Proc. 29th Int. Conf. Low Temperature Physics (LT29)
JPS Conf. Proc. **38**, 011185 (2023)
https://doi.org/10.7566/JPSCP.38.011185

Optical Pumping NMR and Optically Induced Nuclear Spin-Spin Couplings in Semiconductors: Double Resonance NMR Experiments under Light Illumination

Atsushi GOTO[1*], Kenjiro HASHI[1], Shinobu OHKI[1], and Tadashi SHIMIZU[1]

[1]*National Institute for Materials Science, Tsukuba 305-0003, Japan*

**E-mail: GOTO.Atsushi@nims.go.jp*

(Received July 14, 2022)

The two optical effects on the nuclear spins in semiconductors, i.e., hyperpolarization by optical pumping and optically induced nuclear spin-spin coupling, are discussed in connection with their possible applications in NMR quantum computation. In the latter part of the paper, the results of the double resonance NMR experiments used to elucidate the characteristics of the effects, i.e., cross polarization and spin echo double resonance, are described along with their implications.

KEYWORDS: Nuclear Magnetic Resonance, Optical Pumping, Hyperpolarization, Compound Semiconductors, NMR quantum computation.

1. Introduction

As a platform for scalable NMR quantum computers, semiconductors possess favorable features such as well-established nano-fabrication methods for constructing architectures, and long nuclear spin relaxation times of the order of hours favorable for long coherence times [1]. In addition, it is also an important aspect that nuclear spins are controllable by optical means. Optical pumping NMR allows us to create hyperpolarized nuclear spins, which serve as initialized nuclear-spin qubits [2,3]. The scheme is beneficial in that, after the completion of the initialization, the photo-excited electrons can be extinguished by simply shutting off the light.

For the two-qubit operations, nuclear spin-spin couplings are required [1,4,5,6,7]. In general, there are two types of couplings in solids: nuclear dipolar (direct) and electron-mediated (indirect) couplings. The direct couplings are *ubiquitous*, hence they should be intentionally turned off when the two-qubit gates are off. This may require dipolar decoupling/recoupling schemes. By contrast, the indirect couplings are off by default in undoped semiconductors since there are no electrons that mediate the couplings, while they can be created optically; the couplings that emerge upon light illumination are called “optically induced nuclear spin-spin couplings” [8,9]. This feature adds another benefit on the semiconductor-based NMR quantum computation.

The optically induced coupling was first manifested in cross polarization (CP) experiments in undoped GaAs under the optical pumping condition [8]. Recently, this

phenomenon was confirmed in spin echo double resonance (SEDOR) experiments, where the change in the echo decay rate ($1/T_2$) upon light illumination was observed and attributed to the change in the heteronuclear spin-spin couplings [9]. The CP and SEDOR methods are both double resonance NMR schemes that provide us with the information on the couplings between hyperpolarized nuclei. Here, we discuss the optical effects on the nuclear spin systems in semiconductors, mainly focusing on the double resonance NMR experiments used to elucidate the characteristics of the effects. For the detailed experimental setups for the experiments shown here, refer to Ref. [10].

2. Optically induced effects on the nuclear spins in semiconductors

2.1 Optical Pumping NMR

Since its discovery by Lampel in 1968 [11], optical pumping NMR has been recognized and utilized as an effective hyperpolarization method for semiconductors. The process of the optical pumping NMR is as follows [2,3]. The circularly polarized light with the photon energy corresponding to the band gap of the semiconductor excites electrons from the valence bands to the conduction band at the Γ-point, resulting in polarized electrons at the bottom of the conduction band. At low enough temperatures (typically below a few tens of Kelvins), the lifetime of the excited electrons can be shorter than the spin relaxation time, so that net electron spins remain during the excitation-recombination processes. This "net" electron polarization is transferred to nuclear spins. Since the photo-excited electrons are not actively controlled in this transfer process, it proceeds slowly; it takes minutes or even hours to complete the polarization transfer. By contrast, in most of the dynamic nuclear polarization schemes the electron spin states are controlled by microwave irradiation and the transfer proceeds much faster.

Figure 1 shows an example of the optical pumping NMR for undoped GaAs, where the ^{71}Ga signal was measured after the illumination of the circularly polarized (σ^+) light with the photon energy corresponding to the band gap of the undoped GaAs at 10 K (~ 1.5 eV). The negative enhancement of the ^{71}Ga signal reflects the fact that the nuclear spins are polarized in the opposite direction to those in the thermal equilibrium state.

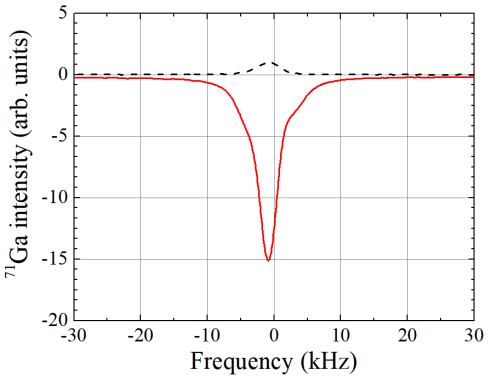

Fig. 1. Solid line: optical pumping NMR spectrum of ^{71}Ga in undoped GaAs measured after the 2-min illumination of infrared light (σ^+, 826 nm, 120 mW). $\omega/2\pi$ = 121.9762 MHz, H_0 = 9.39 T and T = 10 K. Dashed line: ^{71}Ga spectrum measured in the dark.

2.2 Optically induced nuclear spin-spin couplings

The conditions for the emergence of the optically induced nuclear spin-spin couplings are similar to those for the optical pumping, i.e., they emerge under the illumination of the light with the photon energy close to the band gap [8,9]. With

increasing the light power, the couplings become more intense, and reach farther. Although the mechanism of the couplings has not yet been fully elucidated, the couplings may be mediated by optically excited electrons. The indirect couplings in metals are known as the Ruderman-Kittel interaction [12], which has an oscillatory nature as a function of the distance between the two nuclear spins of interest. The optically induced couplings may have a similar nature, but the oscillation period would depend on the light power.

3. Double resonance experiments under light illumination

3.1 Cross-polarization (CP) experiments under light illumination

The optically induced nuclear spin-spin couplings were first discovered in the CP experiments between ^{71}Ga and ^{75}As in undoped GaAs under the optical pumping condition [8]. The ^{75}As polarization built up due to the optical pumping effect during the light illumination for 60 s was transferred to ^{71}Ga in the cross-polarization process under the light illumination. The ^{71}Ga polarization showed a transient oscillation as a function of the contact time, and its peak position changed with increasing the light power. Roughly speaking, the time at which the peak is formed corresponds to the cross-relaxation time T_{IS}^{opt}, which is directly related to the optically induced heteronuclear indirect coupling J_{IS}^{opt}. That is, the cross-relaxation time is expresses as,

$$1/T_{IS}^{\mathrm{opt}} = \frac{\sqrt{\pi}}{4} M_2^{IS} \tau_c, \qquad (1)$$

where τ_c is the correlation time of the CP and,

$$M_2^{IS} = \frac{1}{3} I(I+1) \sum \left(2\pi J_{IS}^{\mathrm{opt}}\right)^2, \qquad (2)$$

is the second moment of the *I*–*S* heteronuclear spectrum due to J_{IS}^{opt}. Figure 2 shows a simple simulation for the transient oscillations. As J_{IS} is increased, the peak position of the oscillation shifts toward shorter contact time as expected from Eqs. (1) and (2).

In the actual experiments, several peaks appeared one after another with increasing the light power, and their positions shifted toward shorter contact time. Each of these peaks was attributed to a specific nearest-neighbor group: the first nearest neighbor, the second nearest neighbor, etc. This observation indicates that the reach of the optically induced nuclear spin-spin coupling expands with increasing the light power.

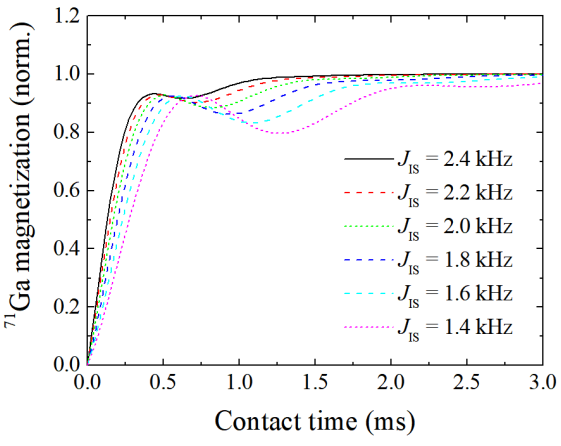

Fig. 2. A simple simulation for the cross-polarization experiments in GaAs with different heteronuclear coupling (J_{IS}). For simplicity, the CP correlation time is assumed to be constant.

3.2 Spin echo double resonance (SEDOR) experiments under light illumination

The cross-polarization experiments shown above revealed qualitative characteristics of the heteronuclear couplings. To understand the overall picture of the couplings including the homonuclear ones, we invoked spin echo decay experiments under light illumination [9]. Here, the ^{71}Ga spin echo signal was measured with the two-pulse sequence: P1(π/2) – t_1/2 - P2(π) – t_1/2 - echo, where P1(π/2) and P2(π) are the first and the second pulses and t_1 is the short delay time. The decay rate $1/T_2$ was determined from the t_1-dependence of the echo intensity. In the SEDOR experiments, an additional π pulse for ^{75}As [P3(π) pulse] was applied concurrently with the P2(π) pulse for ^{71}Ga. The P3 pulse served as a switch for the heteronuclear couplings (^{75}As-^{71}Ga); i.e., both the homo- (^{71}Ga-^{71}Ga) and hetero-nuclear (^{75}As-^{71}Ga) couplings contribute to the decay with the P3 pulse (spin echo double resonance: SEDOR), while only the homonuclear (^{71}Ga-^{71}Ga) couplings contributed to the decay without the P3 pulse (standard spin echo decay) [13]. Hence, by comparing these two cases, the contributions from the homo- and heteronuclear couplings can be distinguished. These experiments were performed under the two light powers of 34 and 68 mW at the sample surface with the spot size of approximately φ5 mm, as well as in the dark. Figure 3 shows an example of the SEDOR experiments under the light illumination. The oscillatory behavior of the peak intensity was observed as a function of the short delay time, which is due to the quadrupolar interaction. By taking this oscillatory behavior into account, the decay time (T_2) was determined.

The SEDOR experiments showed that the decay rate ($1/T_2$) decreased with increasing the light power, which indicates that the sum of the homo- and hetero-nuclear couplings decreased. On the other hand, the standard spin echo decay experiments showed that the change in the decay rate ($1/T_2$) was insignificant compared to that of the SEDOR experiments, which indicates that the change in the homonuclear couplings is small. That is, it is the heteronuclear coupling (^{71}Ga-^{75}As) that decreased with increasing the light power. From these results along with those of the CP experiments shown above [8], it was concluded that, in this range of the light power (below 68 mW), the coupling reaches only the ^{75}As spins at the first nearest neighbor sites. The decrease of the heteronuclear coupling (^{71}Ga-^{75}As) is the consequence of the cancellation between the photo-induced and the dipolar couplings, i.e., the signs of these couplings are opposite to each other.

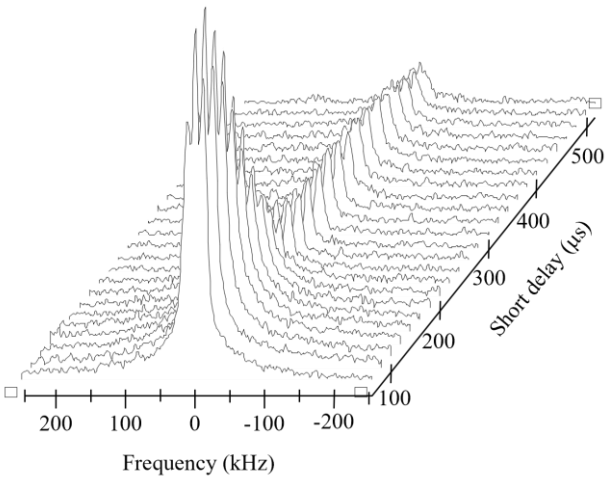

Fig. 3. Short delay time dependence of the ^{71}Ga spectrum measured with the SEDOR sequence after the 5-min illumination of the infrared light (σ^+, 826 nm, 68 mW). $\omega/2\pi$ = 121.9739 MHz, H_0 = 9.39 T and T = 10 K.

4. Conclusion

We have discussed the two distinct optical effects on the nuclear spin systems in semiconductors, i.e., the hyperpolarization by optical pumping and the optically induced nuclear spin-spin couplings, both of which emerge when the light with the photon energy corresponding to the band gap is illuminated. These two effects will be key ingredients of the scalable NMR quantum computers expected to be built on semiconductors in the future. In the elucidation of the characteristics of the optically induced couplings, the double resonance NMR such as CP and SEDOR played essential roles, which proved that the double resonance NMR is a powerful tool to investigate nuclear spin-spin couplings.

Acknowledgments

The experiments shown here were performed with the technical assistance provided by the staff of the NMR station of NIMS. This work was partially supported by JSPS KAKENHI (Grant Number 21K18897).

References

[1] B. E. Kane: Nature **393**, 133 (1998).
[2] R. Tycko and J. A. Reimer: J. Phys. Chem. **100**, 13240 (1996).
[3] S. E. Hayes, S. Mui and K. Ramaswamy: J. Chem. Phys. **128**, 052203 (2008).
[4] I. L. Chuang, N. Gershenfeld and M. Kubinec: Phys. Rev. Lett. **80**, 3408–3411 (1998).
[5] J. A. Jones, and M. Mosca: J. Chem. Phys. **109**, 1648 (1998).
[6] L. M. K. Vandersypen, M. Steffen, G. Breyta, C. S. Yannoni, M. H. Sherwood and I. L. Chuang: Nature **414**, 883 (2001).
[7] A. Goto, T. Shimizu, K. Hashi, H. Kitazawa and S. Ohki: Phys. Rev. A **67**, 022312 (2003).
[8] A. Goto, S. Ohki, K. Hashi and T. Shimizu: Nat. Commun. **2**, 378 (2011).
[9] A. Goto, S. Ohki, K. Hashi and T. Shimizu: npj Quant. Inf. **8**, 59 (2022).
[10] A. Goto, S. Ohki, K. Hashi and T. Shimizu: Jpn. J. Appl. Phys. **50**, 126701 (2011).
[11] G. Lampel: Phys. Rev. Lett. **20**, 491 (1968).
[12] M. A. Ruderman and C. Kittel: Phys. Rev. **96**, 99 (1954).
[13] C. P. Slichter: *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, Heidelberg, New York, 1990) 3rd ed., Chap. 7.21, p. 311.