Optical polarization of nuclear spins in GaAs

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The photon energy, irradiation time, and sample temperature dependences of laser-enhanced NMR spectra from semi-insulating GaAs at 9.4 T were measured. These data were used to test the existing model for the mechanism of optical nuclear polarization—namely, optical excitation of shallow donor states and subsequent spin diffusion of polarization throughout the bulk. Features of the present results, such as their uniqueness to semi-insulating GaAs and pumping data obtained via laser irradiation above the band gap, are inconsistent with this model. An additional model is proposed that includes localized paramagnetic centers as storage sites for electron spin polarization, but relies upon delocalized electron states to accomplish the bulk nuclear spin polarizations. The delocalized states could be free excitons.

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I. OVERVIEW

The crafting of nonequilibrium nuclear spin populations is of increasing scientific and technological interest. Nuclear eigenstate-based computing and sensitivity-enhanced magnetic resonance spectroscopy are examples of emerging technologies that may exploit quantum coherences prepared by transfer of photon angular momentum to nuclear spins. Towards these ends, researchers have employed the optical excitation of semiconductors and semiconductor-based nanostructures to demonstrate exotic NMR-observable nuclear spin populations.[1] For bulk semiconductors, these ''optical pumping'' results have been discussed in the context of angular momentum selection rules for the optical absorption process, followed by perturbation of the nuclear spin populations via cross relaxation with polarized electrons—i.e., the Overhauser effect.[2]

We report observation of new phenomena in the optical polarization of ^{71}Ga and ^{69}Ga nuclear spin states in bulk semi-insulating GaAs which suggest that the present understanding of laser-enhanced NMR is incomplete. We show that optically induced NMR signal enhancements can be observed with irradiation at photon energies up to 30 meV below and 110 meV above the energy of shallow donor states that are the ostensible origin of the enhancements according to previous models.[3,4] Enhancements observed through irradiation at different photon energies show markedly different temperature dependences; high photon energy data are not consistent with indirect population of lower-energy excited states. We further demonstrate that NMR signal dependences on laser irradiation time and photon polarization are suggestive of multiple mechanisms for polarization of bulk nuclear spins, including cross relaxation with localized states at photon energies below 1.50 eV and with mobile or delocalized states at higher photon energies. The phenomena reported here were uniquely observed in semi-insulating GaAs and not in commercially doped GaAs samples or in high-purity molecular-beam-epitaxy- (MBE-) grown layers. The apparent uniqueness of semi-insulating GaAs suggests the importance of a moderate concentration of impurities to increase the spin lifetimes of excited electrons.

II. METHODS

Optically enhanced NMR spectra were collected for wafers of bulk semi-insulating GaAs (thickness 350 μm, surface orientation [100], resistivity greater than 10^7 Ω cm, mobility greater than 6000 $\mathrm{cm}^{-2}/\mathrm{V\,s}$ (American Crystal Technologies) in a 9.4-T magnetic field using the ''saturation recovery'' experimental protocol described in Ref. 5. The sample was irradiated with laser light throughout the whole experiment; no changes in the NMR spectra were observed when the laser was blocked prior to NMR signal acquisition. Each optically enhanced NMR spectrum consisted of a single peak that was indistinguishable in chemical shift and linewidth to GaAs spectra collected without irradiation. Peak integrals alone are therefore sufficient to describe NMR results. When nonzero thermally relaxed intensities were observed with the laser off, the reported values correspond to differences between laser-on and laser-off experiments. Spectra were phase adjusted so that thermally relaxed (''in the dark'' or without laser irradiation) NMR acquisitions yielded a positive peak. A negative signal intensity therefore corresponds to a population inversion in nuclear spin energy levels.

Figure 1 shows a diagram of the equipment used for laser-

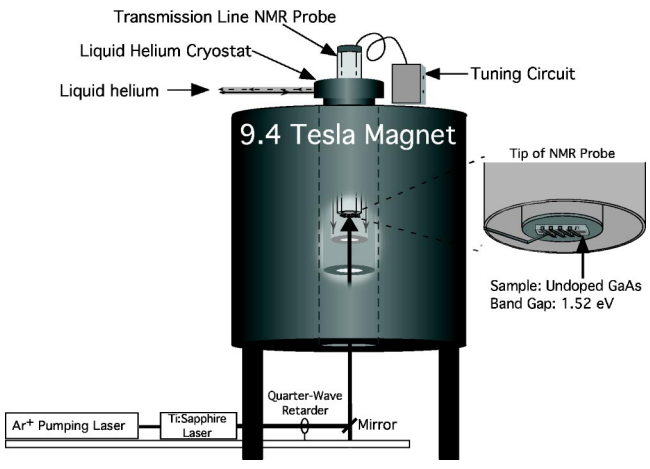

FIG. 1. Equipment diagram.

enhanced NMR. Sample temperature was controlled using a commercial continuous-flow cryostat and laser-induced sample heating was minimized via sapphire heat sinking similar to that employed previously.[6] Masking GaAs samples with silicon in control experiments allowed recreation of the laser-induced temperature gradients in the GaAs without allowing light to penetrate the silicon. ^{71}Ga NMR relaxation times in doped samples were then used to calibrate sample temperatures subject to laser irradiation. A transmission line NMR probe design (with capacitors at room temperature, as shown in Fig. 1) allowed constant probe sensitivity, without the need to retune, between 11 K and 40 K. Constant probe sensitivity was confirmed through measurement of thermal equilibrium NMR intensities in fast-relaxing heavily doped samples; these intensities were proportional to Boltzmann equilibrium magnetizations over the temperature range studied. The NMR probe could be tuned to a variety of NMR frequencies by replacement of the cable between the tuning circuit and transmission line.

In order to evaluate the different excited states populated by laser irradiation, photoluminescence experiments were performed on the semi-insulating GaAs sample in a 7-T magnetic field. In these experiments, sample temperature was also controlled by a continuous-flow liquid helium cryostat. The sample was excited at a photon energy of 1.95 eV with 3.5 mW of laser power focused to a spot size of roughly 10 μm. Luminescence from the sample was analyzed using a high-resolution monochrometer.

III. RESULTS

Optically enhanced NMR signal intensities are characterized herein by two parameters: *A*, the magnitude of intensity modulation by opposite circular polarizations of light ($A = I_{\sigma^-} - I_{\sigma^+}$), and *B*, the offset intensity relative to which this modulation occurs [$B = (I_{\sigma^-} + I_{\sigma^+})/2$]. The parameter *B* represents the NMR intensity observed via irradiation with linearly polarized light, while the parameter *A* quantifies the effects of circular polarization. The excitation energy ''spectra'' of optically pumped ^{71}Ga NMR signals are displayed in Fig. 2 at various temperatures between 11 K and 31 K. The laser penetration depth is expected to range from greater than 20 μm at 1.48 eV to less than 1 μm at 1.60 eV,[7] so features in Fig. 2 are not necessarily proportional to nuclear spin polarizations within the illuminated region. In addition, NMR intensities did vary slightly with laser alignment due to rf field inhomogenieties; error bars in Fig. 2 reflect repeatability within same day experiments. Qualitatively similar behavior was observed when the NMR probe was tuned to ^{69}Ga (insets, Fig. 2) and ^{75}As, although the ^{75}As data were complicated by a strain-induced quadrupolar splitting.

Most qualitative features of Fig. 2 are independent of temperature and Ga isotope observed; the magnitudes of these features, however, are highly dependent on temperature. Below $\sim$1.50 eV, the magnitude of *B* decreases to near zero with sample temperature rise from 11 K to 13 K. Above 1.50 eV, *B* changes sign and its absolute value decreases more slowly as sample temperature is raised from 11 to 31 K. The same trend is true for *A* in the region of subband gap irradiation (below 1.52 eV). Although significantly smaller at 11 K, *A* derived from superband gap (above 1.52 eV) irradiation increases above 11 K and then decreases slowly. The temperature dependence of NMR enhancements is detailed in Fig. 3 for those photon energies marked with arrows in Fig. 2. The most striking differences between the present results and previously obtained optically polarized NMR signals from bulk GaAs (Refs. 3 and 9) are the significant enhancements, and the concomitant photon energy and temperature dependences, observed for superband gap irradiation.

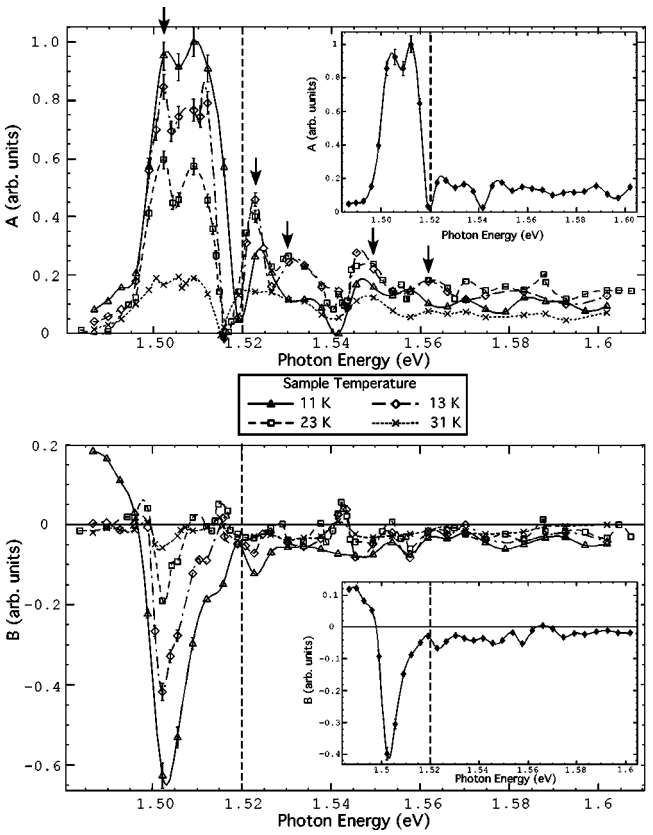

FIG. 2. The parameters *A* (top) and *B* (bottom) defined in the text for ^{71}Ga at 9.4 T as a function of laser photon energy at different temperatures. Laser irradiation time $\tau_l = 4$ min, spot size $= 4$ mm, and power $= 320$ mW. The vertical dashed lines represent the band gap of GaAs below 40 K (Ref. 8). The arrows indicate the photon energies for the data plotted in Fig. 3. The curves are guides to the eye. Unless otherwise specified, estimated errors are approximately equal to the symbol size. Insets: *A* and *B* for ^{69}Ga at $T = 11$ K.

The time dependence of laser-enhanced NMR signals from semi-insulating GaAs was measured over a wide range of time scales (between 0.5 s and several hours). At all sample temperatures and laser irradiation frequencies measured, the time dependence of the NMR signal intensity is well fit by a single exponential: $I_{\tau_l} = I_\infty[1 - \exp(-\tau_l/T_{1,l})]$, where I_{τ_l} and I_∞ are NMR signal intensities evaluated at a finite and infinite optical pumping time, respectively. $T_{1,l}$ represents the characteristic relaxation time of the optically enhanced NMR signal, which was found to be roughly equal to 1 h at 10 K (much less than the dark relaxation time of

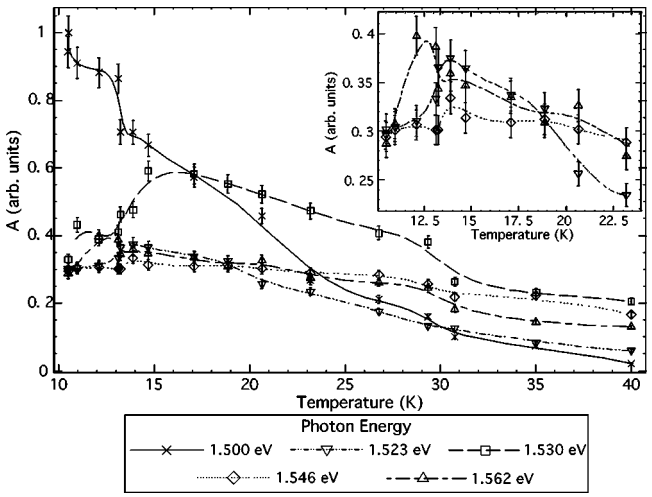

FIG. 3. The temperature dependence of A for ^{71}Ga between 11 K and 40 K. Irradiation time $\tau_l = 4$ min. Inset: data for selected photon energies plotted on a larger scale to demonstrate an increase in intensity between 11 K and 13 K. The curves are guides to the eye.

30 ± 10 h) and 10 min at 30 K (equal to the dark relaxation time). Due to these long relaxation times at low temperatures, errors in $T_{1,l}$ measurements were large, and multiexponential relaxation behavior would not have been detectable if all time constants were of the same order of magnitude. Experimental errors in the $T_{1,l}$ determination were also too large to detect different relaxation times at different photon energies.

Figure 4 shows the photoluminescence spectrum of semi-insulating GaAs at 10 K in a 7-T magnetic field. The broad features between 1.490 eV and 1.505 eV result from free

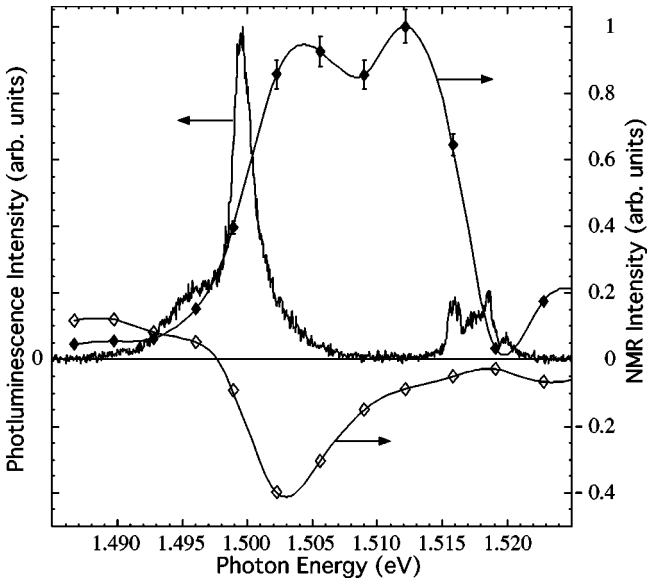

FIG. 4. The photoluminescence spectrum for semi-insulating GaAs at 10 K in a 7-T magnetic field. Excitation photon energy $= 1.95$ eV, laser power$= 3.5$ mW, and spot size ~ 10 μm. On the same axes are superimposed data from Fig. 2: A and B for ^{69}Ga at 11 K.

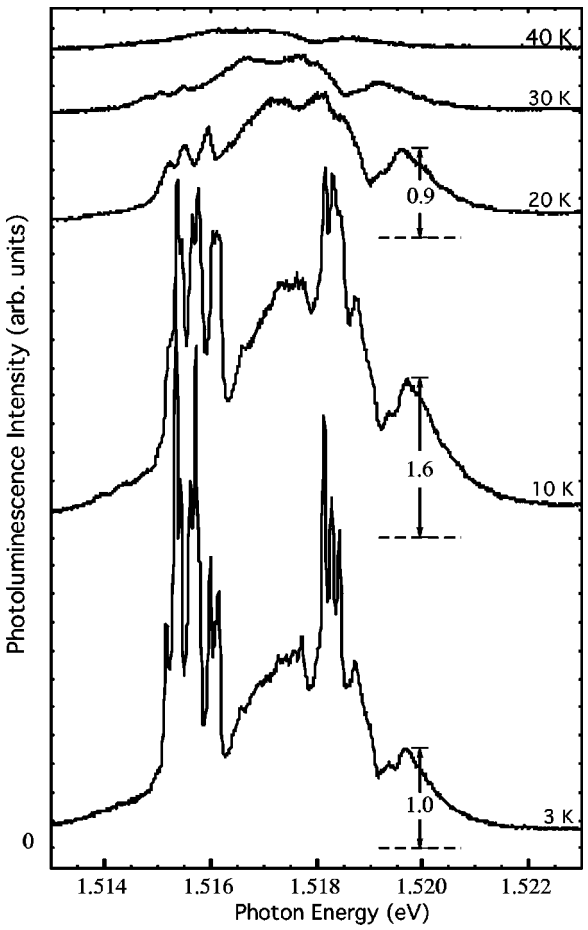

FIG. 5. The temperature dependence of excitonic luminescence from semi-insulating GaAs in a 7-T magnetic field. Experimental parameters are the same as for the photoluminescence data in Fig. 4.

electron-to-acceptor luminescence,[10,11] and the peaks between 1.515 eV and 1.520 eV are attributed to luminescence from excitons.[10] Superimposed on the same axes are the NMR enhancements from Fig. 2. Significant NMR enhancements were observed at photon energies at which there was no photoluminescence, e.g., in the region between the acceptor and excitonic peaks, as well as at energies below the acceptor luminsecence. Figure 5 shows the temperature dependence of the excitonic luminescence. The broad peak centered just below 1.52 eV is assigned to the free exciton polariton.[12] The intensity of this feature is nonmonotonic in temperature. The sharp peaks at lower energy are due to luminescence from excitons associated with impurity sites.[10,12] These peaks disappeared by 30 K due to dissociation of donor- and acceptor-bound excitons.[13] The intensity of all excitonic luminescence decreased significantly by about 40 K.

Finally, we have found that the observation of polarization-dependent optical NMR enhancements depends strongly on the type of GaAs studied. The results in Figs. 2 and 3 appear to be unique to semi-insulating GaAs. Qualitatively similar results were obtained from samples of semi-insulating GaAs produced by other manufacturers,[39] but we have observed *no NMR enhancements* from commercial

samples with doping concentrations (n- and p-type, dopant = Si and Zn, respectively) between 5×10^{17} and 2×10^{18} cm^{-3}. The photoluminescence from commercial n-type GaAs showed a broad, featureless peak spanning from $\sim$1.44 eV to 1.52 eV, without resolved excitonic or acceptor luminescence. We also observed no NMR enhancements from a 6-μm-thick layer of undoped MBE-grown high-purity GaAs that exhibited strong excitonic photoluminescence.

IV. DISCUSSION

Modulation of nonequilibrium nuclear spin populations via circularly polarized optical excitation relies upon two fundamental criteria. First, angular momentum selection rules must exist such that excitation with circularly polarized light results in nonequilibrium electronic spin polarization. Second, the electrons and nuclei must experience a hyperfine interaction so that a transfer of angular momentum to the nuclear spin system occurs. The second criterion alone is sufficient for observation of NMR enhancements that do not depend on light polarization. The satisfaction of both criteria in GaAs is well established,[4,14,15] but no hyperfine shifts have been reported in optically enhanced NMR spectra from bulk GaAs observed through conventional, sample-in-coil NMR detection.[3,9] In previously published models for bulk GaAs optical pumping that invoke nuclear spin diffusion from defect sites, the absence of shifts in the NMR signals prepared via optical pumping was rationalized by the low abundance of nuclei at defect sites relative to the bulk.[3,9]

To our knowledge, there is no definitive identification in the literature of the specific electronic excited states responsible for optical alignment of *bulk* nuclear spins in GaAs.[3,4,16] When NMR enhancements were detected optically, efficient spin exchange between different electronic states prevented identification of specific electronic states that cross relax with nuclei: while optically detected NMR spectra could be extracted from distinct photoluminescence lines, these lines yielded the same optically detected NMR spectrum.[16] The NMR line shapes were consistent with electrons at a fixed defect site coupling strongly with local nuclear spins. Such electrons no doubt experience the strongest nuclear hyperfine fields, but it is not obvious that nuclei near defect sites are representative of bulk nuclear spins. Efficient spin exchange between electrons would render any optical scheme for detection of NMR less sensitive to the polarization of nuclei in the bulk of the crystal.

At the other extreme, sample-in-coil NMR yields a bulk-averaged signal with a limited bandwidth, making it insensitive to the small net magnetization and broad lines anticipated from nuclear spins near defect sites. In previous studies, the insensitivity of laser-enhanced NMR to photon energy below the band gap led to the suggestion that low-lying, localized defect states are responsible for polarization of nuclei; such defect states can be populated indirectly through the electron-phonon cascade.[3,9,17] The expectation of bulk spin polarization through spin diffusion from sites of electronic localization suggests that NMR enhancements should scale with defect density. In our experiments, the lack of signal enhancements from commercially doped samples with higher defect densities than semi-insulating GaAs suggests that the optical polarization effect is more complicated. Furthermore, the dominance of superband gap enhancements over subband gap enhancements at higher temperatures (Fig. 3) indicates the importance of more energetic electrons. We are left with the following question: What are the unique properties of semi-insulating GaAs which lead to strong optical enhancements of NMR? It will be argued that both delocalized and localized paramagnetic electrons contribute to bulk NMR enhancements. The delocalized states interact with large numbers of nuclei and are most efficient at polarization transfer to nuclear spins in the bulk, and fixed paramagnetic centers are necessary to extend spin lifetimes of the delocalized states through spin exchange.[18] The distinct features of Figs. 2 and 3 will be discussed in the context of differing distributions of excited electronic populations.

Under the Solomon formalism for the Overhauser effect, the steady-state nuclear spin polarization under optical excitation is approximated by[19–21]

$$\overline{I_z}=I_0+\frac{\omega_0-\omega_2}{\omega_0+2\omega_{1,I}+\omega_2}\frac{I(I+1)}{S(S+1)}(\overline{S_z}-S_0), \qquad (1)$$

where $\overline{I_z}$ ($\overline{S_z}$) and I_0 (S_0) are the steady-state and thermal equilibrium nuclear (electronic) spin polarizations, and ω_0, $\omega_{1,I}$, and ω_2 are the rate constants for zero-, single-(nucleus), and double-quantum transitions involving coupled electrons and nuclei. The effect of optical excitation is to perturb $\overline{S_z}$ from thermal equilibrium, creating a driving force for polarization transfer. The parameter B is a relative measure of $\overline{I_z}$ for excitation of electrons with no preferred polarization ($|\overline{S_z}|<|S_0|$) via linearly polarized (or unpolarized) light. The parameter A is the response of the nuclear spins to modulation of $\overline{S_z}$ with polarized light: $A\propto[(\omega_0-\omega_2)/(\omega_0+2\omega_1+\omega_2)](S_{z,\sigma^-}-S_{z,\sigma^+})$, where $(S_{z,\sigma^-}-S_{z,\sigma^+})$ is the degree of modulation in S_z induced by the two circular polarizations of light. Equation (1) provides a framework for identifying the specific electronic states that are responsible for polarization of nuclei. As the excitation photon energy is varied, $\overline{S_z}$, $\overline{S_0}$, and the rate constants w_i would change depending on the local symmetries of optical excitation, local electronic g factors, and the nature of electron-nuclear coupling for different excited electronic states. In addition, the magnitudes of NMR enhancements depend on the lifetimes (populations) of excited electrons.

The NMR enhancements presented here appear to be unique to semi-insulating GaAs, suggesting that certain types of defects are essential for these bulk NMR enhancements. The only type of defect we know to be unique to this sample is the carbon acceptor. Carbon acceptors are added in the processing of semi-insulating GaAs to compensate for the donor impurities, such as EL2, which are unavoidable in bulk crystal growth.[22] The presence of this impurity is indicated by the broad photoluminescence peak between 1.490 and 1.505 eV in Fig. 4. Direct excitation at these low photon energies resulted in relatively weak NMR enhancements (Fig. 2). Excitation at the carbon acceptor peak is expected to

promote electrons from carbon acceptor levels into the conduction band; these electrons may or may not relax back to acceptor levels. The fact that NMR enhancements in this region of the photon energy spectrum are not highly dependent on light polarization suggests that light absorption is not highly spin selective.

When the sample is irradiated at photon energies associated with carbon acceptor luminescence, there is a sign change in the polarization-independent component of the NMR enhancement spectrum (B) at 11 K (Fig. 2). This sign change has been measured previously.[3] A sign change in B could be affected in two ways: S_0 could change sign through a change in the electronic g factors of excited electrons or the relative magnitudes of ω_0 and ω_2 could change sign.[19] In the latter case, Eq. (1) would predict a simultaneous sign change in A that is not observed. These results suggest that electronic excited states populated at photon energies below 1.50 eV have g factors opposite in sign to those populated at higher photon energies.

The negative values for B observed throughout most of the photon energy range (above 1.50 eV) are consistent with the negative g factors for electrons at shallow donors and conduction electrons in GaAs.[23] A sign inversion in the effective g factor of the excited electronic spin reservoir as the excitation photon energy is decreased below 1.50 eV suggests a transition to highly localized electronic states. The fact that this sign change is observed only at the lowest temperature suggests that the localized states relax quickly or are easily dissociated. Further investigation of NMR enhancements at lower photon energies is necessary. We are currently looking for evidence of spatial localization of NMR enhancements (nuclear spin diffusion and broadening of the NMR spectrum at short irradiation times) in this range of photon energies.[3,4]

While it is possible that excitation at higher photon energies may lead to similar mechanisms for nuclear spin alignment through indirect population of the same low-energy excited states, the distinct temperature dependence of NMR enhancements at different photon energies suggests a more complicated mechanism. For example, NMR enhancements (both $|A|$ and $|B|$) increased dramatically as photon energy was increased above 1.50 eV. Furthermore, these stronger NMR signals are more robust to increases in sample temperature. Still more striking is the thermally activated behavior of A observed at photon energies above the band gap, and that these enhancements eventually dominate over those observed for subband gap irradiation as temperature was increased (Fig. 3). This final observation is the most indicative of a different mechanism for polarization of nuclei for high-photon-energy excitation: if the only difference between high-photon-energy and low-photon-energy excitation were the indirect population of the same excited states, indirect excitation would not yield stronger NMR enhancements at higher temperatures.

At photon energies above ~ 1.505 eV, the time dependence of the NMR data shows no evidence for electron-nuclear cross relaxation at defect sites and subsequent nuclear spin diffusion to polarize bulk nuclei. First, the temporal dependence of signal enhancements is inconsistent

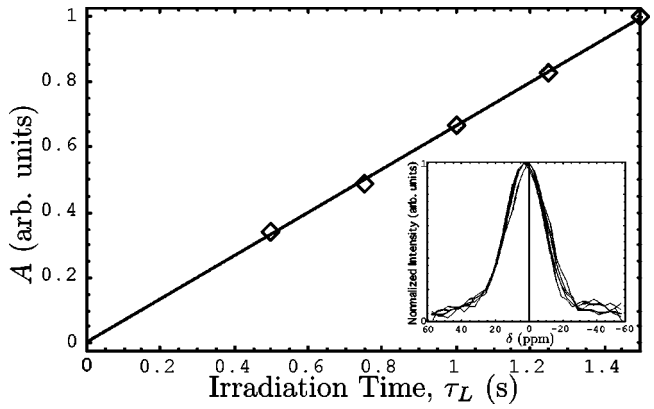

FIG. 6. Short time dependence of A for ^{71}Ga. Photon energy $=1.505$ eV. Temperature $=11$ K. Each datum is the result of signal averaging 500 scans. Inset: NMR spectra collected for this series of irradiation times, normalized and superimposed to show no change in line shape within the noise level. The noisiest spectrum corresponds to the shortest irradiation time. Similar results were observed at other photon energies above 1.505 eV.

with nuclear spin diffusion. Bulk NMR relaxation due to the combination of localized electron-nuclear interaction and nuclear spin diffusion into the bulk has been modeled previously.[24] It was shown that the bulk NMR signal intensity is an exponential function of time at time scales $\tau \gg a^2/D$, where D is the nuclear spin diffusivity and a is the Bohr radius of a defect site. The bulk signal intensity scales with $\sqrt{\tau}$ at short time scales ($\tau \ll a^2/D$) because of the spherical geometry of diffusion, as well as direct interaction between nuclear spins local to the paramagnetic site and the unpaired electron.[24,25] This model thus anticipates three time scales of interest for the present experiments. NMR signals are expected to be nonlinear with irradiation time at short time scales ($\tau_l < a^2/D$), linear at intermediate time scales ($a^2/D \ll \tau_l \ll T_{1,l}$) (due to the linear early-time behavior of the exponential decay function), and nonlinear at longer time scales. Estimating $a \sim 100$ Å (Ref. 26) and $D \sim 3000$ Å^2/s (Refs. 4 and 27), we find $a^2/D \sim 3$ s. Therefore, any signal enhancement that depends upon nuclear spin diffusion from dilute impurity sites should show a nonlinear time dependence for $\tau_l < 3$ s. Figure 6 shows a linear dependence of A on laser irradiation time for τ_l between 0.5 s and 1.5 s, indicating that laser-induced signal enhancements observed in the present experiments are not due to nuclear spin diffusion from dilute impurity sites. A linear growth in signal intensity has been observed previously for even shorter times.[27]

Second, we have observed no shift or broadening of the NMR spectrum, even at the shortest irradiation times measured (inset, Fig. 6), when the NMR signal was ostensibly due to nuclear spins close to paramagnetic sites. Paget showed through optically detected NMR that broadening caused by hyperfine interactions at defect sites should be observable in the NMR spectrum at irradiation times up to 20 s, which is roughly the measured time scale for development of nuclear spin polarization within the defect site itself.[4] In our experiments, even if the NMR signal from nuclei close to paramagnetic centers were broadened beyond

detection, we would expect to have seen the peak gradually shift and narrow into the detection window as nuclear spin polarization diffused away from defect sites. Our bulk-averaged results therefore indicate bulk—rather than localized—nuclear spin alignment; by ''bulk,'' we mean within the illuminated region. In addition, NMR enhancements in our experiments were directly proportional to the laser power up to and including 320 mW. A model relying upon a defect-driven mechanism would be expected to show a nonlinear laser power dependence as the distribution of excited electronic states changes with laser power.[28]

Laser-induced NMR enhancements in bulk GaAs appear to be nonmonotonic in impurity concentration. The lack of enhancements in *p*-type GaAs is an expected result of the efficient Bir-Aronov-Pikus mechanism for thermalization of excited electronic spin.[29] The lack of enhancements in *n*-type GaAs was surprising, since electron spin lifetimes have been shown to be extended in moderately *n*-doped materials.[30] The absence of NMR enhancements in these doped samples suggests that a high concentration of impurities precludes bulk NMR enhancements. At the other extreme, samples that are too pure (undoped MBE-grown layers) do not show NMR enhancements either. For our sample of semi-insulating GaAs, we estimate a carbon acceptor concentration roughly 10^{15} cm^{-3} based on comparison of the room-temperature electron mobility [>6000 $cm^{-2}/(V\,s)$] with the literature.[22] The concentration of EL2 impurities should be on the same order of magnitude. Based on comparison of different GaAs samples, we therefore argue that a model for the observed NMR enhancements must account for the importance of impurities without relying upon localized electron-nuclear cross relaxation.

We propose that the necessity of impurities is to provide paramagnetic centers for storage of excited electronic spin and also that mobile electronic species, such as free excitons, are most effective in polarizing bulk nuclear spins. In the case of semi-insulating GaAs, the specific paramagnetic impurities are likely to be EL2 defects.[31] It is well known that there is strong spin exchange between localized electrons and free excitons,[16] and that impurities extend excited electron spin lifetimes.[18,30] If our argument is correct, a moderate concentration of paramagnetic impurity sites is optimal for the observation of bulk nuclear spin polarizations at high magnetic fields, and the phenomenology described here for semi-insulating GaAs should also be observable in samples of lightly doped ($\sim 10^{15}$–10^{16} cm^{-3}) *n*-type GaAs that exhibit free excitonic luminescence. Excitons in samples that are too pure would quickly lose spin polarization through the electron-hole exchange interaction.[29] Samples with too many impurities may not support free excitons at all,[32] making it difficult for nuclei in the bulk to become spin polarized.

The importance of free excitons could explain the differences in the temperature dependence of enhancements obtained through subband gap and superband gap irradiation (Fig. 3). Electron-nuclear cross relaxation is expected to be strongest if the exciton is in the ground state, because the hyperfine field is expected to drop precipitously as the volume of excitonic states increases.[33] If the laser light populates only higher-order states through superband gap irradiation, NMR signal would only be enhanced if the lowest-order excitonic state is indirectly populated through phonon-assisted spectral diffusion.[17] This process of indirect excitation might explain the thermally activated superband gap NMR enhancements reported in Fig. 3.[17] Superband gap excitation may show stronger NMR enhancements than subband gap excitation by indirectly creating ground-state excitons with athermal momenta and therefore longer lifetimes.[28,40] It is known that free excitonic lifetimes are extended with increasing temperature in the vicinity of 10 K and can also be extended by excitation at higher photon energies.[28] It is important to reiterate that long lifetimes for excited electrons are only beneficial to NMR enhancements if spin lifetimes exceed excited-state lifetimes.[3]

Photoluminescence showed little correlation to NMR enhancements (Fig. 4). This discrepancy could be partially explained by the variable penetration depth of the laser light; strong or weak absorption in a sample that is much thicker than the laser penetration depth would yield the same magnitude of NMR signal, and the intensity features of Fig. 2 must not be overinterpreted.[6] Investigation of a thinner sample (1 μm of thickness would be ideal) would yield a higher-resolution spectrum of NMR enhancements. Still more important could be the distinction between photoluminescence and absorption. The states populated through irradiation at different photon energies may not be well represented by photoluminescence spectra from a sample excited far above the band gap. Dark magnetoexcitonic states, which have the longest lifetimes, may not be detected by photoluminescence at all, though they do become optically active in a magnetic field.[34] It is unclear which type of electronic species is created upon excitation between 1.505 and 1.515 eV. Absorption spectra from the literature do show more broad excitonic features than observed for photoluminescence spectra,[8,35] although 1.505 eV would still appear to be too low for direct excitation of free excitons. Furthermore, it is possible that excitation between 1.505 eV and 1.515 eV may populate delocalized excited states by ionizing electrons from midgap states into the conduction band.[36] Again, penetration depth of the laser light may have exaggerated these NMR intensities, and even a slight absorption from the low-photon-energy edge of the excitonic peak would explain the data.

The temperature dependence of photoluminescence spectra (Fig. 5) is consistent with the temperature dependence of NMR enhancements (Fig. 3). NMR enhancements above 1.50 eV persist to temperatures above 40 K. These high temperatures are above the dissociation temperature of shallow traps. The thermally activated behavior of NMR enhancements through superband gap irradiation is consistent with the nonmonotonic temperature dependence of free excitonic luminescence. The disappearance of NMR enhancements coincides with the loss of excitonic photoluminescence with increasing temperature. While the free electron to carbon acceptor luminescence observed at lower photon energies is expected to persist to higher temperatures,[11] direct excitation of the carbon acceptor did not lead to NMR enhancements that were robust to sample temperature increases.

As a final point, consideration of electron-induced nuclear spin-lattice relaxation rates yielded insights into the nature of the electrons responsible for the NMR enhancements. Nuclear spin relaxation induced by conduction electrons would be expected to result in a Knight shift in the NMR spectrum due to bulk hyperfine fields. Such a shift has been observed in quantum-confined,[37] but not bulk,[3,9] GaAs systems. According to Bloembergen,[38] the relaxation time of nuclei coupled to a nondegenerate electron gas could be estimated by

$$\frac{1}{2T_{1,l}} = 4(2\pi)^{-3/2}\hbar^{-4}v_a^2 A_{fc}^2 m^{*3/2} N(kT)^{1/2}, \tag{2}$$

where v_a is the unit cell volume, A_{fc} is the hyperfine coupling constant through Fermi contact, m^* is the electronic effective mass, and N is the number per unit volume of electrons in the sample. The corresponding Knight shift induced by the same hyperfine coupling is estimated to be[38]

$$\delta_k = \frac{g_e \mu_e}{\hbar \gamma_n} v_a A_{fc} N (kT)^{-1} \frac{\overline{S_z}}{S_0}, \tag{3}$$

where μ_e and g_e are the electronic magnetic moment and Landé g factor [published value -0.44 (Ref. 23)], respectively, and γ_n is the nuclear magnetogyric ratio. The scaling fractor $\overline{S_z}/S_0$ accounts for the nonequilibrium electronic spin polarization excited by polarized light. Using Eqs. (2) and (3), we could not rationalize a conduction-electron-mediated relaxation process with experimental observations: reasonable estimates for N, based on laser power and typical free-electron lifetimes ($\sim$1 ns),[9] could not be rationalized with the measured values for $T_{1,l}$ and the lack of observed Knight shift.[38] However, the same treatment for relaxation due to heavy-hole excitons predicted shorter relaxation times and smaller Knight shifts (below our detection limit) for similar radiative lifetimes due to the larger effective mass of this exciton.[20] We therefore suggest that it is possible for bulk nuclear spins in GaAs to be polarized by direct interactions with mobile excitons without the observation of a Knight shift.

V. CONCLUSION

We have presented new phenomenology in optically enhanced NMR of bulk GaAs. At photon energies below $\sim$1.50 eV, an apparent sign change in the local electronic g factor is suggestive of an interaction with a localized electronic species. At higher photon energies, discrepancies between expectations from previous models and the dependences of the NMR signal on the laser wavelength, temperature, and irradiation time have motivated us to propose that cross relaxation with mobile excitons may be an alternative mechanism for light-induced alignment of bulk nuclear spins. The uniqueness of observed phenomena to semi-insulating GaAs when compared to commercially doped and high-purity GaAs suggests the importance of a moderate concentration of paramagnetic impurities to extend excited electron spin lifetimes. This proposition could be tested by measuring bulk NMR enhancements from samples in which excited electron spin lifetimes are known to be extended by impurities and in which mobile excitons are known to exist. An example of such a sample would be lightly doped (10^{16} cm^{-3}) n-type GaAs.[30]

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[39] In addition to [100] semi-insulating wafers from two other manufacturers, we measured NMR enhancements from a semi-insulating wafer with a [111] surface orientation and another semi-insulating sample mounted so that the unpolished backside of the wafer was exposed to laser light.
[40] Excitonic absorption may also explain the dip in NMR enhancements observed in Fig. 2 at 1.54 eV. Previous workers report that irradiation at this photon energy was necessary to avoid excitation of excitons in semi-insulating GaAs (Ref. 30). At 11 K, we observed a complete loss of NMR enhancements at 1.54 eV, with recovery of signal by tuning the laser just a few meV higher or lower (Fig. 2). As temperature was raised, signal enhancement became nonzero, but 1.54 eV consistently corresponded to a local minimum.