

Proton polarization with *p*-terphenyl crystal by integrated solid effect on photoexcited triplet state

M. Iinuma^{a,*}, Y. Takahashi^a, I. Shaké^{a,1}, M. Oda^{a,2}, A. Masaike^{a,3},
T. Yabuzaki^a, H.M. Shimizu^b

^a Department of Physics, Faculty of Science, Kyoto University, Kyoto 606-01, Japan

^b Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-10, Japan

Received 5 April 2005; revised 25 April 2005

Available online 25 May 2005

Abstract

We have carried out the experiments for polarizing protons in single crystals of *p*-terphenyl doped with 0.1 mol% pentacene. The experiments have been performed in a magnetic field of 3 kG at room temperature or at 77 K. We obtained the polarization of 1.3% for protons in bulk at room temperature by using a pulsed dye-laser with the wavelength of 590 nm, the average power of 150 mW, and the repetition rate of 50 Hz. The polarization at 77 K reached 18% by irradiation with the dye-laser of 500 mW, 50 Hz and the same wavelength. The polarization of protons was measured by the neutron transmission method also. The result was consistent with that measured by the nuclear magnetic resonance.

© 2005 Elsevier Inc. All rights reserved.

PACS: 76.70.Fz; 76.60.-k; 33.25.+k

Keywords: Proton polarization; Photoexcited triplet state; Dynamic nuclear polarization; Integrated solid effect; MIONP; *p*-Terphenyl

1. Introduction

Dynamic nuclear polarization (DNP) is a conventional technique for highly polarizing nuclear spins [1,2]. For studying magnetically ordered nuclear spins in solid state physics [1], or utilizing as a polarized solid target in particle and nuclear physics [3,4], the technique has been applied to various types of solid. Recently, by

efforts of many researchers on quantum computation using nuclear magnetic resonance (NMR), the DNP is attracting attention as a method for improvement of NMR sensitivity in multi-qubits system [5,6]. The great enhancement of NMR signal has also stimulated NMR researches in chemical or biological fields, including, for example, high resolution NMR that are of vital importance for structure analysis of molecules or biopolymers [7].

Methods for the dynamic polarization of protons have been studied extensively, and the resulting highly polarized spin systems are now well understood. In these methods, organic materials [8,9] or ammonia [10] are doped with a small amount of paramagnetic centers. They are irradiated with microwaves in a magnetic field of 25–50 kG at a temperature of 0.3–1.0 K to transfer a polarization of the electrons in the paramagnetic centers to nearby proton spins by the “solid effect.” However,

* Corresponding author. Present address: ADSM, Hiroshima University, 1-3-1, Kagamiyama, Higashi-Hiroshima 739-8530, Japan. Fax: +81 824 24 7018

E-mail address: iinuma@hiroshima-u.ac.jp (M. Iinuma).

¹ Present address: NTT Network Innovation Laboratories, 1-1 Hikari-no-oka, Yokosuka 239-0847, Japan.

² Present address: Sanyo Micro-electronics Laboratories, 180 Ohmori, Anpachi-cho 503-0116, Japan.

³ Present address: JSPS Washington Office, Suite 920, 1800 K Street N.W., Washington, DC 20006, USA.

the “solid effect” is not effective in a low magnetic field or at a high temperature, because the linewidth of electron spin resonance (ESR) is larger than the energy difference between magnetic sublevels of the nucleus. The electron polarization in thermal equilibrium, which is used as a ‘seed’ of the polarization, is not large at high temperature and in low magnetic field. Moreover, the paramagnetic centers then rapidly relaxes the nuclear polarization under such condition to prevent growth of the polarization in a DNP.

In 1988, Henstra et al. [11] proposed a new method for transferring the polarization efficiently in the low magnetic field, “Integrated Solid Effect” (ISE), in which the magnetic field is swept during irradiation with microwaves. In order to get the proton polarization in low magnetic field at high temperature, they also applied the ISE to the polarization transfer on a photoexcited triplet state of pentacene ($C_{22}H_{14}$), which is called “microwave-induced optical nuclear polarization” (MIONP) [12]. Aromatic molecules have a property of a spontaneous alignment of electron spins on the photoexcited triplet state, which provides the electron polarization. The polarization of 0.5% was obtained for protons in a crystal of naphthalene ($C_{10}H_8$) doped with pentacene at room temperature by using a pulsed N_2 -laser ($\lambda = 337$ nm) [12].

To improve the polarization in the crystalline naphthalene, we proposed that the crystal should be cooled down to temperature less than around 250 K, because a slow molecular motion, which is a dominant relaxation process in the naphthalene crystal, can be suppressed at temperature lower than around 250 K [13]. The relaxation rate around room temperature increases significantly with an increase in the laser power, because the relaxation due to the slow molecular motion is very sensitive to the temperature. We reported a great improvement of the proton polarization with the cooled single crystal of naphthalene doped with pentacene (0.001 mol%) by using the pulsed dye-laser, which has the wavelength of 595–605 nm and a long pulse width (800 ns), instead of the pulsed N_2 -laser [14]. The obtained polarization was 32% at 77 K in 3 kG and persisted for a surprisingly long time, 166 m, in a magnetic field close to zero. Some other groups have also obtained high proton polarization at 100 K by irradiating with such long pulse of visible light [6,15,16].

Except for the naphthalene molecule, a *p*-terphenyl ($C_{18}H_{14}$) molecule is a good candidate as a host molecule, because a single crystal of pure *p*-terphenyl have remarkable features for performing this type of the DNP. The concentration of pentacene molecules in the *p*-terphenyl crystal is 10 times as high as that in the naphthalene crystal. It means that a buildup rate of the polarization is practically larger than one in the naphthalene crystal. In addition, the relaxation rate of protons in the pure *p*-terphenyl crystal decreases at high-

er temperature and little changes even if the temperature varies around room temperature [17]. Higher polarization of protons is expected, especially, at room temperature in comparison with that obtained in the naphthalene crystal. However, no experiments are yet to be carried out with *p*-terphenyl crystals doped with pentacene.

In this paper, we report the experimental studies on the DNP in the single crystal of *p*-terphenyl doped with pentacene (0.1 mol%) at room temperature or at 77 K in 3 kG. The polarization of 1.3% was achieved at room temperature by using the pulsed dye-laser with the wavelength of 590 nm, the average power of 150 mW, and the repetition rate of 50 Hz. This value is the highest polarization at room temperature so far. However, we have found that the relaxation rate becomes larger with an increase of the laser power. At 77 K, the polarization of 18% was obtained pumping by the dye-laser of 500 mW, the same wavelength and repetition rate. The proton polarization was measured not only by the NMR but also by the neutron transmission. Preliminary results have been reported in [14].

2. Principle

The DNP is performed on the photoexcited triplet state of pentacene molecules, which play the same role as in the naphthalene crystal [12,14]. On the photoexcited lowest triplet state T_0 of pentacene molecules, the populations of the Zeeman sublevels $|+1\rangle$, $|0\rangle$, and $|-1\rangle$ are 12, 76, and 12%, respectively [18]. The population difference of the electrons on T_0 is transferred to protons in pentacene and *p*-terphenyl by means of the ISE, in which the external field is swept in irradiation with microwaves simultaneously. Pentacene decays from T_0 into the ground state with the decay constant of about 20 μ s [19]. Since the electron spin–lattice relaxation time is longer than the decay time of T_0 , it is expected that the influence of the electron spin relaxation to the proton spin is small. It is noticed that the population difference on the triplet state depends on the direction of the magnetic field. The field is needed to be aligned parallel to the long molecular axis of pentacene for the occurrence of such population difference.

The maximum proton polarization is determined by the balance between the buildup rate and the relaxation rate of the polarization. In general, the time evolution of the polarization is given as the phenomenological formula

$$\frac{dP_p}{dt} = A(P_e - P_p) - \Gamma(P_p - P_{pth}), \quad (1)$$

where P_p is the proton polarization, P_e the electron polarization, and P_{pth} the proton polarization in thermal equilibrium. A is the buildup rate of the polariza-

tion, and Γ the relaxation rate. This formula means that the proton polarization approaches the electron polarization P_e with the buildup rate A , whereas it has a tendency to decay spontaneously to the thermal polarization P_{pth} with the relaxation rate Γ . The following relations are derived from Eq. (1).

$$P_p = P_{p0}(1 - \exp(-(A + \Gamma)t)), \quad (2)$$

where

$$P_{p0} = \frac{A}{A + \Gamma} P_e. \quad (3)$$

Here P_{pth} is neglected, since P_{pth} is quite small, that is 10^{-6} at room temperature in 3 kG. In order to obtain high proton polarization, the buildup rate should be large and the relaxation rate should be small.

The buildup rate can be written as

$$A \propto C\alpha(\lambda) \frac{E}{S} \beta \varepsilon R, \quad (4)$$

where $\alpha(\lambda)$ is the optical absorption coefficient of pentacene at the wavelength of λ , R the repetition rate, and ε the transfer rate of polarization from an electron to a proton for every sequence. C is the concentration of pentacene, β the transition rate from the first excited singlet state to the lowest triplet state, E the energy of the laser pulse, and S the area of the laser beam on the crystal. Methods for an increase of the buildup rate include an increase of the pulse energy of the laser beam and the concentration of pentacene and an use of the laser optimized for the wavelength.

3. Experiment

3.1. Sample

A pure *p*-terphenyl crystal has a feature of changing the crystal structure at 193 K. The molecular rotation is most active at this temperature, so that the relaxation rate of protons becomes maximum at 193 K [17,21,20]. The relaxation time at room temperature is longer than that at 193 K and about 8 min in 46 kG [17]. The crystal, whose space group is $P2_1/a$ at higher temperature than 193 K, has site A and site B. In the pentacene-doped crystals, one *p*-terphenyl molecule on site A or site B is replaced with one pentacene molecule. In order to prepare pentacene-doped crystals we made a crystal growth by the typical Bridgeman technique after the *p*-terphenyl were purified by recrystallization and zone melting.

Typical concentration of pentacene in *p*-terphenyl crystals is 0.1 mol%, whereas it is 0.01 mol% in naphthalene crystals. The relaxation time of protons in the *p*-terphenyl crystal is shorter than that in the naphthalene crystal [12,14]. However, in higher temperature region than 193 K, it does not become shortening even if the temperature rises [17]. Therefore, it is expected that high

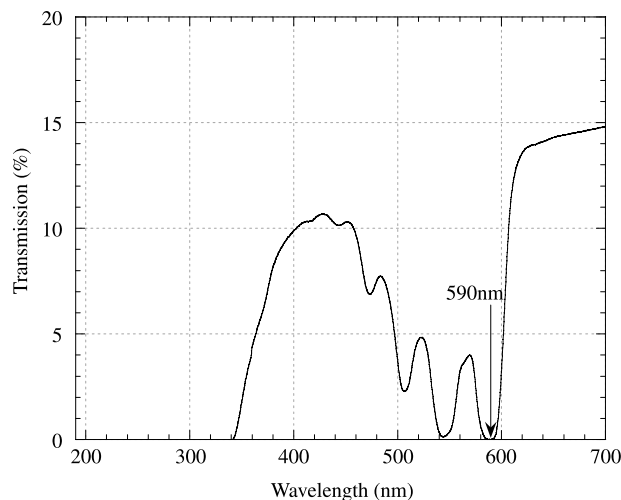


Fig. 1. Absorption spectrum in a single crystal of *p*-terphenyl doped with pentacene at room temperature: the thickness of the crystal was 2.2 mm. The spectrum was obtained with the spectrophotometer (Shimadzu, MPS-2000).

polarization is obtained at room temperature if a powerful laser beam is used as a pumping beam.

Typical absorption spectrum of a sample is shown in Fig. 1. A large absorption of ultraviolet rays by *p*-terphenyl molecules does not allow the excitation of only pentacene molecules. The wavelength for the most efficient excitation was found to be 590 nm at room temperature. At 77 K, a width of the dips in absorption is narrower than that at room temperature and the dip position can be generally shifted. The absorption curve of the crystals at 77 K showed that the shift was negligibly small. The laser whose wavelength is approximately 590 nm is most suitable for exciting pentacene molecules at 77 K and at room temperature.

3.2. Experimental apparatus

3.2.1. Pulsed laser

A pulsed laser is advantageous over a CW laser because pumping by the CW laser reduces the population difference between the Zeeman sublevels on the lowest triplet state. The populations of the Zeeman sublevels $|+1\rangle$, $|0\rangle$, and $|−1\rangle$ in excitation of pentacene by the CW laser are calculated to be 30.6, 38.8, and 30.6, respectively. For an increase of the population on T_0 , the pulse width longer than the decay time of S_1 to the ground state (~ 20 ns) and shorter than the decay time of T_0 ($\sim 20 \mu\text{s}$) is preferable, where the S_1 is the first excited single state of pentacene [14]. In this experiment, we used the pulsed dye-laser with the pulse width of about 800 ns (Cynosure, Model LFDL-3) as well as in the experiments of naphthalene crystals. The maximum energy per one pulse is 10 mJ and the maximum repetition rate is 50 Hz. The wavelength is valuable from 590 to 605 nm.

3.2.2. ESR system

The experimental apparatus is the same as in the experiments with naphthalene crystals [13]. A synthesized sweep generator was used as a microwave source. The output power was 63 mW and the frequency was tuned to the resonance frequency of the cavity, which was 9.3 GHz without a sample, but slightly shifted in presence of the sample. By monitoring the ESR signals, the direction of pentacene molecule could be adjusted. The way for the adjustment is similar to in the naphthalene experiments [13]. Typical linewidth of the ESR spectrum is about 30 G.

3.2.3. ISE system

The ISE system is also same as in the naphthalene experiments. The CW microwaves were pulsed with a diode switch and the pulse width was longer than 10 μ s. They were amplified by a TWT power amplifier with the gain of 39.4 dB. A typical power of the pulsed microwaves was about 30 mW.

The magnetic field was swept with the internal coil in the cavity. The maximum drive current for the field sweep was chosen to be ± 25 A, which corresponded to ± 21 G. The time width of the field sweep was about 10 μ s. The ISE system and the laser system were synchronized with the trigger pulse.

3.2.4. NMR system

We measured the proton polarization with a conventional pulsed NMR system, which could detect a signal of the free induction decay (FID). The frequency of the RF pulse was 12.95 MHz and the power of RF pulses was adjusted with attenuators and the RF power amplifier. The pulse width of the 90° pulse was 1.8 μ s.

The amplitude of FID just after applying the 90° pulse ($t = 0$) corresponds to the area of NMR spectrum, which is proportional to the proton polarization. In order to obtain the absolute value of the polarization, we detected the FID signal in thermal equilibrium. The comparison of the enhanced signal with that in the thermal equilibrium could be done without complicated shape analysis, since the shape of both the FID signals were similar even the sizes were so much different.

The relaxation time of the protons T_{1p} is measured by following two methods. One is to obtain the decay time of the polarization from the decay curve measured by using the weak RF pulse after the DNP. The other one is to measure the recovery time of the polarization from zero to the thermal value by using the 90° pulse. The second one could be applied without performing the DNP.

We also checked the linearity of the receiver. The dynamical range for the measurement of FID signals is about 10^4 . The signal enhancement higher than 10^4 could be detected by using the 90° pulse and the weak RF pulse.

4. Experimental results

4.1. Experiments with NMR

In single crystals of pure *p*-terphenyl, the relaxation time of proton spins at room temperature does not become short, even if the temperature rises around room temperature. Therefore, it is expected that the increase in temperature by the optical absorption of high power laser beam does not induce a strong relaxation to proton spins. In the experiments with *p*-terphenyl crystals, we achieved the polarization of 1.3% at room temperature with the dye-laser of 590 nm, 150 mW, and 50 Hz after only 1 h. This polarization corresponds to the enhancement of 13,000, which is 10 times as high as the one in naphthalene crystal with the dye-laser of 595 nm and 100 mW [14]. The relaxation time of protons in presence of the dye-laser of 150 mW, 590 nm, and 50 Hz was 7.6 min, which was similar to the one in naphthalene crystal by using the same laser of 100 mW and 595 nm. The improvement is ascribed to the fact that the *p*-terphenyl crystals can be doped with pentacene of 10 times higher concentration than that in naphthalene crystals.

However, we could not obtain higher polarization by irradiation with the laser power higher than 150 mW, because the relaxation time was shortened with such laser power. Fig. 2 shows a plot of the relaxation rates obtained from the measured decay curve at room temperature as a function of the laser power. They have a tendency to increase with higher laser power. This is in disagreement with the expectation.

We studied the relation between the relaxation rate and the temperature in two different conditions. In

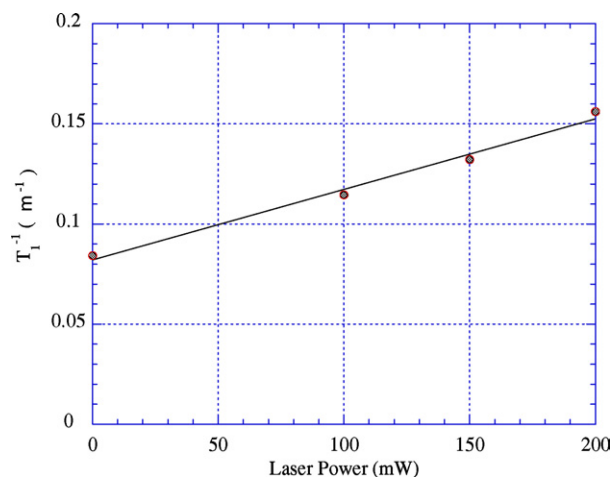


Fig. 2. Laser power dependence of the relaxation rate of protons in a crystal of *p*-terphenyl doped with 0.1 mol% pentacene in 3 kG at room temperature with the pulsed dye-laser of 590 nm. The measurement of the relaxation rate was performed after polarizing protons by the DNP. The data were fitted to the linear function shown by the solid line.

Fig. 3, the relaxation rates in thermal equilibrium without performing the DNP are shown with the marks of solid circles. These values were given as the recovery time from zero to the thermal value. In the same figure, the relaxation rates in the identical sample, but after polarizing protons by the DNP, are also plotted with the marks of open squares. These values were obtained from the decay curve of polarization after polarizing to 0.1%. Both measurements covered temperature region higher than 300 K. Fig. 3 shows that the relaxation rates without performing the DNP around room temperature do not enlarge with an increase in temperature. This result is consistent with our expectation. However, the relaxation rates after the DNP tend to increase significantly as the temperature is rising in the temperature region higher than 300 K. This behavior is different from the expectation and a main reason why the irradiation with higher laser power does not lead to higher polarization at room temperature. In the temperature region from 200 to 300 K, the relaxation rates after the DNP decrease at higher temperature, which are the same behavior as ones without the DNP.

To improve the polarization, therefore, cooling the sample down to temperature less than 193 K is effective. $1/T_1$ in a pure crystal is about $1/30 \text{ m}^{-1}$ at 77 K [17]. The polarization at 77 K in the crystal doped with 0.1 mol% pentacene reached about 18% after 2 h irradiation with the pulsed dye-laser of 590 nm, 500 mW, and 50 Hz. The relaxation time measured by the NMR was 33 m. With higher power laser, the improvement of the polarization at 77 K is promising, because the relaxation rate was not changed in presence of the irradiation with the current laser.

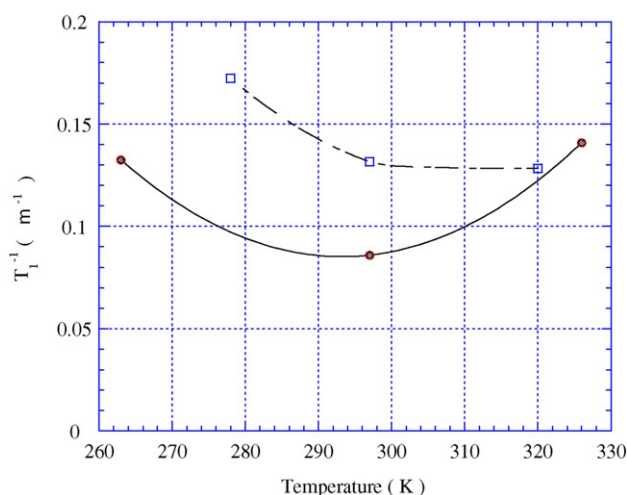


Fig. 3. Temperature dependence of the relaxation rate of protons in the crystal of *p*-terphenyl doped with pentacene in 3 kG. The solid circles show the experimental results for polarized protons after getting the polarization of about 0.1% by the DNP. The open squares show the results in thermal equilibrium without the DNP.

It is interesting to consider the unexpected behavior of the relaxation rates. There is a possibility that the temperature dependence of the relaxation rates in pentacene molecules is different from the one in *p*-terphenyl molecules. In the low temperature region, the temperature dependence of pure *p*-terphenyl crystals might be dominant, whereas in the high temperature region, it seems that the dependence in pentacene molecules is dominant, if we assume that the observed signals are mainly from pentacene's protons after the DNP.

4.2. Measurements by neutron transmission

The proton polarizations at 77 K were measured by the neutron transmission in the crystal. The values can be compared to the ones obtained by the NMR measurement.

In low energy neutron–proton scattering, the scattering cross-section for the neutron whose spin is parallel to the proton spin σ_{para} is 10 times as large as the one whose spin is anti-parallel to the proton spin σ_{antipara} . The polarization of protons can be determined from the neutron transmission in the polarized crystal [16,22,23].

We carried out the experiments in the cold neutron beam line SAN at KEK-KENS. The energy of the neutron was 1–3 meV and the beam intensity was $2 \times 10^4 / \text{cm}^2/\text{s}$. The beam was collimated to be $0.6 \text{ cm} \times 0.3 \text{ cm}$ at the filter with two collimators made of cadmium. The crystals were 0.8 cm high, 0.5 cm wide, and 0.3 cm in thickness. They were put in a quartz-glass dewar which was filled with liquid nitrogen.

First, the protons in the *p*-terphenyl crystal immersed in liquid nitrogen were polarized with the pulsed dye-la-

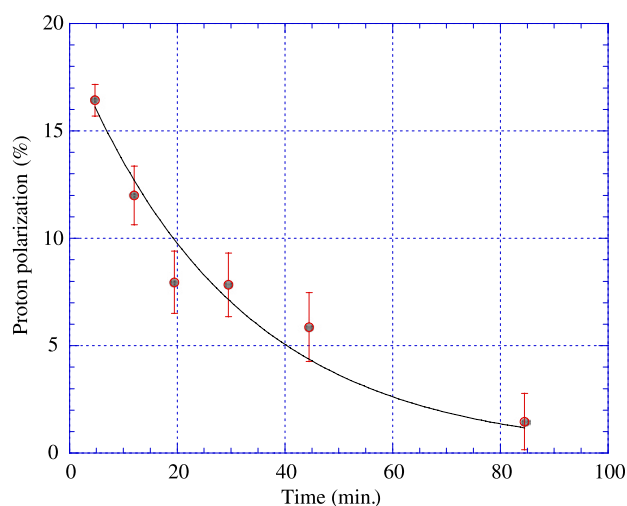


Fig. 4. Proton polarization in *p*-terphenyl in 3 kG at 77 K as a function of time measured by the neutron transmission method. The solid line shows the curve fitted to an exponential function. The proton polarization and the relaxation time were $18.9 \pm 1.2\%$ and $30.0 \pm 5.5 \text{ m}$, respectively.

ser of 500 mW. After irradiation with the laser beam and microwaves for about 2 h, we measured the decay curve of the neutron transmission without presence of the microwaves and the laser beam. In order to obtain the proton polarization, the transmission of the unpolarized neutron through the unpolarized target is necessary. It was obtained through the extrapolation of the decay curve on the transmission of unpolarized neutrons. The relaxation time of protons was measured in the field of 3 kG. The proton polarization as a function of time is shown in Fig. 4. From this curve, the initial polarization was determined to be $18.9 \pm 1.2\%$ and the relaxation time of 30.0 ± 5.5 m was obtained. The values are consistent with ones by the NMR.

5. Conclusion

We have carried out the experiments to polarize protons in single crystals of *p*-terphenyl doped with 0.1 mol% pentacene by using the pulsed dye-laser. The experiments were performed in the magnetic field of 3 kG at room temperature or at 77 K.

Although the laser power dependence of the relaxation rates in the crystal is not so strong as that in naphthalene crystal at room temperature, the laser beam has to be optimized for the power. We obtained the proton polarization of 1.3% at room temperature with the pulsed dye-laser of 590 nm, 150 mW, and 50 Hz. The polarization of 18% was obtained at 77 K with the dye-laser of 590 nm, 500 mW, and 50 Hz.

The proton polarization obtained at 77 K was also measured by the neutron transmission using neutrons with the energy of 1–3 meV. The polarization and the relaxation time are consistent with those by the NMR measurements.

To obtain higher proton polarization, the optimization of the pentacene concentration and the power of the dye-laser is necessary at room temperature, whereas a more powerful laser is useful at 77 K.

Acknowledgments

We are grateful to Professor N. Hirota and Professor M. Terazima for useful discussion and their helpful comments on the method of the crystal growth and the photoexcited state of pentacene. We are also thankful for Dr. Abe to give his help for establishment of the crystal growth. We thank Professor M. Furusaka, Dr. T. Oku, and Mr. Y. Ogawa for their supports on neutron transmission experiment. This work is partially supported by the Grant-in-Aid for Scientific Research of the Ministry of Education of Japan under the Program Nos. 04244101 and 06220202. One of the author (M.I.) is supported by Fellowship of the Japan Society

for the Promotion of Science for Japanese Junior Scientists.

References

- [1] A. Abragam, M. Goldman, Nuclear Magnetism: Order and Disorder, Clarendon Press, Oxford, 1982.
- [2] C.D. Jeffries, Dynamic Nuclear Orientation, Interscience Publishers, New York, 1963.
- [3] S. Ishimoto, S. Hiramatsu, S. Isagawa, K. Morimoto, A. Mसाike, A spin-frozen polarized target of proton and deuteron, Jpn. J. Appl. Phys. Pt. 1 Regular papers and short notes 28 (1989) 1963–1972.
- [4] S. Ishimoto et al., Slow neutron polarization by longitudinally polarized proton filter, JJAP Lett. 25 (1986) L246–L248.
- [5] See, for example M.A. Nielsen, I.L. Chuang, Quantum Computation and Quantum Information, Cambridge University Press, Cambridge, 2000.
- [6] K. Takeda, K. Takegoshi, T. Terao, Dynamic nuclear polarization by electron spins in the photoexcited triplet state: I. Attainment of proton polarization of 0.7 at 105 K in naphthalene, J. Phys. Soc. Jpn. 73 (2004) 2313–2318.
- [7] M. Mehring, High Resolution NMR in Solids, Springer-Verlag, New York, 1983.
- [8] A. Mसाike, H. Glattli, J. Ezratty, A. Malinovski, High proton polarization at 0.5 K, Phys. Lett. Sect. A 30A (1969) 63–64.
- [9] S. Mango, Ö Run lfsson, M. Borghini, A butanol polarized proton target, Nucl. Instrum. Methods 72 (1969) 45–50.
- [10] T.O. Niinikoski, J.-M. Rieubland, Dynamic nuclear polarization in irradiated ammonia below 0.5 K, Phys. Lett. Sect. A 72A (1979) 141–144.
- [11] A. Henstra, P. Dirksen, W.Th. Wenckebach, Enhanced dynamic nuclear polarization by the integrated solid effect, Phys. Lett. Sect. A 134 (1988) 134–136.
- [12] A. Henstra, T.-S. Lin, J. Schmidt, W.Th. Wenckebach, High dynamic nuclear polarization at room temperature, Chem. Phys. Lett. 165 (1990) 6–9.
- [13] M. Iinuma, I. Shaké, R. Takizawa, M. Daigo, H.M. Shimizu, Y. Takahashi, A. Mसाike, T. Yabuzaki, High proton polarization in crystalline naphthalene by dynamic nuclear polarization with laser excitation at room temperature and liquid nitrogen temperature, Phys. Lett. Sect. A 208 (1995) 251–256.
- [14] M. Iinuma, Y. Takahashi, I. Shaké, M. Oda, A. Mसाike, T. Yabuzaki, H.M. Shimizu, High proton polarization by microwave-induced optical nuclear polarization at 77 K, Phys. Rev. Lett. 84. (2000) 171–174.
- [15] K. Takeda, K. Takegoshi, T. Terao, Dynamic nuclear polarization by electron spins in the photoexcited triplet state: II. High polarization of the residual protons in deuterated naphthalene, J. Phys. Soc. Jpn. 73 (2004) 2319–2322.
- [16] M. Iinuma, Y. Takahashi, I. Shaké, M. Oda, A. Mसाike, T. Yabuzaki, H.M. Shimizu, High proton polarization at high temperature with single crystals of aromatic molecules, Nucl. Instrum. Methods Phys. Res. Sect. A 529 (2004) 199–203.
- [17] K. Kouda, N. Nakamura, H. Chihara, Proton magnetic relaxation study of phase transition in crystalline *p*-terphenyl, J. Phys. Soc. Jpn. 51 (1982) 3936–3941.
- [18] D.J. Sloop, T.-L. Yu, T.-S. Lin, S.I. Weissman, Electron spin echoes of a photoexcited triplet: pentacene in *p*-terphenyl crystals, J. Chem. Phys. 75 (1981) 3746–3757.
- [19] A.J. Van Strien, J. Schmidt, An ESR study of the triplet state of pentacene by electron spin-echo techniques and laser flash excitation, Chem. Phys. Lett. 70 (1980) 513–517.

- [20] B. Toudic, J. Gallier, P. Rivet, H. Calteau, Critical slowing down of fluctuations in *p*-terphenyl and *p*-quaterphenyl observed by proton spin–lattice relaxation, *Solid State Commun.* 47 (1983) 291–295.
- [21] T. Gullion, M.S. Conradi, A. Rigamonti, Critical proton and deuteron spin–lattice relaxation at the phase transition in *p*-terphenyl, *Phys. Rev. B* 31 (1985) 4388–4393.
- [22] V.I. Lushchikov, Y.V. Taran, F.L. Shapiro, Polarized proton target as a neutron polarizer, *Sov. J. Nucl. Phys.* 10 (1970) 669–677.
- [23] S. Hiramatsu et al., Slow neutron polarization by polarized proton filter using ethylene glycol, *J. Phys. Soc. Jpn.* 45 (1978) 949–953.