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Development of closed-cycle dynamic nuclear polarization system for small-angle neutron scattering and neutron reflectometry

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We develop a closed-cycle dynamic nuclear polarization (DNP) system for spin-contrast-variation (SCV) small-angle neutron scattering (SANS) and neutron reflectometry (NR) to increase the use of these techniques. Compared with our cryogen-filled DNP system, the closed-cycle system is made compact and can change the sample in a comparable time-scale, but achieved proton-polarization is only 11.2 and 20±3% for bulk and thin-film samples, respectively, whereas 32–37% is achieved with the cryogen-filled system. This is because cooling power of the recycling cold helium gas in the closed-cycle system is lower than that of superfluid helium in the cryogen-filled one. In order to improve the polarization with the closed-cycle system, we have to improve thermal contact between the sample and cold helium gas to minimize microwave heating of the sample.

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1. Introduction

Spin contrast variation (SCV) is a technique to determine structure of composite materials using polarized neutrons and proton-polarized sample [1]. Since coherent scattering length of thermal and cold neutrons for protons remarkably depends on relative direction of their spins, the scattering profile of polarized neutrons for soft materials such as polymers and biological systems, which are composed mainly of hydrogen, varies as a function of the proton-polarization P_H. Multiple form and structure factors of these composite materials can be determined from the multiple polarized-neutron scattering profiles measured at different P_Hs. Such multiple form and structure factors of composite materials have been determined by deuterium contrast variation, which utilize the difference in neutron scattering length between proton and deuterium, so far. However, this technique is tightly limited to the samples whose partially-deuterated simulation samples having the same morphology can be prepared. In contrast, SCV opens the way to determine the structure unless the deuterated simulation samples are prepared. The goal of our study is to establish the SCV as a general technique to determine structure of composite materials.

Small-angle neutron scattering (SANS) using the SCV technique is firstly demonstrated by Knop et al. in 1989 [2], but have not been used as a general technique so far. We consider that it is mainly due to poor usability of dynamic nuclear polarization (DNP) system for the proton polarization of the samples. In general SANS measurements of soft materials, plural number of samples in a sample changer are measured in succession within a few hours. In contrast, it takes days to change the sample in a dilution refrigerator of the DNP apparatus in Ref. [2]. van den Brandt et al. [3] developed a compact DNP system for SANS, which enables changing the sample within 2 hours by omitting the dilution refrigerator. Following their basic design, we have developed a DNP system for the SANS-J diffractometer at Japan Research Reactor (JRR-3) and TAIKAN (BL15) at the Materials and Life Science Experimental Facility (MLF) in Japan Proton Accelerator Research Complex (J-PARC), and then carried out SCV-SANS measurements [4-7]. However, our first-made cryogen-filled DNP system is still large and tough to operate for the people who do not have a special skill of cryogenics. As shown in Figure 1, we have to carry-in and set such large system including the cryogen injection and pumping systems, and refill liquid helium more than 80 liter everyday. Due to such low usability and high running cost, the system cannot be served as a shared device for external users in neutron facilities.

In order to overcome the problem, we are developing a closed-cycle DNP system for SCV-SANS and SCV neutron reflectometry (NR). This system is compact including helium circulation system and does not consume any cryogen. Matsuki et al. [8] developed a low running cost and long-term stable closed-cycle solid-state DNP-NMR system, which promotes

Figure 1: Cryogen-filled DNP system carried in J-PARC MLF.

broader application of the DNP technique. Pierce et al. [9] developed a closed-cycle DNP system for neutron protein crystallography. We believe that our closed-cycle DNP system will make the SCV technique as a commonly usable technique for structure determination of composite materials. In this paper, we report the development of the system.

2. Experiment

Figure 2 (a) shows our closed-cycle DNP system. It is built by inserting a DNP cell, mounting the letter-size microwave (94 GHz, VCSS GDO-10-9417F, Keycom MPA95GHz-01) and NMR (143 MHz) curcuits, and connecting their controllers and detectors in a single rack to the closed-cycle split-pair transverse magnetic field superconducting magnet and cryostat (Cryogenic Ltd.). The sample in the cell is cooled by splaying cold helium gas that is recondensed by the cryocooler of the magnet (Sumitomo 415D) [10]. The sample can be changed by pulling the cell above the gate valve on the magnet while keeping cryogenic temperature in the insert.

Figure 2 (b) is the seal-type aluminum DNP cell (Cell b) for SCV-SANS measurement. The microwave is guided through a 6 mm-inner diameter stainless cylindrical waveguide to the cell with 24 mm-long, 30 mm-wide, and 8 mm-thick inner volume. In (c), the flat cover of the Cell b is replaced to a perforated plate with thickness of 0.5 mm and bore diameter of 1 mm, which is smaller than half wavelength the 94 GHz microwave (1.6 mm), to introduce the cold helium gas into the cell while sealing the microwave (Cell c). The cell in (d) having aluminum radiator plates at the front, rear, and bottom covers is for the SCV-NR measurement (Cell d) [10]. The microwave is guided through the WR-28 cupronickel rectangular waveguide to the cell with 20 mm-long, 20 mm-wide, and 5 mm-thick inner volume.

Using the NMR circuit, we measure P_H of 20 mm-long, 20 mm-wide, and submillimeter-thick bulk polystyrene (PS) sample doped with 33 mM 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO), which is the model sample for the SCV-SANS measurements, in Cells b and c. We also measured NMR signal of the bulk PS sample enclosed in Cell d as a reference for tuning the

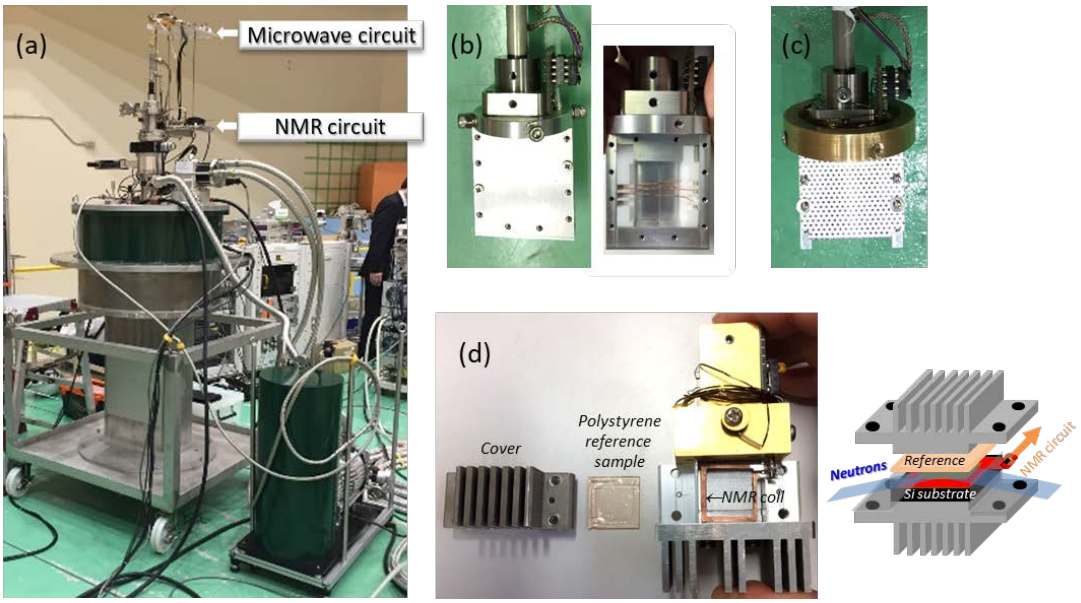

Figure 2: (a) Closed-cycle DNP system [10], (b) Cell b for SCV-SANS, (c) Cell c for SCV-SANS, and (d) Cell d for SCV-NR [10].

DNP condition. The sample for the SCV-NR measurement is submicrometer-thick poly(styrene-*block*-polyisoprene) (PSPI) film sample, which is spin-coated on a 20 mm-long, 20 mm-wide, 3 mm-thick single crystalline Si substrate adhered to the aluminum radiator plate at the inner wall of the cell, and sealed in Cell d with the bulk PS reference sample. Since the thin-film sample is too thin to measure with the NMR system, we determine P_H from the variation of the oscillation period in the SCV-NR profile that is measured at J-PARC MLF BL17(SHARAKU) [10].

3. Results

Figure 3 shows P_H of the bulk PS sample in the Cells b, c, and d as a function of microwave power at the exit of the microwave power amplifier of the closed-cycle DNP system. P_H increases with increasing the microwave power up to 6.8% at 200 mW in Cell b, 11.2% at 200 mW in Cell c, and 9.3% at 600 mW in Cell d but it decreases with the power above due to microwave heating of the sample. P_H decreases with increasing temperature T according to the increase of the spin-lattice relaxation rate. It should be stressed that these values are remarkably smaller than P_H of the thin-film PSPI sample in Cell d [10]. The maximum P_H of the thin-film PSPI is twice as high as that of bulk PS.

Figure 4 compares the maximum P_H using the closed-cycle and cryogen-filled DNP systems. As shown by the results of the cryogen-filled DNP system at 1.1 K, the P_H values of bulk PSPI and bulk PS are close to each other as long as they are set to the same environment. This result indicates that the remarkable difference in P_H between thin-film PSPI and bulk PS is not due to difference in chemical component but due to that in environment.

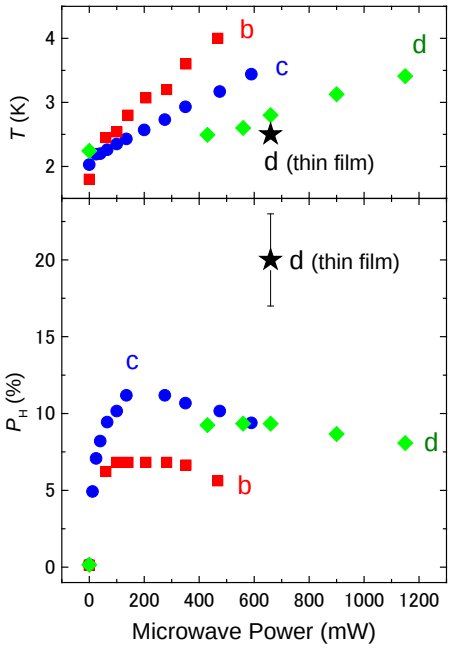

Figure 3: Temperature of the cells and P_H of the bulk PS in Cell b (square), c (circle), d (diamond) and thin-film PSPI in Cell d (star) [10] as a function of microwave power of the closed-cycle DNP system.

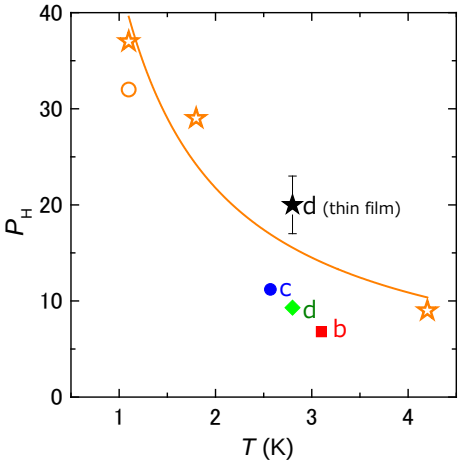

Figure 4: Filled symbols, P_H of bulk PS in Cell b (square), c (circle), d (diamond) and thin-film PSPI in Cell d (star) [10] of the closed-cycle DNP system; Open symbols, P_H of bulk PS (circle) [11] and bulk PSPI (star) [6] with curve fit using $P_H \propto 1/T$ relation.

4. Discussion

We consider that temperature of the bulk PS sample in the closed-cycle DNP system becomes remarkably higher than that of the cold helium gas in the cryostat due to poor thermal contact with the cell wall and cold helium gas. P_H in Cell c is higher than that in b, because cold helium gas is directly introduced inside the sample cell. Following the idea, P_H of the thin-film sample is higher than that of the bulk one in Cell d, because the heat of the thin-film sample is more effectively removed through the Si substrate and the adhered radiator plate than the bulk one whose cooling rate is limited by poor thermal conduction of the helium gas sealed inside of the cell. Such temperature gradient is not expected in the cryogen-filled system because of enough heat conduction of liquid helium especially below superfluid transition temperature. The P_H value of the thin-film sample in the closed-cycle system is close to or even better than that of the bulk samples expected at 2.2 K in the cryogen-filled system. This result suggests that the microwave heating of the thin-film sample in the closed-cycle DNP system is effectively removed due to the ideal thermal contact with the radiator. In contrast, P_H of the bulk samples in the closed-cycle system is lowered by the poor thermal conduction. It can be increased by improving thermal contact among the bulk sample, cell wall, and the spraying cold helium gas in the cryostat.

5. Summary

Using the close-cycle DNP system, we achieved P_H = 11.2 and 20 ± 3 % of the bulk and thin-film samples for SCV-SANS and SCV-NR measurements, respectively. In the closed-cycle system, effective removal of microwave heating of the sample with the spraying cold helium gas is essential to achieve higher P_H, whereas temperature of the sample is kept equal to that of superfluid helium in the cryogen-filled system. We are currently developing a new DNP cell for bulk samples which improves the thermal contact among sample, cell, and the spraying cold helium gas.

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