau_c^2} \cdot \exp\left(\frac{-4r}{a_B}\right) \end{aligned} \quad (5)$$

235 where μ_0 is the permeability of free space; g_0 is the free-electron g -factor; μ_B is the Bohr magneton; γ_δ is the nuclear isotope gyromagnetic ratio ($6.4323 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ for ^{69}Ga and $10.841 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ for ^{31}P); d_δ is the electronic density at the nuclear isotope, δ , ($d_{^{69}\text{Ga}} = 5.8 \times 10^{25} \text{ cm}^{-3}$ in GaAs [2] and $d_{^{31}\text{P}} = 3.26 \times 10^{25} \text{ cm}^{-3}$ in InP [44]); v_0 is the volume of the GaAs or InP unit cell;
 240 a_B is the Bohr radius for a localized electron in GaAs or InP; $\Gamma(z, E_{\text{ph}})$ is the probability of occupation of an ORD, where z is the depth from the surface of the sample; ω_I and ω_S are the nuclear and electronic Larmor frequencies, respectively; and τ_c is the electron-nuclear correlation time [40]. The quantity in

brackets in Eq. (5) represents the hyperfine coupling constant for the isotope δ .

245 From the final term in Eq. (5), it is evident that the coupling is much stronger for those nuclei within the Bohr radius of an occupied ORD (10 nm in GaAs [40] and 8.3 nm in InP [45]).

For the situation where spin diffusion is ignored, *i.e.*, $D = 0$, the following analytic solution can be obtained for Eq. (4) [21]:

$$\begin{aligned} \langle I_z(r, z, E_{\text{ph}}) \rangle &= \frac{I(I+1)}{S(S+1)} (\langle S_z(E_{\text{ph}}) \rangle - S_0) \\ &\times \left[1 - \exp\left(\frac{-\tau_L}{T_1^{II}(r, z, E_{\text{ph}})}\right) \right]. \end{aligned} \quad (6)$$

250 Equation (4) provides us a direct estimate of average nuclear polarization, $\langle I_z \rangle$. The fixed parameters used in the simulation are $B_0 = 4.7$ T, $T = 6.0$ K and $P_{\text{las}} = 2$ W cm⁻². The recombination time, τ_e , was set to ≈ 10 ns [23] and the ratio τ_e/T_{1e} was allowed to vary between 1.0 to 10.0 [46]. The final value used for the simulation was $\tau_e/T_{1e} = 2.0$, corresponding to the best intensity match to the experimental data. The correlation time, $\tau_c \approx 15 \times 10^{-12}$ s, was allowed to vary by factors of 10 [21, 40]. As demonstrated previously for subgap irradiation, we include the calculated energy-dependent optical absorption coefficient of the material, $\alpha(E_{\text{ph}}, B_0)$, to predict fluctuations in Γ as a function of E_{ph} and B_0 as well providing a method to model the decay of laser intensity (and therefore Γ) as the laser penetrates into the sample [18].

260 Equation (6) can be considered valid for short irradiation times, where the diffusion distance is small. A diffusion distance, d , can be approximated as [11]:

$$d = \sqrt{D \cdot \tau_L}. \quad (7)$$

The spin diffusion coefficient for ⁶⁹Ga in GaAs and ³¹P in InP is $D \approx 30$ nm² s⁻¹ [11, 265 40], giving a diffusion distance of $d \approx 60$ nm with 120 s of optical pumping (τ_L). Using this solution, artificial limitations can appear on the signal growth at long values of τ_L as nuclei within the hyperfine coupling region ($\sim a_B$) of the electron become completely polarized, while nuclei outside this region see no effect (since spin diffusion is treated as absent). This assumption depends on

270 the magnitude of the hyperfine coupling constant. For the coupling values used
in our simulations, an irradiation time of 120 s remains below this saturation
regime. In other words, with no diffusion, maximum polarization will be reached
in an artificially short time.

The OPNMR signal intensity is proportional to $\langle I_z(r, z, E_{\text{ph}}) \rangle$. The relative
275 OPNMR signal (Ξ) is calculated by the following:

$$\Xi(E_{\text{ph}}) \propto \iint \gamma_{\delta} F_{\delta} n_s(r) \langle I_z(r, z, E_{\text{ph}}) \rangle dr dz, \quad (8)$$

where F_{δ} is the isotopic abundance (0.604 for ^{69}Ga and 1.00 for ^{31}P isotopes),
 $n_s(r)$ is the number of nuclei contained in a shell of radius r from the ORD,
and z is the depth from the irradiated surface of the sample.

In Fig. 4, we compare the two models of OPNMR phenomena developed thus
280 far with the experimental data overlaid. A better match between experiment
and the model of OPNMR phenomena is found when $S_{\text{opt}}(E_{\text{ph}})$ is calculated
and permitted to vary with respect to E_{ph} . The red lines depict this new
model using both calculated $S_{\text{opt}}(E_{\text{ph}})$ and magnetoabsorption. In contrast,
the earlier OPNMR model we developed [28] used the *fixed* ± 0.25 factor in
285 place of $S_{\text{opt}}(E_{\text{ph}})$ and experimental magnetoabsorption data. These results
demonstrate that the electron spin polarization has an important contribution
from the photon energy-dependent (E_{ph}) term.

Across much of the range, $\mathcal{P}_{\text{opt}}$ is *close* to ± 0.5 . However, where it devi-
ates strongly are regions with “peaks” and “valleys”. We find good agreement
290 between model and experiment at these sharp features, notably in the agree-
ment between sharp minima in the OP signal profile and regions of light-hole
absorption (regions where $\mathcal{P}_{\text{opt}} \rightarrow 0$). Referring to Fig. 3, features in the “dif-
ference” spectrum that are coincident with light-hole transitions are the most
easily resolved.

295 This research modifies the prior work [18, 21, 47] by incorporating the pho-
ton energy dependence of the optically-induced electron spin polarization into
the established model for the OPNMR signal intensity. Comparing our mea-
surements with the theoretical predictions of the spin-dependent Landau level

Figure 4: (Color available online.) ^{69}Ga OPNMR photon energy dependence at 4.7 T for σ^- (top) and σ^+ (bottom) irradiation. Symbols are experimental data, and lines correspond to models of the OPNMR phenomena. Shown in red is the model using calculated $S_{\text{opt}}(E_{\text{ph}})$ and calculated magnetoabsorption (long-dash and solid line), while results modeled using constant $S_{\text{opt}} (\pm 0.25)$ and experimental magnetoabsorption [19] are depicted in black (short-dash and dot-dash curves). The following light hole-to-conduction band Landau level transitions are labeled: LH⁰-CB⁰ (A), LH¹-CB¹ (B), LH²-CB² (C), LH³-CB³ (D), LH⁴-CB⁴ (E), LH⁵-CB⁵ (F).

Parameter	Units	Value	
		GaAs (^{69}Ga)	InP (^{31}P)
E_g	eV	1.519 [48]	1.424 [49]
g_{eff}	—	−0.44 [29]	+1.20 [50]
v_0	nm^3	0.1806	0.3444
a_B	nm	9.8 [51]	8.3 [51]
τ_e/T_{1e}	—	2.0	3.5
d_δ	cm^{-3}	5.8×10^{25} [2]	3.26×10^{25} [44]
τ_c	s	15×10^{-12} [40]	2.9×10^{-12} [9]

Table 3: Summary of simulation parameters used for GaAs and InP. Values of InP were compiled from various literature references (see text for details).

transitions, it can be readily seen that electron spin polarization involving the
300 light hole-to-conduction band transitions deviate the most from the previous
assumption of constant 50 % polarization at the band edge.

5. Application to InP

We seek to demonstrate the generality of this model for OPNMR phenomena
by applying it to other direct-gap semiconductors. This application to other
305 semiconductors requires the modification of only a few input parameters (Table
3). One such demonstration is to a ^{31}P OPNMR profile recorded for σ^+ and σ^-
irradiation on a sample of InP:Fe by Michal and Tycko [10]. (InP is a direct-
gap semiconductor that is intrinsically n -type, but samples can be compensated
through the addition of iron.) Like GaAs, InP adopts a zinc-blende structure
310 and has a direct energy gap.

The experimental data were obtained with the following set of conditions:
 $B_0 = 9.39 \text{ T}$, $T = 8.0 \text{ K}$, $\tau_L = 60 \text{ s}$, and $P_{\text{laser}} = 4.6 \text{ W cm}^{-2}$. Figure 5 shows a
comparison between the experimental ^{31}P OPNMR data (blue circles) extracted
from Ref. [10] and the simulated signal (red lines). The parameters used for

315 the simulation are shown in Table 3. There is excellent agreement between
the experimental data and the prediction of “peaks” and “valleys” in the InP
OPNMR profile, with prominent dips due to the LH transitions.

In contrast to the simulation for GaAs, Eq. (2) for InP required the addition
of a vertical offset. This offset translates both curves downward by a fixed
320 amount in order to correctly simulate the σ^+ and σ^- OPNMR data. The offset
value was adjusted and applied uniformly to the OPNMR profile simulations
to capture the asymmetry between signal intensities for both helicities of light,
and a similar offset has been shown previously by Pietrass and coworkers arising
from carriers/doping in GaAs [7]. The value used in the final simulation was
325 -0.06 (not large when compared to the size of the term pertaining to S_0 , -0.34).

Further generalization of such offsets are worthwhile to study. Several quan-
tities in the expression for S_0 could account for such an offset. For example, a
modification of one of the following values that contribute to the thermal equi-
librium polarization ($\mathcal{P}_0$, see Supplementary Materials, Eq. 3) results in the
330 same change in $\langle S_z \rangle$ (and hence, $\langle I_z \rangle$ and Ξ):

$$\begin{aligned} g_{\text{eff}} = 1.20 & \implies g_{\text{eff}} = 1.75, \text{ or} \\ B_0 = 9.39 \text{ T} & \implies B_0 = 13.7 \text{ T}. \end{aligned}$$

Optical pumping experiments in InP samples have shown electron g -factors
which range from 1.26 (conduction electrons [52]) to ~ 2 (electrons bound to Fe
or P_{In} antisite [53]). Thus, a change in the g -factor could reflect a localization
335 of the electrons at one defect site versus another. On the other hand, a change
in B_0 could be attributed to the creation of internal fields in the sample. These
fields could be generated via large nuclear alignments which occur during optical
pumping, as suggested in optically-detected NMR experiments [2]. We also note,
fields on the order of several tesla have been observed in semiconductor materials
340 doped with magnetic ions [54]. The effects of such fields should be visible in
NMR lineshapes, but no lineshapes were reported in the InP work.

Figure 5: (Color available online.) ^{31}P OPNMR photon energy dependence at 9.4 T for σ^- (top) and σ^+ (bottom) irradiation. Symbols are experimental data, and lines correspond to models of the OPNMR phenomena. Shown in red is the model using calculated $S_{\text{opt}}(E_{\text{ph}})$. The following light hole-to-conduction band Landau level transitions are labeled: $\text{LH}^0\text{-CB}^0$ (A), $\text{LH}^1\text{-CB}^1$ (B), $\text{LH}^2\text{-CB}^2$ (C), $\text{LH}^3\text{-CB}^3$ (D).

6. Conclusion

We have incorporated a photon-energy dependent S_{opt} term in the expression for $\langle S_z \rangle$ to simulate the intensity dependence of the OPNMR signal as a function of laser photon energy used for optical pumping in excess of E_g , and we have
345 applied this model to a new material, InP. Whereas in prior studies, the fixed values of optically generated electronic spin polarization of ± 0.25 captured many of the features, here we show a better match to experiments by using the photon energy dependent S_{opt} in models of OPNMR phenomena. In addition, with
350 the change of only a few adjustable parameters, and using referenced values for constants and physical measurements, excellent agreement is found for OPNMR profiles for both ^{69}Ga in GaAs and ^{31}P in InP:Fe.

Using S_{opt} is a more accurate representation of the conditions that result from optical pumping. In prior work, where we used a fixed value for electron po-
355 larization, the sub-band gap behavior is depicted well but the transitions above the band gap were not well-modeled. By using the *difference* between light-hole and heavy-hole transitions, as opposed to their sum, the above gap transitions are matched better by the simulations. The electron polarization is reflected in the difference in absorption between light-hole and heavy-hole transitions,
360 rather than their conventional sum (as the optical absorption spectrum), owing to the phase imparted by these different states. Excellent agreement on the photon energies where OPNMR peaks and valleys occur for both GaAs and InP lend credence to the model of opto-electronic behavior. The “offset” reflecting the average position of σ^+ and σ^- pairs of OPNMR data offers intriguing av-
365 enues of study, since the origin is still not definitively understood. Local nuclear fields, occupancy of ORD’s with different g -factors, and the effect of carriers (n - and p -type) are all areas to be explored.

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