Can nuclear magnetic resonance resolve epitaxial layers?

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The recently demonstrated technique of time-sequenced optical nuclear magnetic resonance in GaAs has made possible the detection of spectra free of the line shape distortions that accompanied earlier steady-state methods with an improvement in sensitivity as well. This work examines the possibility of even higher spectral resolution by means of selective averaging with radio frequency-optical multiple-pulse techniques with the aim of isolating the site-specific changes in the spin Hamiltonian associated with excitation to localized states of the conduction band, as in quantum wells. Simulations are presented to evaluate the approach proposed. It is concluded that such experiments are capable of the sensitivity and resolution to resolve individual epitaxial layers in high-quality structures and would provide unprecedented detail on the electronic structure and its uniformity by way of the nuclear quadrupole and spin-averaged hyperfine interactions.

I. INTRODUCTION

Nuclear magnetic resonance (NMR), particularly in solids, typically requires macroscopic samples due to the low sensitivity of detecting radio frequency (rf) emission. For over two decades, it has been known that irradiating a III–V semiconductor with circularly polarized light creates electron spin polarization of the photocarriers.[1–5] The nonequilibrium electron spins then polarize the lattice nuclei through the hyperfine interaction, as in the Overhauser effect. The resulting nuclear polarization is also optically detectable; precession of the photocarrier angular momentum about the hyperfine nuclear field B_N may be detected as a change in the degree ρ of circular polarization of the luminescence, which is directly proportional to the component of electron spin in the observation direction, a type of Hanle effect.[1,8] Steady-state experiments on bulk GaAs and $Ga_{1-x}Al_xAs$ have demonstrated sensitivity enhancements relative to ordinary high-field NMR of at least five orders of magnitude, making possible NMR in sample volumes of $\cong 10^{-7}$ cm^3. However, the spectral resolution obtained in these early studies was an order of magnitude worse than expected from ordinary NMR.[6,7]

Two very recent developments have vastly improved the prospects for optical NMR of GaAs semiconductors. The first was the extension of the steady-state methods to quantum wells (QWs) and heterostructures.[9–12] These studies demonstrated that sensitivity down to a single QW ($\cong 10^{11}$ nuclei) is readily possible. One interpretation[10,11,13] is that the electron localization inherent in the structures could provide the strong hyperfine coupling that in the bulk is associated with defect states. Again, however, the linewidths observed exceed those of ordinary NMR in the bulk.

The second development is a new experimental procedure, time-sequenced optical NMR (TSONMR), in which the three physical processes of optical nuclear polarization (ONP), NMR, and optical detection (OD) are separated into successive time intervals[13,14] as sketched in Fig. 1. This has the consequence that each process can be separately optimized both for sensitivity and for spectral resolution. In this way it has been possible[13] in bulk p-GaAs to obtain the intrinsic linewidth due to spin–spin couplings and to do so with nuclear polarizations less than 10^{-3} of those reported in previous work.

The resolution and sensitivity advantages of TSONMR are distinct and separable. The resolution advantage already realized has several contributions: the absence of optical Knight shifts in the NMR spectrum, if it is encoded in the dark;[13,14] the absence of rf power broadening present in many of the early steady-state experiments; and the ability to manipulate the fractional contribution of distinct, but nearly isochronous, sites to the signal.[14] Additional resolution advantages proposed here come from the adaptability of TSONMR to multiple-pulse and multidimensional experiments related to those in use in ordinary NMR.

The relative sensitivity advantage of TSONMR is not fully characterized because the sensitivity of the steady-state methods is only qualitatively described.[4] Figure 2 experimentally compares the continuous-wave (cw) steady-state method used by previous workers with a Fourier-transform variant[14] of our time-sequenced experiment on such a weakly polarized[13,14] sample. A quantitative analysis applicable to both bulk and heterostructure samples has been given[13] which relates the sensitivity of the optimized TSONMR experiment to readily measured magnetic parameters and the luminescence photon counting rate. Applied to GaAs/GaAlAs QW samples, this analysis conservatively predicts sensitivity to a small fraction of a monolayer ($< 10^{10}$ nuclei). We are currently preparing such experiments.

II. RESOLVING SITES BY SPIN INTERACTIONS

This article presents some ideas and calculations which motivate the experiments and predict some aspects of the results anticipated. Important *a priori* insight can be gleaned from existing observations of NMR in GaAs. Given the sensitivity, one needs a spin interaction capable

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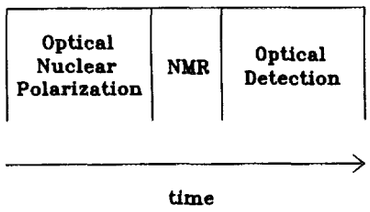

FIG. 1. The three epochs of TSONMR. First, the nuclei are polarized optically in the field B_0, typically until a steady-state nuclear polarization is reached. Next, the spins are irradiated with rf which depolarizes resonant spins and lowers the nuclear field B_N encoding the NMR as a function of a frequency or time variable. The band gap light is not needed during this time and introduces shifts if present. Finally, the resulting B_N is measured optically, by way of the Hanle effect. The direction and magnitude of the magnetic field may be varied in the three epochs to optimize sensitivity,[13] but this is not essential to the resolution issues. The three steps are repeated for each value of the NMR frequency or time variable.

of distinguishing different layers or sites. The nuclear quadrupole interaction,[15] which measures the electric field gradient (efg) tensor at the nucleus, vanishes in an ideal GaAs lattice due to the cubic symmetry. The TSONMR method was able to show[13] that even sites with efg unobservably

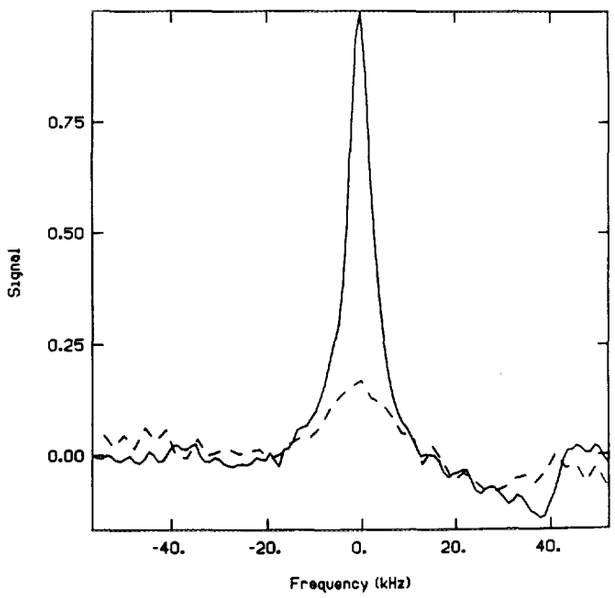

FIG. 2. Equal time comparison of Fourier-transform time-sequenced optical detection with the cw steady-state method. The two spectra show the resonance of ^{71}Ga in $\cong 10^{-7}$ cm^3 of p-GaAs (Zn doped 4×10^{17}/cm^3). The dashed trace was obtained with the magnetic field along the optical axis swept through resonance in the presence of continuous optical and rf irradiation. The solid trace was obtained with a Fourier-transform variation[14] of the time-sequenced method[13] in which the field direction is rotated between polarization and detection periods, and the light is off during the rf irradiation which encodes the NMR. The y-axis scales were adjusted to give equal noise levels. The resolution of the steady-state experiment was optimized by lowering the rf power level until power broadening was negligible. Both the resolution and the sensitivity of the time-sequenced experiment are superior in this example by factors of 3 and 8, respectively.

perturbed by proximity to the optically relevant defect (ORD) are optically detectable. This suggests that around a point defect the range of perturbation of the efg in either the valence or conduction band is small compared to the range ($\cong 10$ nm) of the hyperfine interaction which is switched on by optical excitation as a result of the s-orbital character of the conduction band. On the other hand, for sites within a few bonds of an isovalent defect (or presumably an interface) the nuclear quadrupole interaction can be the dominant spin-dependent term. On the basis of observations in the bulk both by optical[16] and by ordinary[17–19] NMR, this is predicted to give rise to satellite resonances as far as several megahertz away from the Larmor frequency. Because all of the principal nuclei (^{27}Al,^{69}Ga,^{71}Ga,^{75}As) are half-integral, a central transition remains in the neighborhood of the Larmor frequency. This can also be used to characterize the efg, as it experiences a second order quadrupole shift in the high field analysis.[15]

Another benchmark is provided by pressure-dependent studies of the quadrupole interaction, which suggest that the strain associated with the interface should also lead to readily observable splittings. In a QW experiment, the quadrupole interaction was induced by a uniaxial strain on the sample and the observed splittings were on the order of 10 kHz.[10,11] The splittings seen in this study are considerably less than the predicted strain caused by the lattice mismatch between the GaAs and GaAlAs layers.[20]

The question then arises of why spectral resolution by the efg was not already seen in the steady-state optical NMR of epitaxial structures. This can be rationalized by considering the differential sensitivity of the steady-state methods. Because both the ONP and the detection processes are weighted by the hyperfine coupling,[8] sites in regions of low electron probability, such as those near the interface or in the barrier, are not effectively detected. The time-sequenced method provides a route to mitigating this discrimination; by arranging for spin diffusion in the dark to carry polarization and depolarization to and from regions of low hyperfine coupling,[5,14] it will be possible to enhance the fractional contribution of their resonances to the detectable nuclear field. Another way to enhance the contribution of interfacial sites is by the use of double resonance methods, long established in ordinary NMR.[21–24] In this way the resonant contribution of dilute or distant sites can be made fractionally large, since each such site can destroy the nuclear field contribution of many (up to 10^5) neighbors.

The next largest spin interaction is the hyperfine interaction itself. The Fermi contact hyperfine Hamiltonian is[25]

$$\mathcal{H}_{HF} = (2/3)\mu_0 g_0 \mu_B \gamma_N \hbar |\Psi(\mathbf{r}_k)|^2 \mathbf{I}\cdot\mathbf{S}, \quad (1)$$

where g_0 is the free electron g-factor, μ_B is the Bohr magneton, γ_N is the nuclear gyromagnetic ratio, and $|\Psi(\mathbf{r}_k)|^2$ is the electron density evaluated at the nucleus at position $\mathbf{r}_k$. Since the excited state lifetime is on the order of 10^{-10}–10^{-9} s,[1] the hyperfine interaction is rapidly fluctuating. The fluctuating part of the hyperfine interaction is responsible for ONP, and the average value is responsible

for the Knight shift of the NMR line.[25] The average of the hyperfine interaction acts as an additional field B_e experienced by the nuclei. This electron field or Knight shift has been observed in bulk GaAs,[4,9] and a p-channel $Al_xGa_{1-x}As/GaAs$ heterojunction ($x = 0.36$).[12] Its magnitude is proportional to the electron density at the nucleus. For bulk GaAs, the Knight shift is understood to be due to the localization of excited electrons at donor sites (the ORD) of unproven identity.[8] The wave function for these donor states is modeled as hydrogenlike with an effective Bohr radius of $a_0^* = 10$ nm.[8] For nuclei at distance r from a localized electron, the Knight shift for nuclear species α is $\gamma_\alpha B_e^\alpha(r_\alpha) = \gamma_\alpha b_e^\alpha(0)\langle S_z\rangle \exp(-2r_\alpha/a_0^*)$, where $\gamma_\alpha b_e^\alpha(0)\langle S_z\rangle$ is the Knight shift at the donor site. The Knight shift near the ORD has been measured to be $b_e^\alpha(0)\langle S_z\rangle \simeq 2$ mT[4,9] (for $\langle S_z\rangle \simeq 0.1$) which is in agreement with theoretical estimates.[8] The Knight shift of the free photocarriers has not been measured in GaAs, but is estimated to be orders of magnitude smaller. Rapid spin exchange between the localized and free electrons has been proposed.[4]

III. RESOLUTION OF KNIGHT SHIFTS WITH TWO-DIMENSIONAL LOCALIZATION

In the heterojunction the Knight shift was attributed to electrons localized in the interface since the luminescence was detected on a line originating from the interfacial region.[12] Spin exchange with the localized electrons can be ruled out in this case, because a difference in the electron spin polarization was seen for different luminescence lines. The Knight shift here was found to be 4.4 kHz for the ^{75}As nuclei ($\langle S_z\rangle = 0.4$). Given this interpretation, this value for the Knight shift could be taken as a lower bound for that due to electrons experiencing two-dimensional (2D) localization in a QW, which can have a narrower localization width and a higher spin polarization. By detecting the luminescence on a line due to 2D electrons in the QW, it should be possible to measure the resulting Knight shift for the $n = 1$ level, though no positive or negative result on this has been reported to date. The Knight shift for this case is expected to be[11,26]

$$\gamma_\alpha B_e^\alpha(z) = \gamma_\alpha b_e^\alpha(0)\langle S_z\rangle \cos^2(\pi z/d), \qquad (2)$$

where d is the well width.

Figure 3 shows a pulse sequence and simulation of a TSONMR experiment designed to resolve individual layers of ^{75}As atoms in a QW. This experiment takes advantage of a multiple-pulse line-narrowing sequence designed to average the dipolar and quadrupole interactions to zero as well as to remove the resonance offset.[27-30] The result of this sequence would be a narrow line at zero offset. The Knight shift information is obtained by turning the light on during the windows of the line-narrowing sequence as illustrated in Fig. 3(a). This type of experiment is most closely analogous to a solid-state NMR imaging experiment where dc gradient pulses are given in the windows to encode the spatial dependence of the gradient,[27,29] but uses a 16 pulse rf line-narrowing sequence used for rf gradient imaging.[30]

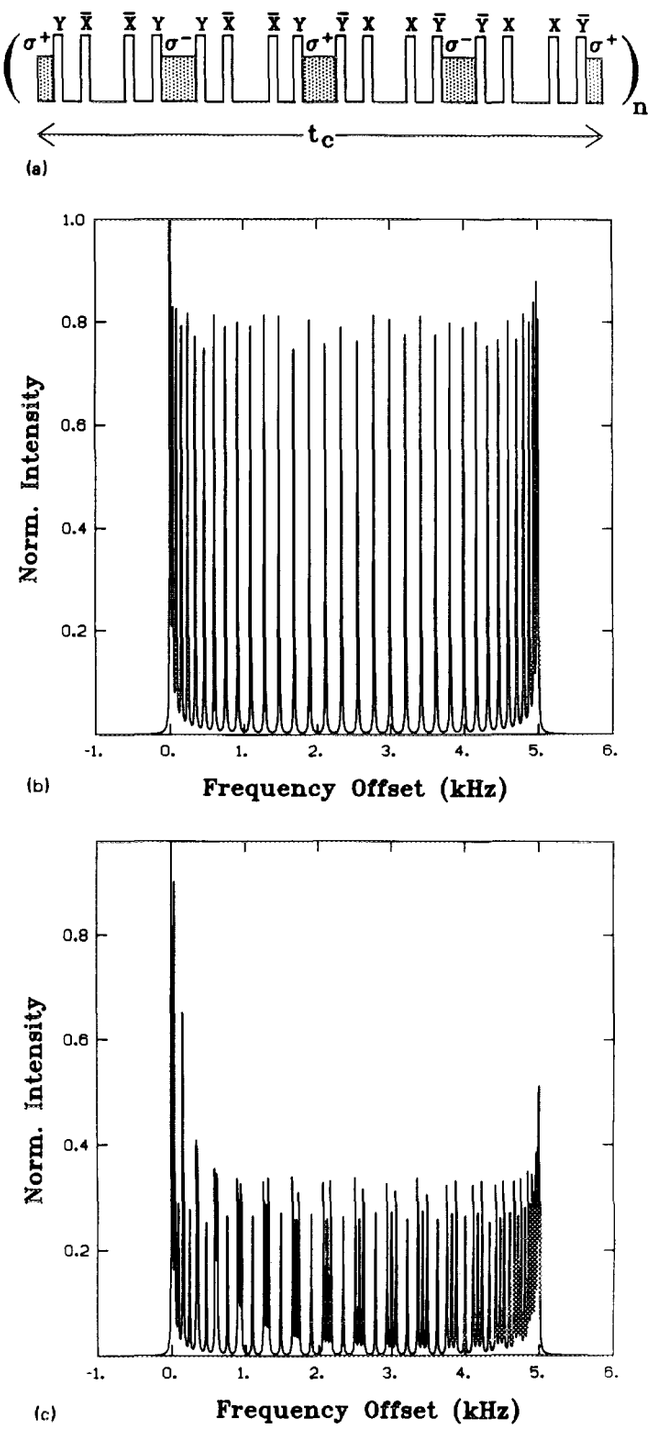

FIG. 3. Simulation of the optical Knight shift of the ^{75}As resonance in a GaAs QW. The line-narrowing pulse sequence shown in part (a) is performed during the NMR part of a TSONMR experiment. Line-narrowing of the ^{75}As resonance to the order of 10 Hz is expected. The simulation in part (b) is for an ideal QW of 36 layers of As layers and 36 Ga layers ($d \simeq 10$ nm). Each resonance line represents the Knight shift of a single layer of As atoms with all 36 layers resolved. The simulation of part (c) represents the average of three well widths $d \simeq 10$ nm $\pm$ 1 ML which is expected for a real sample. There should be a total of 18 + 19 + 36 = 63 lines. Only the nuclei between the center of the well and the interface remain resolved. The Knight shift at the center of the well is assumed to be 15 kHz which is scaled down by the pulse sequence to 5 kHz.

The success of the line-narrowing experiment depends on the amount of nuclear spin relaxation that occurs during the length of the pulse sequence. The relaxation time of interest is spin-lattice relaxation in the rotating frame $T_{1\rho}$ which has been measured to be in excess of 10 ms for bulk GaAs.[14] If the well contains 36 layers of As atoms arranged symmetrically about the center and each layer is assumed to contribute equally to the spectrum then only 18 lines are expected. If the As atoms are arranged asymmetrically about the center of the well then all 36 lines are expected. Figure 3(b) shows a simulation for the asymmetric ($d \simeq 10$ nm) case assuming line-narrowing down to 10 Hz and a center shift $\gamma_a b_e^{\alpha}(0)\langle S_z\rangle = 5$ kHz, all 36 layers are resolved. For a real sample the well width fluctuates ± 1 ML,[31] and in this case the spectrum is an average of three different well widths and is illustrated in Fig. 3(c). The resolution of the atoms near the center of the well and near the interface has been decreased by the averaging, but the layers in between the center and the interface are still resolved.

Optical NMR in GaAs materials has proven to be an effective way of circumventing the sensitivity problem of conventional NMR. The TSONMR method is essential for the study of GaAs layers in GaAs heterostructures, an area where the quasi steady-state ODNMR technique has been inadequate. By using the quadrupole and hyperfine interactions as a way of distinguishing different sites in a GaAs epitaxial layer, valuable information about the structure as well as the excited electronic states can be obtained. The more sophisticated multiple-pulse and 2D NMR techniques are now accessible with optical methods making optical NMR an informative tool for studying GaAs semiconductors.

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