Trends

Nuclear hyperpolarization in solids and the prospects for nuclear spintronics

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Abstract

Nuclear hyperpolarization can be achieved in a number of ways. This article focuses on the use of coupling of nuclei to (nearly) pure quantum states, with particular emphasis on those states obtained by optical excitation in bulk semiconductors. I seek an answer to this question: “What is to prevent the design and analysis of nuclear spintronics devices that use the extremely long-lived hyperpolarized nuclear spin states, and their weak couplings to each other, to affect computation, memory, or informational technology schemes?” The answer, I argue, is in part because there remains a lack of fundamental understanding of how to generate and control nuclear polarization with schemes other than with rf coils.

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1. Introduction

Nuclear magnetic resonance (NMR) spectroscopy and magnetic resonance imaging (MRI) have impacted virtually every field of science and engineering. Magnetic resonance methods enjoy a plethora of applications, ranging from medicine and biological sciences, physical sciences and engineering, to industrial sensing and process control. A particularly limiting feature of these methods, however, is the miniscule magnitude of the expectation value for bulk nuclear spin orientation. The resulting lack of sensitivity has largely confined the vast majority of NMR and MRI methods to bulk systems enclosed by enormous magnets.

I am interested in the expectation value for bulk nuclear spin orientation (a.k.a. polarization, or “signal”) for two reasons. First, analytical NMR spectroscopy is not routinely available at the place and time where it is needed most. The low sensitivity of NMR precludes its use in combinatorial synthesis and screening, chemical and pathogen detection, portable NMR and MRI for “in-field” use as chemical sensors or emergency medical diagnosis, localized in vivo spectroscopic studies of targeted tissues, and with force and other nanoscale microscopies. Secondly, nuclear spin polarization is a limiting factor for emerging devices that use either electron or nuclear spins as active components in computational devices. For example, considerable excitement...
was generated when manipulations of the couplings between nuclear spins in small molecules provided for algorithms in a quantum computer [1]. The error algorithms that must be invoked to deal with thermal polarization in such schemes, however, are prohibitive. These concerns would be addressed with routinely available hyperpolarization of nuclear spins.

I am also interested in non-inductive control of NMR polarization once hyperpolarization is generated. Spintronics [2] is an emerging field whereby designers employ the systematic control of electron spin angular momentum for the development of novel computational and information-storage devices. Spintronics is also providing new discoveries in fundamental science and puzzling phenomenology that challenge explanations. Of principal interest in this emerging field is the control and manipulation of electron spin angular momentum via a combination of materials design and the creation of devices manipulating electron spin angular momentum via means other than traditional Zeeman-resonant methods. In these endeavors light excitation and application of electric fields (or currents) are common. Why cannot these same strategies be employed to control nuclear spin polarization? Indeed, what is to prevent the design and analysis of nuclear spintronics devices that use the extremely long-lived hyperpolarized nuclear spin states, and their weak couplings to each other, to affect computation, memory, or informational technology schemes? Nuclear spintronics is challenging in part because there remains a lack of fundamental understanding of how to generate and control nuclear polarization with schemes other than with rf coils.

Finally, spintronics device design is challenged by the (unwanted) decoherence of electron spins owing to weak coupling to the nuclear spins; long electron spin decoherence times are desirable in spintronics so that many quantum operations (in excess of 10,000) can be performed before the quantum coherence decays. In order to address the decoherence problem researchers envision using either nuclear control schemes for decoupling or diluting nuclei from each other [3,4] and from electrons spins [5], or by using triplet states formed by pairs of electrons [6], and by constructing materials platforms for such devices, including the NV- center in diamond [7] and quantum dots and rods [8]. In these applications the weak fluctuations and couplings of electrons to the nuclear polarization limit the quantum mechanical lifetimes of coherent electron spins, potentially precluding nano-scale device development. The development and control of nuclear hyperpolarization seems to be a prerequisite for control of the decoherence of electron spins.

The primary purpose of the Trends article is to broadly consider the generation and control of nuclear polarization in solids [9], then pose suggestions for future work. Several examples of hyperpolarization methods are already well-documented in the literature, and I will highlight those as briefly as possible. I focus more attention on the generation of hyperpolarization with optical pumping, and its subsequent control with electrical currents. Many of these strategies are only partly realized. Of particular importance is the electron–nuclear interaction in semiconductors, and the consequences this interaction has on the preparation of highly spin polarized nuclei. Spatial patterning of optically prepared nuclear hyperpolarization has already been realized in optically detected magnetic resonance, yet has not been demonstrated for induction detection in instruments that most of the SSNMR readers are accustomed to using. Electric control of bulk nuclear polarization is tantalizingly close.

2. An overview of hyperpolarization—how to get more signal

Consider the following quantitative example [10] of the limitations associated with Zeeman nuclear spin polarization. Conventional NMR begins with $M$ oriented along the z-axis with a magnitude proportional to the ensemble average expectation value of $I_z$. The value at thermal equilibrium is given by Boltzmann statistics:

$$\langle I_z \rangle_{eq} = \sum_n \frac{n!}{n!} \frac{e^{-n/kT}}{\sum_n e^{-n/kT}},$$

(1)

where $e_n$ and $I_{zn}$ are the $n$th eigenvalue of $H_z$ and $I_z$, respectively. For the Zeeman Hamiltonian, $e_n = -I_{zn} \Delta E_n$, thus

$$\langle I_z \rangle_{eq} = \sum_n \frac{n!}{n!} \frac{e^{-n/kT}}{\sum_n e^{-n/kT}} \frac{I_{zn} \Delta E_n}{kT} = \sum_n \frac{e^{n/kT} I_{zn} \Delta E_n}{\sum_n e^{n/kT}} I_{zn} \Delta E_n/kT.$$ (2)

For the case of $^{71}$Ga in semiconducting GaAs, a spin-3/2 nucleus, Eq. (2) becomes:

$$\langle I_z \rangle_{eq} = \frac{1}{2} \frac{\Delta E_n}{kT} + \frac{\Delta E_n}{kT}.$$ (3)

The behavior for $(\Delta E_n \ll kT)$ is captured in the Maclaurin Series for Eq. (3) in $\Delta E_n/kT$ taken to second order:

$$\langle I_z \rangle_{eq} = \frac{5 \Delta E_n}{4kT} + \frac{\Delta E_n}{kT}.$$ (4)

The temperature dependence of $\langle I_z \rangle_{eq}$ for $^{71}$Ga spins in a 9.4 T magnet is plotted in Fig. 1. One can see from this figure that the “high temperature approximation” is accurate above $mK$ temperatures. Therefore, at nearly all experimentally accessible sample temperatures, nuclear spin populations are considered to be in the high temperature limit.

The resulting nuclear spin polarizations at anything other than pathological temperatures is miniscule. For example, for $^{71}$Ga in a 9.4 T magnet at $T = 300 K$, $\langle I_z \rangle_{eq} = 2.43 \times 10^{-5}$, meaning that 61,500 $^{71}$Ga atoms would have the effective magnetization of a single atom oriented with $B_0$. Practically speaking, a sample typically requires at least $10^{16}$ nuclear spins in order to show a detectable NMR signal, and even then signal averaging for hours, if not days, is often required. As a result, dilute spin systems (e.g., surface atoms and atoms at defect sites) are usually inaccessible to solid state NMR. Substantial athermal alignment of nuclear spins would provide NMR enhancement factors on the order of $10^5$, and would therefore provide NMR with the sensitivity necessary to address the wide variety of problems discussed in the Introduction.

2.1. Nuclear refrigeration

Engineers are comfortable with the principles surrounding the refrigerator: energy is used to lower the entropy of a system by...
transferring heat against a thermal gradient. A generalized scheme for preparation of highly athermal nuclear polarization, then, would be a nuclear spin refrigeration system in which the nuclear spin temperature is lowered by rejecting heat into a higher temperature reservoir using an engine. Fig. 2 details this generalized scheme for hyperpolarization strategies. The engine for this refrigeration process is the unique symmetry of the para-H$_2$ molecule when it hydrogenates unsaturated bonds. The denouement of this elegant process is the (symmetric) chemical reaction of parahydrogen across double bonds whereupon the pure spin states of the hydrogen nuclei are preserved. The resulting signal enhancement for protons in the target molecule can be substantial, and there are practical polarization transfer schemes to less abundant nuclei such as $^{13}$C. Clinical imaging employs such schemes [14].

PHIP is just one example of an emerging class of methods that exploit the selection of vibrational or rotational states in the gas phase, which in turn provide pure nuclear spin states. Both HF and HCl molecules have been prepared recently in highly athermal nuclear spin states via laser excitation of specific vibrational and rotational lines [15,16].

The Haupt effect [17] is the third refrigeration scheme, and this method couples the nuclear spin system to the rotational eigenfunctions of the methyl group in the solid state. The A ($I = \frac{3}{2}$) and E ($I = \frac{1}{2}$) symmetry states defined by the proton triad in methyl groups form the basis for the refrigeration engine. Owing to the very slow exchange of population between these A and E states, a sudden jump in sample temperature leads to a highly athermal distribution of A and E populations. Cross-relaxation between A and E states is mediated by a simultaneous proton spin flip, thus forming the mechanism by which the refrigeration “engine” couples to the nuclear spin system. The net result is that highly athermal proton spin populations can result when monitoring proton signals after a temperature-jump of the sample from approximately 10 to 60 K [18]. As with PHIP, the Haupt approach has also been used to hyperpolarize rare nuclei [19] via suitable application of multiple resonance pulse schemes. It seems certain that further applications of this method will be forthcoming.

A fourth refrigeration scheme exploits dynamic nuclear polarization. “DNP” has a rich history, recently resuscitated by new strategies for implementation in imaging and medicine at high magnetic fields [20]. The principles underlying DNP have been documented in classic texts [21]. In brief, the large gyromagnetic ratio for electrons relative to nuclei (e.g. ~660 compared to protons) means that high field NMR instruments with appropriate isolated free radicals have a large thermal polarization of electrons that might cross relax with NMR-active nuclei. The trick is to facilitate most effectively this cross-relaxation. A large number of recent papers [22], as well as commercial equipment [23], describe methods for implementing this strategy for hyperpolarization of nuclei. Effective as the DNP strategy might be, it is ultimately limited to the thermal polarization of the electron spins. I will not address this important research endeavor in this article, other than evoke it for situations where electrons spins are prepared with athermal polarizations.

“Optical pumping” is another scheme for nuclear hyperpolarization and the primary focus for the remainder of this article. In brief, optical absorption selection rules in semiconductors, or selection rules within radiative and non-radiative decays following absorption, lead to electron spin states characterized by highly athermal polarizations. The fundamental mechanism by which nuclear spins are polarized in this process involves the Overhauser Effect, or cross-relaxation between nuclei and electrons. This process has been known since 1968 [24]. A recent example of this method of hyperpolarization can be found in studies of bulk
diamond imbibed with nitrogen-vacancy defects. These spin-1 defects may be prepared in a nearly pure quantum state via optical excitation coupled to a fortuitous arrangement of radiative and non-radiative decays. Dipolar couplings of weakly interacting, and highly athermally populated, NV- centers induces nuclear spin transitions, with a concomitant hyperpolarization of naturally abundant $^{13}$C nuclei in the diamond [25].

There are no doubt thousands of potential cases whereby electrochemical and/or photo-physical processes at defects, surfaces, or interfaces, lead to nearly pure quantum states; cross-relaxation schemes, either inherent or forced, can lead to nuclear hyperpolarization. We need to find more of these schemes; the literature suggests that any mechanism whereby the electron spin polarization becomes athermal might result in nuclear cross-relaxation with subsequent hyperpolarization of nuclear spins.

3. Manipulation of nuclear spin states—how to get more control with light and/or electrical current

3.1. Optical pumping

Optical pumping in compound semiconductors has been reviewed twice in the recent literature [26,27]. This process was originally modeled [28] using phenomenological rate equations which produced a useful equation that serves as a pedagogical and predictive tool for optically pumped NMR and related phenomena:

$$\langle I_{z} \rangle - \langle I_{o} \rangle_{eq} = \left( \frac{\omega_{0} - \omega_{2}}{\omega_{0} + 2\omega_{1} + \omega_{2}} \right) \left( \frac{I(I+1)}{3S(S+1)} \right) \langle I_{z} \rangle - \langle I_{o} \rangle_{eq},$$

(5)

where $\langle I_{z} \rangle$ is the ensemble-average expectation value of $\langle I_{z} \rangle$ for nuclei with spin $I$, $\langle I_{o} \rangle_{eq}$ is the thermal equilibrium value for $\langle I_{z} \rangle$ (similarly for electron spins $S$), and $\omega_{0}$, $\omega_{1}$, and $\omega_{2}$ are the rate constants for zero, two, and one-quantum transitions amongst the nuclear and electron Zeeman sublevels. In this expression the Overhauser effect is defined to be the changes in the NMR signal intensity, proportional to $\langle I_{z} \rangle$, upon perturbation of $\langle I_{z} \rangle$. The rate constants in Equation (5) are affected by the detailed nature of the electron–nuclear couplings (Fermi contact, dipolar, indirect), which in turn may also be affected by the experimental design [26]. The literature reports that this scheme for nuclear hyperpolarization can be realized by manipulating $\langle I_{z} \rangle$ via light modulation [26], application of fields [29], injection of electrons [30,31,32], EPR saturations [33], and other effects [34].

Optical pumping in the bulk semiconductors [9] (“OPNMR”) is rich in phenomenology, yet remains poor in atomistic understanding. This is best illustrated by consideration of what is known as the “OPNMR profile.” In these experiments the induction signal from a bulk semiconductor is monitored (usually near liquid helium temperatures) as a function of optical excitation frequency and light helicity. “Spectra,” or OPNMR profiles, represent the compilation of bulk NMR signal intensities on the ordinate and laser energy on the abscissa, as shown in Fig. 3 (taken from [10]). These spectra are parsed qualitatively into three regimes: “sub-gap,” “mid-gap,” and “super-gap” OPNMR profiles. In the case of GaAs at $\approx 5$ K, these regimes are less than 1.505 eV (sub-gap), 1.5–1.52 eV (mid-gap), and in excess of 1.52 eV (super-gap). These same features appear in the OPNMR profiles of all bulk compound semiconductors [26]. Quantitative models for some aspects of these regimes are described in the literature.

Taking Eq. (5) as the operating description for the OPNMR phenomenology, the peaks and valleys of OPNMR profiles are given by variations in $\langle I_{z} \rangle$, and thus all modeling efforts begin with this quantity. The simplest and most commonly invoked picture from which to understand $\langle I_{z} \rangle$ starts with optical absorption generating free electrons, which in turn bind to shallow donors. Rapid spin-exchange equalizes the steady-state electron spin polarizations of the free and donor-bound electron reservoirs [35]. The result is

$$\langle I_{z} \rangle = \langle I_{z} \rangle_{0} + \langle I_{z} \rangle_{eq} \frac{T_{1e}}{1 + T_{1e}},$$

(6)

where $\langle I_{z} \rangle_{0}$ is the initially excited electron polarization, $\langle I_{z} \rangle_{eq}$ is the equilibrium Zeeman electron polarization, and $T_{1e}$ is the spin–lattice time for the electrons governed by a single recombination time, $\tau$. Models for equation (6), therefore, begin with models for $\langle I_{z} \rangle_{0}$; this quantity, in turn, is understood from optical absorption coefficients within the bulk semiconductor. (There are many subtleties, however, in employing models that go from optical absorption to the quantity $\langle I_{z} \rangle_{0}$ [36].) All phenomenological models for the OPNMR process then, follow the same strategy: measure optical absorption, determine $\langle I_{z} \rangle_{0}$ and thus $\langle I_{z} \rangle$, then employ Eq. (5) to determine $\langle I_{z} \rangle$. A spin–diffusion transport model is then used to predict bulk measurements.

Elegant data [37,38] and a sophisticated model [39] have been presented for super-gap OPNMR profiles. The features of these profiles are well accounted for by variations in optical absorption due to the presence of Landau energy levels [40] for the initial and final photo-absorption states. Quantitative modeling of these data require magneto-optical absorption coefficients, with the resulting fits to data being splendidly sensitive to the near-gap electronic structure of the semiconductor.

OPNMR in this mid-gap regime is closely related to photoconductivity. In this situation, the optical absorption process was modeled [41] by specific consideration of electron recombination kinetics: a first-order (in photoelectron concentration) rate process whereby recombination occurs at defects, and a second-order process whereby electrons collide with each other to recombine. Both processes are known to be important for near-band-gap optical absorption. For a photon flux ($\phi$) decaying exponentially with the depth $x$ into the sample, $\phi = \phi_{0} e^{-x/\lambda}$, the generation rate of free electrons in a volume element is

$$k_{1} N_{n} n^{2} = -\frac{d\phi}{dz} = \frac{\phi_{0}}{\lambda} e^{-x/\lambda}.$$  

(7)

Here $N$ and $n$ are the concentrations of defect traps (assumed constant) and free electrons, respectively, and $k_{1}$ are the rate constants. In this way the generation of the electron spin reservoir $\langle I_{z} \rangle_{0}$ given in Eq. (6) is accounted for. This phenomenological model accounts well for both photoconductivity data and the “peak” in mid-gap OPNMR profile. The rate constants and defect concentrations can be measured or estimated from the literature.

The low energy regime of the OPNMR profile is poorly understood. Consider the GaAs optical pumping studies wherein
linearly polarized laser excitation frequency was varied and the resulting Ga NMR signal monitored \[42^*\]. Fig. 4 shows representative results, along with Eq. (5) for comparison. The observed bulk-averaged Ga polarization, proportional to \(\langle I_z \rangle\), changes sign as the laser frequency is decreased well below the band gap. This result is rationalized on the basis of the sign of the electron g-factor that determines \(\langle S_z \rangle\). Cross-relaxation from electrons in GaAs proceeds via the hyperfine contact interaction \[10\], and thus the \(\omega_2\) term in Eq. (5) is equal to zero. Since algebra determines that the first term on the right hand side of (5) is positive, then a sign change in \(\langle I_z \rangle\) as the laser wavelength decreases must be due to a sign change in \(\langle S_z \rangle\). Electrons localized at shallow donor sites are known to have positive g-factors, conduction elections are known to have negative g-factors. Thus sub-gap OPNMR profile is believed to emanate from nuclei proximate to localized electrons that are not undergoing rapid spin-exchange with conduction elections. It is worth noting that this rationalization is not substantiated by independent measurements.

The modeling process for the OPNMR profile is not complete until the local \(\langle I_z \rangle\) that results from cross-relaxation is allowed to transport throughout the remaining spins in the bulk by spin diffusion. This transport process has been modeled many times by various groups \[43–45,41^*\,36\], with the main difference between them being how the boundary conditions are satisfied for the governing generation-diffusion-loss equation:

\[
\frac{\partial \langle I_z \rangle}{\partial t} = D \nabla^2 \langle I_z \rangle + \frac{1}{T_{1\text{H}}} (I_z - \langle I_z \rangle) - \langle I_z \rangle/\tau_{1\text{L}},
\]

where \(I_z\) is the theoretical maximum nuclear polarization achievable through cross-relaxation, \(D\) is the nuclear spin diffusivity, \(T_{1\text{H}}\) is the (spatially dependent) hyperfine cross-relaxation time, and \(T_{1\text{L}}\) is the (spatially dependent) nuclear spin–lattice relaxation time by all other mechanisms. In this equation the Boltzmann nuclear polarization is neglected because typical experiments begin with saturation of the equilibrium signal. During this microscopic evolution, the bulk NMR signal grows in proportion to the total nuclear z-angular momentum \(\langle I_z \rangle\), found by integrating \(\langle I_z \rangle\) over all space.

I urge caution, however, in assuming that successful match of observation with phenomenological models means that analysis is finished and design of materials for hyperpolarization is underway. Practitioners of OPNMR face a dizzying array of non-idealities, dopant types, and surface cleaning are excellent examples of poorly controlled variables in historical studies of OPNMR profiles (see InP, for example \[46\]). With exception of the NV- center in diamond, the “molecular” identity of those defects responsible for the pumping process are unknown in all the bulk semiconductors.

### 3.2. Electrical control

Unusual NMR hyperpolarization effects due to the presence of electrical currents have been observed for decades. The effect of electron acceleration (“hot electrons”) on nuclear polarization under applied fields was demonstrated \[29,47\] via the application of dc electric fields in indium antimonide. More recently, two groups have published phenomenological results that show nuclear spin polarization is controlled by the application of electrical currents in GaAs \[48,31^*\]. Both recent papers show sign changes in \(^{71}\text{Ga}\) NMR signals with application of dc current. Although the experiments are different, they both attribute the sign change to the same effect: cross-relaxation occurs with electrons with a positive g-value located at a defect, yet upon application of the dc current, the defect electron spin exchanges with conduction electrons that have a negative g-value. These conduction elections may exhibit a polarization that is “hot” relative to the equilibrium Zeeman polarization in the experimental NMR instrument. The ability to invert nuclear spins with application of electric fields could be particularly useful as it provides a scheme for isolating only those NMR signals associated with the region under electric field control. One imagines preparing bulk inorganic semiconductors with micro-fabricated electric gates that are under control of the experimenter. With such a device spatial patterns of nuclear polarization could be generated and such patterns may be allowed to evolve in time for a variety of purposes. In addition to information storage and quantum computing, such spatial patterns could be used for multiplexing NMR on the semiconductor for enhanced sensitivity and selectivity.

The phenomenon associated with injected current in the presence of optical pumping in GaAs \[26\] is instructive as it portends both the opportunities and challenges in such electrical control schemes. The phenomenon \[31^*\] is summarized in Fig. 5 \[49\]. Upon pumping at 1.49 eV with linearly polarized light, an inversion in sign of the Ga NMR signal occurs when approximately 50 V per centimeter is applied to the sample (caution: at higher currents/voltages significant Ohmic heating of the sample may occur, obfuscating the effects of electron spin injection effects). There are several possible mechanisms for this effect.

A mechanism whereby a change in sign of the electronic g-factor for the electron spins coupled to the nuclei was suggested \[10,31^*\] in 2005, where the authors posited that application of voltage releases, through impact ionization, electrons with opposite g-factor \((g < 0)\) from the prevailing one at low voltage \((g > 0)\). This proposal was motivated by the fact that the observed non-Ohmic conductivity was consistent with impact ionization of defects over the voltage range that the NMR signal was inverted, shown in Fig. 5B (inset). However, while impact ionization is very likely going on at high voltage, it is not at all clear that at zero voltage the nuclear polarization originates from cross-relaxation with \(g > 0\) electrons. Large photoconductivities have been observed for photon energies \(E < 1.495\) eV at low voltage, so there are delocalized (free) charge carriers around even at voltages where there is no NMR signal inversion. Also, electron-DNP in the absence of optical pumping \[48\] was found to be highly dependent on which sample was employed: highly
insulating or highly doped samples showed no DNP effects. Those authors concluded that the relationship between transport properties and DNP effects are “not straightforward.” At the time of this writing the most compelling argument for the change in g-factor with the passage of electrical current comes from comparison with optical pumping studies cited above and shown in Fig. 4. This association is hardly a compelling case for a deep understanding of the relationship between electron transport of OPNMR profile.

4. Proposals for future work

There has been excellent progress in the preparation of highly polarized nuclear spins in semiconductors via the use of optical absorption processes. It has also been demonstrated that nuclear spin polarization can be further manipulated by the application of electrical currents. The design of nuclear spintronic devices, however, remains elusive because several fundamental studies that I believe are essential for device design have not yet been accomplished. In the sections below, I outline a few Ph.D. theses that could provide the fundamental understandings necessary to consider nuclear spintronics devices.

4.1. Ph.D. #1—the role of localization in OPNMR

Optical pumping in the bulk compound semiconductors likely proceeds via the mechanisms given in Eqs. (6) and (8). What is missing, however, are definitive experiments that show localization of the electron that yields nuclear magnetization. There are methods in the literature that provide tests for the localized mechanism, and they exploit the quadrupolar splittings present in hyperpolarized samples exhibiting small lattice strains [50]. In compound semiconductors, lattice strain produces internal electric field gradients at nuclear sites. If the nuclear spins are hyperpolarized and possess a quadrupole moment, then the population differences across the various quadrupolar transitions will be asymmetric, and a noticeable intensity difference can be seen in the satellite transitions. The ratio of satellite intensities is a function of the population differences between the corresponding nuclear spin energy levels. For the case of spin-\(\frac{3}{2}\),

\[
P_{-1/2} - P_{-3/2} = \exp\left( -\frac{2\hbar\gamma_n B_0}{kT_n} \right),
\]

where \(p_m\) represents the population corresponding to the Zeeman energy level with quantum number \(m\), \(\gamma_n\) is the nuclear magnetogyric ratio, \(B_0\) is the external magnetic field, and \(T_n\) is the nuclear spin temperature. This effect is shown in Fig. 6, where the intensity differences, as manifest as an asymmetry of the quadrupolar-split NMR line, determine local spin temperature.

Fig. 7 shows a proposed rf pulse sequence [49] for measuring the degree of localization of optical nuclear polarization. The sequence begins with a saturation comb that destroys any nuclear magnetization. The semiconductor is then irradiated for a period \(t_L\) with near-band-gap light of selected polarization. The light is then blocked for a period \(t_D\), and finally, the NMR interferogram is measured.

Fig. 6. Left: The \(^{71}\text{Ga}\) NMR spectrum of semi-insulating GaAs at \(\approx 10\) K. Right: \(^{71}\text{Ga}\) NMR spectrum of the same sample bathed in \(\sigma+\) light of 200 mW intensity for 4 min. Quadrupolar satellites of unequal intensity are clearly visible. Adapted from [10] and [50].
Figs. 7(B) and (C) show the predicted evolution of the bulk nuclear polarization $\langle I_z \rangle$ for two scenarios for hyperpolarization: cross-relaxation from conduction electrons (7B) and electrons associated with localized shallow donors (7C) [49]. Not only are the qualitative shapes of the predicted profiles different, but the timescales over which the profiles change are dramatically different. These qualitative differences in experimental results should be used to differentiate the role of localized versus delocalized centers in the nuclear hyperpolarization process. Indeed, the critical parameter for the nuclear polarization models given in Fig. 7 is the initial fractional drop-off rate of the observed signal with $\tau_D$; this rate scales inversely with $D/L^2$, where $D$ is the nuclear spin-diffusion coefficient and $L$ is the length-scale for the initial nuclear polarization from the localized or delocalized source. Thus, if the spin-diffusion coefficient is known, then the fractional drop-off rate provides a quantitative measure of $L$. Mapping out the fractional drop-off rate as a function of the optical pumping time, then, would allow one to map out the dependence of $L$ on optical pumping time. The ability to measure the nuclear polarization localization length could provide a measure of the degree of electron confinement in, for example, quantum Hall systems [51, 52], quantum wells, quantum wires, or quantum dots, or in bulk systems where there may be a distribution of defect Bohr radii [53] or where the Zeeman magnetic field induces a shrinkage of defect wavefunction [54]. To date, these measurements have not been performed and should be done on a variety of semiconductors containing quadrupolar nuclear spins, such as Al, Ga, As, In, Sb, or N, whose satellite transitions can be made to occur at different energies with a lattice–strain-induced electric-field gradient.

4.2. Ph.D. #2—the relationship to photoconductivity

The strong relationship between photoconductivity and OPNMR profiles have been noted in the literature, and exploited to develop models for OPNMR [41]. Photoconductivity data often give rise to hysteresis effects, particularly for mid- and sub-gap irradiation, as shown in Fig. 8. Here, we see hysterisis in the photoconductivity vs. photon–energy curve while sweeping from low to high energy then back down to low energy, where 8(B) shows the percent change between the two sweeps. These data suggest “photobleaching” of the optical absorption process.

It seems clear that if photoconductivity exhibits hysteresis effects due to photobleaching of defects, then there should be an effect of photobleaching on OPNMR signals, and that the dynamics of this effect could help in identifying the defect(s) responsible for hyperpolarization. An NMR pulse sequence has been proposed to assess this effect [49] and is shown in Fig. 9. If the NMR detection sensitivity is very good, then the effect of photobleaching on the hyperfine NMR shift may also be investigated.

The effects of light helicity on photoconductivity and OPNMR profiles are also not clear. The recombination rate of electrons and holes will depend on magnetic field strength in a phenomenon known as spin-dependent recombination. According to this phenomenon, optical pumping with circularly polarized light determines the spin polarization of the charge carriers. Recombination rates will follow the usual selection rules, and the result is photoconductivity being either suppressed or enhanced. A detailed study of photoconductivity in GaAs attributed spin-dependent recombination in semi-insulating GaAs to a site known as the “EL2” defect [55]. This defect dominates the sub-gap optical absorption in semi-insulating GaAs, and undergoes a physical transformation upon irradiation with infrared light to metastable EL2*. The metastable state (EL2*) is not paramagnetic, does not absorb in the near infrared, nor does it contribute to photoconductivity [56]. For these reasons, EL2* is sometimes referred to as the photo-bleached or photo-quenched state of EL2. The EL2 defect is widely believed to contain the arsenic anti-site. Previous works [55] suggested that EL2 is dynamically polarized by photoelectrons and that this is responsible for his observed difference in luminescence intensities for $\sigma$ and $\pi$ polarized light. Photobleaching of deep defects has been reported in unpublished works [49], yet physical mechanism responsible for the photoconductivity decay, and the effect of this phenomenon on OPNMR, remains to be determined.

4.3. Ph.D. #3—Systematic materials investigations

Commercial GaAs sources provide wafers with a variety of different doping levels. The scientific literature, however, does not dwell on missing or non-reproducible results. A few papers and (mostly) anecdotes from researchers suggest that $n$- or $p$-type wafers show no OPNMR effects, yet semi-insulating GaAs wafers do. Discrepancies remain in the literature regarding the OPNMR
signals from InP, either “undoped” (intrinsically n-type) or Fe-compensated [26]. No systematic investigation of OPNMR in a broad class of semiconducting systems has ever been published, and the wide variation in material electro-optical properties afforded by alloying and doping has yet to be explored by OPNMR. There have also been no attempts to determine which defect in a compound semiconductor is associated with the hyperpolarization process by systematic control of dopant type and concentration. There is a critical need to acquire large amounts of phenomenological data in a variety of well-chosen systems, with the intent of using these data to make broad assertions about the types of systems that can be enhanced via optical pumping.

An excellent starting point for such an investigation would be collaboration between NMR researchers and materials scientists that prepare very carefully controlled compound semiconducting films. Molecular beam epitaxy, for example, can provide undoped GaAs in micron-thick heteroepitaxy layers on many substrates using lattice-matching composition changes that overcome substrate mismatch. What is needed for these studies, however, would be systematic variation of a shallow donor (Si or C, for example), while the Fermi level of the material is pinned with a deep level impurity (Mn, for example). In this way the electron conductivity, and perhaps $T_1$ and $\tau$, could be kept as constant as possible while the shallow donor concentration varies over several orders of magnitude. OPNMR profiles, as well as effects of light helicity, could then be monitored.

GaAs could also serve as an excellent starting point for systematic studies of band gap effects. I suggest an investigation of OPNMR enhancements in bulk GaAs$_{1-x}$P$_x$ purchased from commercial sources. At small values of $x$, OPNMR phenomena are not expected to differ significantly from those observed in GaAs; small amounts of phosphorous are not expected to affect crystalline symmetries and band structure. As phosphorous content increases, the samples will undergo a transition from direct to indirect band gap, and it would be fascinating to measure the effect of this transition on OPNMR signal enhancements. OPNMR intensities are expected to diminish in indirect band gap samples as the indirect band gap semiconductors are expected to support bound, rather than free, excitons. This factor may or may not be masked by slower electron recombination rates in indirect gap semiconductors. The role of direct versus indirect gap systems, then, warrants careful experimental attention.

Bulk InP and GaAs materials are most efficiently pumped when they are prepared to have large numbers of defects, yet few free carriers. This set of properties is also met in the broad class of amorphous semiconductors, many of which can be prepared with a host of spatially localized defects near mid-gap, yet are quite electrically insulating. Amorphous silicon in the form a-Si:H is an excellent example of a material that exhibits properties identical to that of a direct gap semiconductor, including the ability to host excitons. If long-range crystalline order is not necessary for the OPNMR phenomena, it would seem these systems are ripe for experimental exploration. Moreover, amorphous semiconductors are readily prepared in thin film form with varying composition (Ge, C for example) and doping levels.

Optical pumping in a-Si:H and related materials also suggests the intriguing possibility that clusters of nuclei may be pumped. For some years it has been well established that device-quality a-Si:H contains microporoids dressed with hydrogen, typically 6-hydrogen atoms per microvoid [57*]. OPNMR in a-Si:H thin films could, in fact, result in the preparation of highly polarized 6-atom clusters of hydrogen, an ideal scenario for conducting nuclear quantum computation schemes.

4.4. Ph.D. # 4—Bulk relaxation effects

The present paradigms for OPNMR treat the nuclear spin–lattice relaxation times as irrelevant to the optical pumping process. In some cases, such as the pumping of bulk diamond [25*], this assumption may be justified. In the case of compound semiconductors containing quadrupolar nuclei, however, this assumption is not so clear. Very recent theoretical work [58] has shown that the presence of light can induce nuclear spin relaxation by modulation of local electric field gradients due to
photoelectron trapping and recombination at the localized recombination sites. The resulting calculations for the modulating nuclear quadrupolar interaction show a substantial decrease in the local nuclear polarization field at the shallow defects, with an implied corresponding loss in OPNMR efficiency. This relaxation model needs to be tested experimentally with systematic investigations of relaxation times and OPNMR efficiencies as a function of laser power and other pumping parameters. I am unaware of any systematic T1 measurements in GaAs or other materials with light exposure.

This issue is also critically important to the effects shown in Fig. 5, i.e., in schemes that portend electrical control of OPNMR polarization. All of the NMR data in that system were acquired in the presence of linearly polarized light excitation. The appearance of large positive signals (i.e., the same polarization as normal Zeeman polarization) may be obfuscated by light-induced relaxation effects in the saturation comb pulse and pumping scheme used to acquire the data [31\*]. In other words, is the sign change with changing current a spin-exchange effect, or is it a scheme used to acquire the data? In other words, is the sign change with changing current a spin-exchange effect, or is it a manifestation of the light-induced nuclear T1 effects? It is clear to me that a systematic study of T1 needs to be made as a function of laser power and current in these systems.

4.5. Ph.D. # 5—polarization transfer

One of the ultimate goals of OPNMR has been the transfer of nuclear polarization from pumped materials to other spin reservoirs, such as adsorbed molecules [59]. There has yet to be a report in the literature, however, of bulk polarization transfer from OP-enhanced compound semiconductors to specified target nuclei. In the case of solids two polarization transfer methods dominate the literature: cross-polarization and Overhauser enhancement from polarized gases such as xenon (SPINOE) [60]. Cross-polarization methods require multiple resonances of schemes, necessitating the ability to irradiate both the target and source nuclei. SPINOE uses the dynamic dipole–dipole interaction and hence requires source and/or target nuclei to possess a dynamic dipolar interaction.

Cross-polarization transfer from OPNMR systems will require conventional sample-in-coil methods to fully excite the semiconductor source nuclei near an interface; nuclei at or near surfaces are expected to experience large electric field gradients, thereby enormously broadening and/or shifting the NMR transitions of source nuclei. Moreover, the presence of a chemical barrier, such as a thermal oxide, might preclude this method altogether as such an interface might make the dipolar interaction too small to be effective for polarization transfer. One strategy to overcome this limitation would be to use the MBE synthesis methods mentioned previously to prepare multiple layers (though bulk-like in their electronic properties) of GaAs (GaAs,P), InP (InP), so that polarization transfer could be assessed (e.g. from Ga or As in GaAs to P in GaAs(P)) in systems that have well-defined interfaces yet changing band structures. Once this process is better understood, schemes for transfer across a more complicated interface, such as proteins adsorbed on InP [59], would be more tractable.

SPINOE transfer from OPNMR-derived target nuclei to mobile species at a surface may be the best strategy for preparing finite volumes of highly polarized solvents. My strategy would be preparation of athermal polarization via OPNMR of bulk or thin film semiconducting materials, and then employ SPINOE to transfer polarization to overlayers of simple solvents. While simple to propose, such a scheme is fraught with uncertainty owing to the lack of understanding of the OPNMR process in the first place. Particularly vexing is the problem of the cryogenic temperatures presently used to produce the OPNMR effects. Even at very low temperatures, however, substantial proton enhancement via SPINOE from xenon has been established [60,61], and freeze-thaw cycles may be used to store larger quantities of polarized solvent. The case of pumped diamond is also worth considering; it seems that OPNMR associated with the NV[–] center is dictated only by penetration depth, and not electron relaxation times [25\*]. Isotopically 13C-enriched diamond, with appropriate nitrogen doping and annealing, could produce an excellent platform for SPINOE from bulk-to-solvent. The availability of such solvents greatly enhance analytical, and bio-analytical, NMR spectroscopy and MRI.

4.6. Ph.D. # 6—spin-injected NMR (SINMR)

Electron spins may be made athermal by passage through a magnetic material, and this phenomenon is the basis for a large number of spintronics [2] devices. Should these spins be injected into a target material, there exists the opportunity to have the electrons cross-relax with nuclei in the target material, thereby producing spin-injected NMR (SINMR) signals. This effect was proposed [30] in the year 2000, but to my knowledge has never been demonstrated in bulk systems. The effect has been documented via electroluminescence in quantum heterostructures [32,62]. Sufficient theoretical knowledge exists to predict bulk systems for which the effect could be measured. One particular system would be a compelling study, namely ferromagnetic semiconductors such as doped ZnSe “spin filters.” The synthetic abilities afforded by MBE mentioned previously may be used to generate simple multi-layer structures from Mn-doped ZnSe contacts. At low temperatures, where the Zeeman-splitting of the band-edge states in doped ZnSe are huge, pure spin-aligned electrons may be injected into MBE-grown layers of compound semiconductors and Solomon-type cross relaxation observed in via NMR in traditional induction geometries. Further optimization of this effect, including the use of higher temperature ferromagnetic semiconductors, suggest the tantalizing possibility of significant nuclear polarization in bulk at more modest temperatures. Indeed, the use of conducting liquids as a metal contact may afford the possibility of significant nuclear polarization in solvents. Such schemes would also require an ability to transfer nuclear polarization subsequent to, or during, the spin-injection process, as described for Ph.D. student # 5. SINMR might be the most effective way to produce bulk quantities of hyperpolarized solvents. It also may be the most effective strategy for integrating nuclear hyperpolarization into semiconductor device processing and information technologies of the future.

5. Conclusions

Of all the hyperpolarization schemes presented to date, OPNMR (and its hoped-for cousin, SINMR) are the least understood at a fundamental level, yet afford compelling opportunities for greatly enhancing the sensitivity of traditional NMR and delivering new devices based upon spatial patterning of nuclear hyperpolarization. The challenges towards understanding OPNMR fundamentals are great, but schemes and theories have been presented that may be easily implemented and provide tests for present and future theories. Opportunities for collaboration with material engineers and device physicists are also possible, thereby bringing solids state NMR to yet another scientifically and technologically engaging community. I am hopeful this Trends article compels you to make it so.
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