Light-induced hyperfine ^{69}Ga shifts in semi-insulating GaAs observed by optically polarized NMR

Kannan Ramaswamy, Stacy Mui, and Sophia E. Hayes
Department of Chemistry and Center for Materials Innovation, Washington University, St. Louis, Missouri 63130, USA
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We report the observation of ^{69}Ga NMR light induced hyperfine shifts at 6 K in semi-insulating GaAs detected by optically polarized nuclear magnetic resonance in a magnetic field of 4.7 T. The main features of the observed shift are a systematic change in the absolute shift value as the irradiation time is increased, and the sign of the hyperfine shift changes with polarization. The shift dependence on irradiation time can be understood as a combination of the hyperfine interaction of localized electrons with the surrounding nuclear spins and nuclear spin diffusion.

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Optical pumping of a semiconductor results in orientation of the electron spin system which subsequently polarizes the nuclear spins. Nuclear magnetic resonance (NMR) of these polarized spins can be observed with radio-frequency detection (termed "OPNMR")[1–13] or optical detection (termed "ODNMR").[14–21] The ability to manipulate both electron and nuclear spin polarization with light opens up potential applications in spintronics and quantum computing.[22]

In this paper, we report experimental observations of ^{69}Ga hyperfine shifts in bulk GaAs by OPNMR, critical for determining the mechanism of polarization transfer between electron and nuclear spins. Phenomenological models exist[7,12,23,24] that explain experimental observations obtained using OPNMR in bulk GaAs and InP, such as the dependence of optically enhanced NMR signal intensity on magnetic field, illumination time, intensity of light, and the phase of the NMR signal with respect to helicity of light. However, the roles played by localized and delocalized electrons in creating the nuclear polarization are not fully understood. Recent OPNMR experiments in semi-insulating GaAs (Ref. 12) suggest the importance of both types of electrons in creating nuclear polarization. The results reported here highlight the role of localized electrons, evidenced by the temporal evolution of the hyperfine shifts.

We present a model that explains the dependence of the ^{69}Ga shift with illumination time, based on electron-nuclear cross relaxation and nuclear spin diffusion. In metals and semiconductors or in materials containing paramagnetic impurities, a shift in the nuclear Larmor frequency can be observed due to the presence of electrons coupled to the surrounding nuclei through a hyperfine interaction, termed a "Knight shift" for coupling to conduction electrons or "paramagnetic shift" for coupling to an unpaired electron spin at a paramagnetic site.[25] With optical pumping, it is believed that enhanced nuclear polarization results from electron-nuclear cross relaxation due to the hyperfine interaction between the trapped electrons at optically relevant defects (ORD) and the nuclear spins within a Bohr radius of these sites.[16] The electron-nuclear hyperfine interaction which is responsible for the nuclear polarization is also expected to produce a shift in the nuclear Larmor frequency.[25] Nuclear spins in regions outside the Bohr radius are polarized by nuclear spin diffusion.[17] Simulations invoking these two domains of nuclear spins were able to explain experimental observations.[7] Surprisingly, the theoretically predicted shift has not been observed in a number of previous OPNMR investigations of bulk II-VI (Refs. 5 and 9) and III-V semiconductors,[8,10–12] with the exception of one study on InP.[26] A Knight shift has been previously reported via ODNMR alone in bulk GaAs[16,18] and via both OPNMR and ODNMR in quantum confined GaAs systems.[3,21,27]

The material studied is undoped single-crystal semi-insulating GaAs (ITME, Warszawa, Poland). The sample characteristics are: mobility 5630 $\frac{cm^2}{Vs}$, resistivity $2.3 \times 10^7\ \Omega$ cm, and carrier concentration 4.9×10^6 cm^{-3} at room temperature. The growth direction of the wafer is along [100]. Small rectangular-shaped samples were cleaved from a 400 μm thick wafer for the experiment. Typical sample dimensions were 10 mm$\times$3 mm. The sample was cleaned with methanol and attached to a sapphire base using Apeizon type-N grease. The sapphire base was used as a thermal heat sink and also for positioning of the GaAs sample within the NMR coil. The sample's growth direction was parallel to the external magnetic field.

^{69}Ga OPNMR experiments were recorded at a Larmor frequency of 48.09 MHz (B_0=4.7 T). The spectra were recorded at 6 K using a continuous flow liquid helium cryostat (Janis-200 Supertran), outfitted with optical Suprasil quartz windows. The temperature near the sample space was controlled using a temperature controller (Lakeshore, 340S) and was monitored using a Cernox temperature sensor attached near the cryostat's heat exchanger. The data acquisition and processing were carried out using a Tecmag Apollo console.

The ^{69}Ga NMR spectra were collected using sequences consisting of a saturating radio-frequency (rf) train; a period of laser irradiation, τ_L (1-1000s); and a Bloch decay or Hahn spin echo rf pulse sequence followed by signal acquisition.[2] The laser was only shuttered during the saturating train; therefore, the laser was on during the signal acquisition, in contrast to numerous prior OPNMR studies.[3–6,8,9,26] The saturating train consisted of twenty-five $\frac{\pi}{2}$ rf pulses separated by 1 ms. Typical $\frac{\pi}{2}$ pulses were 4.5–6.6 μs, and spin echo delays were 10–50 μs. No significant shift differences were observed between the spin echo and Bloch decay sequences. Data were acquired with a single transient except where noted, and four-step phase cycling was employed when mul-

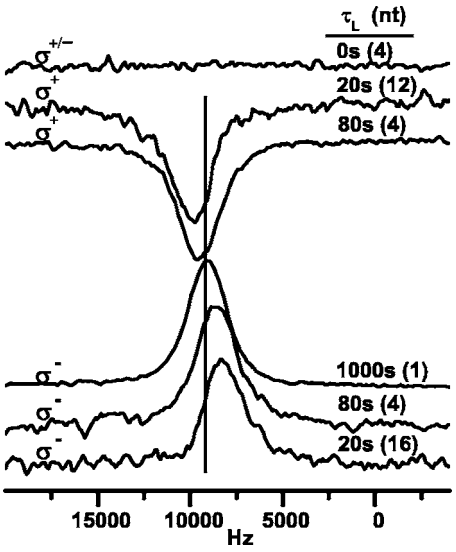

FIG. 1. ^{69}Ga OPNMR spectra. Helicity of the light, illumination time (τ_L), and the number of transients (nt) recorded are indicated on the figure. All spectra were apodized with exponential line broadening of 200 Hz. The black vertical line is a guide at the position of the reference spectrum.

tiple transients were recorded. A Ti:sapphire continuous wave ring laser (Coherent, 899-21) pumped by a Millenia diode laser (Spectra Physics) was used as the excitation source at 1.568 eV (λ=790 nm). (The band gap energy, E_g, is approximately 1.521 eV at 6 K.[28]) The sample was irradiated with the incident beam parallel to the external magnetic field, and the spot size was approximately 5±1 mm, power 2.5 $\frac{W}{cm^2}$. A quarter-wave retarder was used to convert the linearly polarized light into right (σ^+) or left (σ^-) circularly polarized light.

^{69}Ga NMR spectra of semi-insulating GaAs are presented in Fig. 1. All of the spectra are phased with respect to a conventional Bloch decay NMR reference spectrum at 6 K, reflecting the populations determined by Boltzmann statistics at that temperature (spectrum not shown). The OPNMR spectra show a shift with respect to the reference that depends on the length of irradiation, and the sign of the shift is dependent on the helicity of light. The shift in the ^{69}Ga resonance for τ_L=20 s is −0.95 kHz for irradiation with σ^- light and 0.65 kHz for σ^+ light.

The dependence of this shift with irradiation time, τ_L, is depicted in Fig. 2. The ordinate is the frequency offset between the OPNMR spectra and that of the reference spectrum. This shift difference was calculated by comparing the centroids of the two spectra, fit to Lorentzian functions. For both helicities, the frequency offset is greatest for short τ_L and lessens with increasing irradiation time. In addition, the linewidth of the spectra change as a function of τ_L (see inset Fig. 2). Resonances at short τ_L are the broadest, narrowing with increasing τ_L.

NMR signal intensities are proportional to the fractional difference in populations between nuclear spin energy levels. For conventional NMR experiments, these nuclear spin populations are dictated by Boltzmann statistics; therefore, at a given magnetic field, signal intensity can be increased by

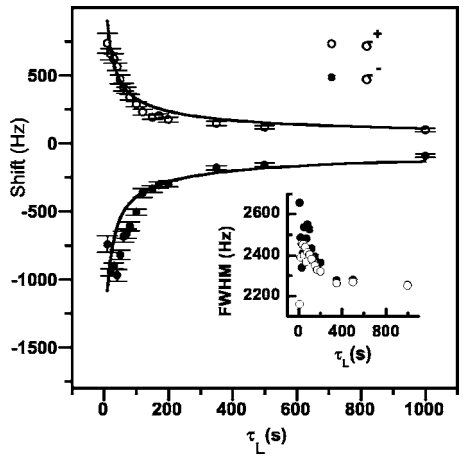

FIG. 2. Experimental and simulated ^{69}Ga OPNMR shift offset. Experimental points obtained with σ^+ light (○), with σ^- light (●). The solid line is the simulated shift offset using Eq. (4). The inset is full width half maximum of the spectra versus τ_L.

lowering the temperature of the sample. In certain semiconductors it is possible to alter the thermal equilibrium Boltzmann distribution by means of polarized light. This is due to deep cooling of the nuclear spin system (~100 mK) by oriented electrons resulting in higher NMR signal intensities.[29] The amount of cooling depends on many factors, among them is the degree of polarization of electron spins. In the following, I and S refer to nuclear spin and electron spin species, respectively.

In the case of semi-insulating GaAs, the average z component of electron spin polarization, $\langle S_Z \rangle$, is given by the following equation when excited by a photon energy, $h\nu < E_g + \Delta$ (where Δ is the spin-orbit splitting):[29,30]

$$\langle S_Z \rangle_{\sigma^{\mp}} = \frac{\pm 0.25}{\left(1 + \frac{\tau_e}{T_{1e}}\right)} + \frac{0.5 S_0}{\left(1 + \frac{T_{1e}}{\tau_e}\right)}. \quad (1)$$

In Eq. (1), τ_e is the electron lifetime, T_{1e} is the electron spin-lattice relaxation time, and S_0 is the thermal equilibrium electron polarization, $S_0 = \frac{-S(S+1)}{3} \frac{g^* \mu_B B_0}{k_B T}$. Both S_0 and T_{1e} are dependent on the external magnetic field, B_0.[14,15] The second term of Eq. (1) tends to dominate with increasing magnetic field. In general, for semi-insulating GaAs under our experimental conditions (T=6 K, B_0=4.7 T), the value of $\frac{\tau_e}{T_{1e}} < 1$ (typical $\tau_e \sim 10$ ns, $T_{1e} \sim 100$ ns).[31] The maximum possible value for $\langle S_z \rangle$ is therefore 0.25 for radiation at E_g.

An electron excited into the conduction band of GaAs by circularly polarized light interacts with the surrounding nuclei, and the Hamiltonian for the interaction is given by[25,27]

$$H = B_0 \mu_B g^* S_z + B_0 \gamma_I I_z^i + \sum_i a_{Ni} \vec{S} \cdot \vec{I}^i. \quad (2)$$

In Eq. (2), $\vec{S}$ and $\vec{I}^i$ are the electron and nuclear spin operators, respectively; μ_B is the Bohr magneton; g^* is the effective g factor, which is −0.44 for conduction electrons in bulk GaAs,[30] $a_{Ni} = \frac{8\pi}{3} \hbar^2 v_0 \gamma_I \gamma_S |\Psi_i(r)|^2$ is the hyperfine coupling

constant for the ith nuclear spin; v_0 is the volume of the unit cell; and $|\Psi_i(r)|^2$ is the electron probability density at the nucleus normalized over the sample volume. The first two terms of the Hamiltonian are the nuclear and electronic Zeeman energies, and the third term is the hyperfine interaction between the electron and nuclear spins. As long as the hyperfine interaction is smaller than the nuclear Zeeman term, it is possible to observe NMR but with a shift determined by the average electronic field at the nucleus.[25] In GaAs nuclear spins are subject to effective magnetic fields from two types of electrons, namely the itinerant electrons in the conduction band and electrons localized at trapping centers. The field created by itinerant electrons is independent of the position of the nucleus, whereas the field due to localized electrons depends on the distance of the nucleus from the localization center.[16] The effect on nuclear polarization due to contact hyperfine interaction of free electrons with the nuclei is negligible and therefore will not be considered in the analysis.

The hyperfine term in Eq. (2) is responsible for dynamic nuclear polarization (DNP). A mechanism invoked in earlier studies[16] treated the source of polarization in GaAs to electrons localized at shallow donor sites (below E_g). It is well known that DNP arises via electron-nuclear cross relaxation[32] that has a characteristic time constant for localized electrons in semiconductors, T_{1r}, given by $T_{1r}=T_1(0)\exp\left(\frac{4r}{a_0^*}\right)$, where $\frac{1}{T_1(0)}=\Gamma_t^{69}\Omega^2\frac{2\tau_c}{1+\omega^2\tau_c^2}=100\ \mathrm{sec}^{-1}$.[17] Γ_t is the probability of occupation of the donor, which we assume here to be equal to 1, ${}^{69}\Omega={}^{69}\gamma b_e$ is the magnitude of the interaction which is responsible for relaxation, b_e is the maximum magnetic field produced by a localized electron at a ^{69}Ga nuclear site, τ_c is the correlation time of the fluctuating electron-nuclear hyperfine interaction, $\hbar\omega$ is the energy required for a simultaneous reversal of both an electronic and a nuclear spin, r is the distance of the nuclei from the ORD, and a_0^* is the Bohr radius of the localized electron. $b_e(0)$ is the magnetic field created by the electrons trapped at the ORD. For ^{69}Ga nuclei in GaAs, b_e is ~ -130 G (-133 kHz).[16]

In Ref. 16 DNP is ascribed to electrons localized at shallow donor sites populated with photons at energies just below the band gap. In the data reported here, a frequency shift is observed for electron states populated by photon energies in excess of the band gap energy. We posit that electrons become localized at a state when pumped above some threshold energy; such localized states can be described by the wave function $\Psi(r)=\sqrt{\frac{v_0}{\pi a_0^{*3}}}u_{\vec{k}=0}(r)e^{-r/a_0^*}$ where $u_{\vec{k}=0}$ is the $\vec{k}=0$ Bloch state. The frequency shift (in kHz) in the ^{69}Ga NMR spectra due to the contact hyperfine interaction with these localized electrons is given by ${}^{69}\nu_S(r)=-133\langle S_z\rangle\Gamma_t e^{-2r/a_0^*}$.[7,16] The sign of ${}^{69}\nu_S(r)$ depends on the sign of $\langle S_z\rangle$ arising from the different spin angular momentum of the polarizing photon as observed here. The time evolution of the average z component of DNP, $\langle I_Z(r,\tau_L)\rangle$, at a given distance, r, from the ORD can be calculated from the following equation:[6,17]

$$\frac{\partial\langle I_Z(r,\tau_L)\rangle}{\partial\tau_L}=D\nabla^2\langle I_Z(r,\tau_L)\rangle-\frac{[\langle I_Z(r,\tau_L)\rangle-I_\infty]}{T_1(r)}. \quad (3)$$

In Eq. (3), I_∞ is the steady state nuclear polarization, which is given by $I_\infty=\frac{I(I+1)}{S(S+1)}[\langle S_Z\rangle-S_0]$, and D is the isotropic nuclear spin diffusion coefficient. We have calculated a value of $D=2300\ \frac{\text{Å}^2}{sec}$ for ^{69}Ga in the present study, based on previously reported values for ^{75}As and ^{71}Ga.[6,17]

We have fit the variations in hyperfine shift with respect to laser illumination time (see Fig. 2) by numerical resolution of Eq. (3) for $\langle I_Z(r,\tau_L)\rangle$ using appropriate boundary conditions.[7] The NMR signal arises initially from hyperfine-coupled nuclear spins surrounding the ORD site and at longer irradiation times from spins located remotely, polarized through nuclear spin diffusion. The observed signal is a weighted average of these two domains asymptotically approaching the bulk value at long irradiation times. This result is significant because it supports previous experiments where spin diffusion was utilized to explain the intensity of the NMR spectra with respect to τ_L.[9,10] We have incorporated spin diffusion into our model as a result of the variation of the observed ^{69}Ga NMR resonance with irradiation time.

In order to calculate this weighted average and the corresponding NMR chemical shifts, it is necessary to know the relative number of nuclear spins that experience each type of interaction. First, we consider the volume over which the electron wave function extends to determine the hyperfine-coupled species.[6,7] We computed the number of gallium species in a face-centered-cubic lattice to give the radial distribution of ^{69}Ga nuclear spins, $N(r)$, at a distance, r, from the ORD. The distribution of gallium sites has a $51r^2$ dependence, obtained from numerical computation; therefore, $N(r)=0.60\times 51r^2$, where 0.60 is the natural abundance of ^{69}Ga. The average nuclear magnetization $\langle M_Z(r,\tau_L)\rangle$ at a distance r from the ORD is given by $\langle M_Z(r,\tau_L)\rangle={}^{69}\gamma\hbar N(r)\times\langle I_Z(r,\tau_L)\rangle$. Therefore the observed shift in the NMR spectra can be given as follows:

$$\langle\nu_S(\tau_L)\rangle=\frac{\sum_r\langle M_Z(r,\tau_L)\rangle{}^{69}\nu_S(r)}{\sum_r\langle M_Z(r,\tau_L)\rangle}. \quad (4)$$

The best match was obtained for $\langle S_Z\rangle$ values of -0.10 (for σ^+), and 0.14 (for σ^-), where $\frac{\tau_e}{T_{1e}}=0.8$. Such differences in the average electron spin polarization are possible when $\frac{\tau_e}{T_{1e}}$ is on the order of 1, such that the second term of Eq. (1) also contributes to $\langle S_Z\rangle$.

The source of electron spin polarization with optical pumping has been the subject of some debate, since free electrons are present for irradiation $\geqslant E_g$. However, even if all the photogenerated carriers behave as free electrons, the magnetic field produced will be much less than 1 G. It has been shown experimentally that the hyperfine magnetic field produced by $\sim 10^{15}$ fully oriented free electron spins in InSb, which has a stronger hyperfine interaction compared to GaAs, is 1 G.[33] Furthermore, the fact that the shift changes

with increasing illumination time cannot be accounted for by invoking free electrons; the shift due to free electrons should be independent of illumination time.

In summary, our results indicate that the observation of a hyperfine shift in bulk semi-insulating GaAs is possible using OPNMR under suitable conditions. In addition, the shift is dependent on the helicity of light, reflecting the sign of the z component of the polarized electron spins. We have presented a quantitative model of OPNMR that utilizes the hyperfine interaction, between localized electrons and surrounding nuclei, and nuclear spin diffusion. At short irradiation times, the observed chemical shift is dominated by the hyperfine interaction due to nuclear relaxation caused by the electrons trapped at the ORD. This is the case for which nuclear spin states populated by spin diffusion are not contributing significantly to the observed signal. At longer τ_L times, spin diffusion must be introduced, and those nuclear spins begin to dominate the observed spectra. Our results give compelling evidence that the hyperfine shift is due to localized, and not itinerant, electrons. These observations of hyperfine shifts in bulk GaAs will contribute to a better understanding of the mechanism of optical pumping.

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[1] G. Lampel, Phys. Rev. Lett. **20**, 491 (1968).
[2] S. E. Barrett, R. Tycko, L. N. Pfeiffer, and K. W. West, Phys. Rev. Lett. **72**, 1368 (1994).
[3] S. E. Barrett, G. Dabbagh, L. N. Pfeiffer, K. W. West, and R. Tycko, Phys. Rev. Lett. **74**, 5112 (1995).
[4] T. Pietrass, A. Bifone, T. Room, and E. L. Hahn, Phys. Rev. B **53**, 4428 (1996).
[5] T. Pietrass and M. Tomaselli, Phys. Rev. B **59**, 1986 (1999).
[6] P. L. Kuhns, A. Kleinhammes, T. Schmiedel, W. G. Moulton, E. Hughes, S. Sloan, P. Chabrier, and C. R. Bowers, Phys. Rev. B **55**, 7824 (1997).
[7] C. R. Bowers, Solid State Nucl. Magn. Reson. **11**, 11 (1998).
[8] C. A. Michal and R. Tycko, Phys. Rev. B **60**, 8672 (1999).
[9] I. J. H. Leung and C. A. Michal, Phys. Rev. B **70**, 035213 (2004).
[10] A. K. Paravastu, S. E. Hayes, B. Schwickert, L. N. Dinh, M. Balooch, and J. A. Reimer, Phys. Rev. B **69**, 075203 (2004).
[11] A. Goto, K. Hashi, T. Shimizu, R. Miyabe, X. Wen, S. Ohki, S. Machida, T. Iijima, and G. Kido, Phys. Rev. B **69**, 075215 (2004).
[12] A. K. Paravastu and J. A. Reimer, Phys. Rev. B **71**, 045215 (2005).
[13] A. S. Verhulst, I. G. Rau, Y. Yamamoto, and K. M. Itoh, Phys. Rev. B **71**, 235206 (2005).
[14] V. I. Berkovits, A. I. Ekimov, and V. I. Safarov, Sov. Phys. JETP **38**, 169 (1974).
[15] M. I. D'yakonov and V. I. Perel', Sov. Phys. JETP **38**, 177 (1974).
[16] D. Paget, G. Lampel, B. Sapoval, and V. I. Safarov, Phys. Rev. B **15**, 5780 (1977).
[17] D. Paget, Phys. Rev. B **25**, 4444 (1982).
[18] S. K. Buratto, D. N. Shykind, and D. P. Weitekamp, Phys. Rev. B **44**, 9035 (1991).
[19] G. P. Flinn, R. T. Harley, M. J. Snelling, A. C. Tropper, and T. M. Kerr, Semicond. Sci. Technol. **5**, 533 (1990).
[20] J. A. Marohn, P. J. Carson, J. Y. Hwang, M. A. Miller, D. N. Shykind, and D. P. Weitekamp, Phys. Rev. Lett. **75**, 1364 (1995).
[21] S. W. Brown, T. A. Kennedy, D. Gammon, and E. S. Snow, Phys. Rev. B **54**, R17339 (1996).
[22] B. E. Kane, Nature (London) **393**, 133 (1998).
[23] A. Patel, O. Pasquet, J. Bharatam, E. Hughes, and C. R. Bowers, Phys. Rev. B **60**, R5105 (1999).
[24] R. Tycko, Mol. Phys. **95**, 1169 (1998).
[25] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1961).
[26] C. A. Michal and R. Tycko, Phys. Rev. Lett. **81**, 3988 (1998).
[27] M. Eickhoff, S. Fustmann, and D. Suter, Phys. Rev. B **71**, 195332 (2005).
[28] M. B. Panish and H. C. Casey, J. Appl. Phys. **40**, 163 (1969).
[29] F. Meier and B. P. Zakharchenya, *Optical Orientation* (North-Holland, New York, 1984).
[30] C. Weisbuch and C. Hermann, Phys. Rev. B **15**, 816 (1977).
[31] I. Zutic, J. Fabian, and S. Das Sarma, Rev. Mod. Phys. **76**, 323 (2004).
[32] A. W. Overhauser, Phys. Rev. **92**, 411 (1953).
[33] A. Willig and B. Sapoval, Solid State Commun. **11**, 1077 (1972).