



Improvement of a Time-of-Flight Spectrometer AGNES at JRR-3 Using Supermirror Techniques

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(Received May 21, 2024; accepted July 1, 2024; published online August 21, 2024)

AGNES is a direct geometry chopper-type time-of-flight neutron spectrometer installed at the cold neutron guide (C3-1-1) of JRR-3 (Tokai, Japan). This instrument is well-suited for studies on low-energy excitations of powdered and amorphous samples, and quasi-elastic scattering with an energy resolution of 120 μeV (standard mode) or 50 μeV (high-resolution mode). During the long shutdown period of JRR-3 due to the Great East Japan Earthquake in 2011, AGNES was significantly improved through the installation of supermirror-coated neutron guide tubes and collimator, installation of a new-type top-loading cryo-furnace, and renewal of data acquisition electronics and software. As a result, the neutron intensity has increased by 7.7 times in the standard mode and by 3.2 times in the high-resolution mode. These enhancements facilitate experiments with small amounts of samples, and under special environments, which have previously been challenging.

1. Introduction

Neutron scattering is a technique that can measure dynamics in a time scale of about 6 orders of magnitude, ranging from 0.1 ps to 100 ns.^{1–3)} Only backscattering and spin echo instruments can measure the region of more than 100 ps, but many instruments based on various principles can measure the region below 100 ps. In this time region, there exist various relaxation phenomena such as diffusion of liquids, jump motions of ions and molecules in solids, and rotational motions of segments and side chains of polymers. These are observed as quasi-elastic neutron scattering (QENS), corresponding to broadening of elastic scattering peaks. Of course, inelastic neutron scattering (INS) is also observed by these instruments. These are generally referred to as low-energy excitations ($E < 10$ meV), such as phonon and magnetic spin excitations.

AGNES⁴⁾ (Angle-focusing cold neutron spectrometer) is a chopper spectrometer installed at the most upstream beam-line of the C3 cold guide of JRR-3 (JAEA, Tokai). This instrument was built by Shibata and Kajitani in 1995.⁴⁾ This article will introduce the structure and performance of AGNES, focusing on the improvement which was conducted during the long shutdown period after the Great East-Japan Earthquake in 2011.

2. Structure of AGNES

Figure 1 shows overview photo and schematic drawing of the structure of AGNES. Neutrons with a wavelength of 4.22 Å (for the standard mode) or 5.50 Å (for the high-resolution mode) are selected by an array of five PG(002) monochromators and pulsed by a Fermi chopper rotating at a rate of 6400 rpm (standard mode) or 8770 rpm (high-resolution mode). The anti-frame-overlap chopper which rotates at a half rotation speed is used only for the high-resolution mode. The pulsed neutrons are irradiated to a sample and the scattered neutrons are detected by 328 ³He tube detectors arranged in a wide detector bank covering scattering angles of 10–130°. The time of the flight from the chopper to detectors (ca. 2.4 m) is measured by time

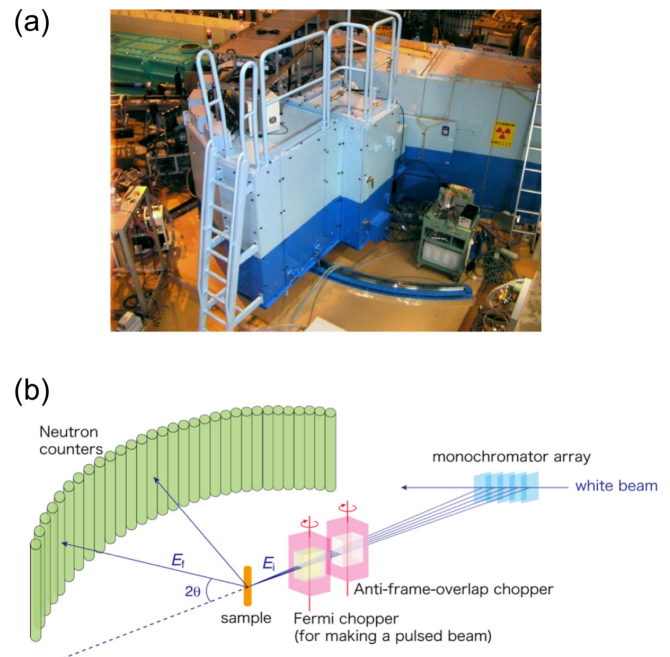


Fig. 1. (Color online) (a) Overview photo and (b) schematic drawing of the structure of AGNES.

analyzers with a resolution of 4 μs (standard mode) or 2 μs (high-resolution mode). From the neutron counts as functions of time-of-flight t_f and scattering angle 2θ , the dynamic structure factor $S(Q, E)$ is obtained. The energy transfer E and the momentum transfer Q are calculated by the following equations:

$$k_i = (2m_n E_i)^{1/2} / \hbar \quad (1)$$

$$k_f = m_n L / \{ \hbar (\Delta t_i + t_f - t_e) \} \quad (2)$$

$$E = \hbar^2 (k_f^2 - k_i^2) / (2m_n) \quad (3)$$

$$Q^2 = k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta \quad (4)$$

Here, k_i and k_f are the incident and scattered wave numbers. m_n is the mass of a neutron, E_i is incident energy of neutrons

Table I. Spec of AGNES.

	STD mode	HR mode
Monochromator angle/deg	78	110
Wavelength/Å	4.22	5.50
Energy range/meV	−4–20	−2–6
Energy resolution/μeV	120	50
Q -range/Å ^{−1}	0.2–2.7	0.15–2.1
Beam size/cm	4 (vertical) × 2 (horizontal)	
T -range/K	0.7–800	

(fixed by monochromators), $\hbar$ is the reduced Planck constant, L is the distance between the sample and detector, Δt_i is the time required for the flight for the distance L , t_e is the time-of-flight for the elastic scattering.

The energy resolution, energy range, and Q range in the standard mode and high-resolution mode are listed in Table I. In the future, we plan to use a Mica(002) monochromator ($\lambda = 8$ Å) to measure with an energy resolution of about 15 μeV.

Experiments suitable for AGNES include: 1) Low-energy excitations of powder and amorphous samples, 2) quasi-elastic scattering with an energy resolution of 120 or 50 μeV, corresponding to the relaxation with a time scale of 0.5–100 ps, and 3) in-situ experiments under special environments such as high-pressure (liquid: <500 MPa, gas: <200 MPa), gas atmosphere (any gas), and light-irradiation (UV etc.).

3. Improvement of AGNES during the Long Shutdown Period of JRR-3

During the shutdown period of JRR-3 due to the East Japan Earthquake, the C3 guide tube of JRR-3 and collimator of AGNES were replaced with those attached with $3Q_c$ supermirrors. We also installed a new top-loading cryostat (which can cool down to 3 K in 3 h), and upgraded the high-speed chopper, detector circuit, and measurement control system. In this chapter, we will discuss the significant increase in intensity due to the supermirror and the performance of the new cryostat.

3.1 Installation of supermirror-coated neutron guide tube and collimator

As shown in Fig. 2(a), the C3 guide tube in JRR-3 consists of a 15 m upstream bent guide tube for fast neutron rejection and an 11 m downstream straight guide tube. For both of these, the previous normal guide tubes whose inside surface is coated with Ni were replaced with $3Q_c$ supermirror guide tubes (Mirrotron, Hungary), which have Ti/Ni multilayer coating and total reflection up to 3 times Q_c (critical momentum transfer) of the normal guide tube. One unit of supermirror is rectangular and measures 52 mm inside height, 24 mm inside width, and 880 mm length. The units are joined together with naphthotherm adhesive to create the tube. The inside of the tube is constantly evacuated by a dry pump to create a vacuum of 10 Pa or less. Figure 2(b) shows the actual photo of the guide tube. The guide tube is fixed from the top and bottom using a sturdy steel base and horizontal strut. A monochromator is installed at the exit of the guide tube.

Figure 2(c) shows the result of a simulation of the wavelength dependence in intensity at the monochromator

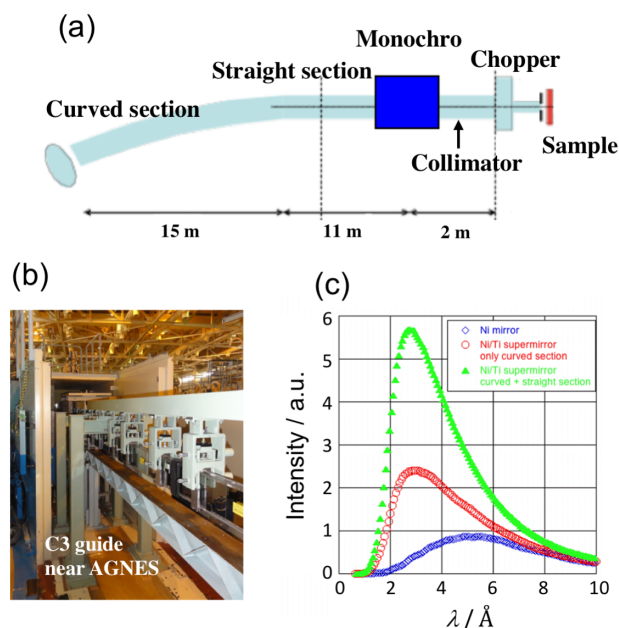


Fig. 2. (Color online) (a) Schematic drawing and (b) photo of C3 guide tube. (c) Simulation results for the enhancement of neutron intensity due to installation of supermirror guide tube. The blue curve is the intensity with Ni mirror guide tube (previous condition), the red curve is the intensity with supermirror guide tube installed only in the curved section, and the green curve is the intensity with supermirror guide tube installed both in the curved and straight sections.

position caused by the change of the guide tube. The blue curve is the intensity with Ni mirror guide tube (previous condition), the red curve is the intensity with supermirror guide tube installed only in the curved section, and the green curve is the intensity with supermirror guide tube installed both in the curved and straight sections. The simulation was performed using McStas software,^{5,6)} which is commonly used for the neutron intensities in neutron scattering instruments. For 4.2 Å neutrons used in the standard mode, the intensity is expected to increase by a factor of about 5 by changing the guide tube, and by a factor of 2.5 for 5.5 Å neutrons used in the high-resolution mode.

A tunnel-like device called collimator is installed between the monochromator and the chopper. A supermirror was also attached on the inner wall of the collimator. A detailed structure and photograph of the supermirror collimator are shown in Fig. 3. The supermirrors are mounted only on the top and bottom inner surfaces of the collimator as shown in the red line in Fig. 3(a). To suppress horizontal beam divergence, which results in the reduction of Q resolution, the boron carbide (B_4C)/epoxy resin sheet is attached to both inner sides of collimator, as shown in the blue line in Fig. 3(b).

3.2 Enhancement of neutron intensity after supermirror installation

Figure 4 shows the data of elastic scattering intensities from the standard sample ($\phi 13.7$ Vanadium rod) before the supermirror installation, after the installation of only the supermirror-coated neutron guide tubes, and after the installation of both the supermirror-coated neutron guide tubes and collimator. Figures 4(a) and 4(b) are for the standard mode and the high-resolution mode, respectively.

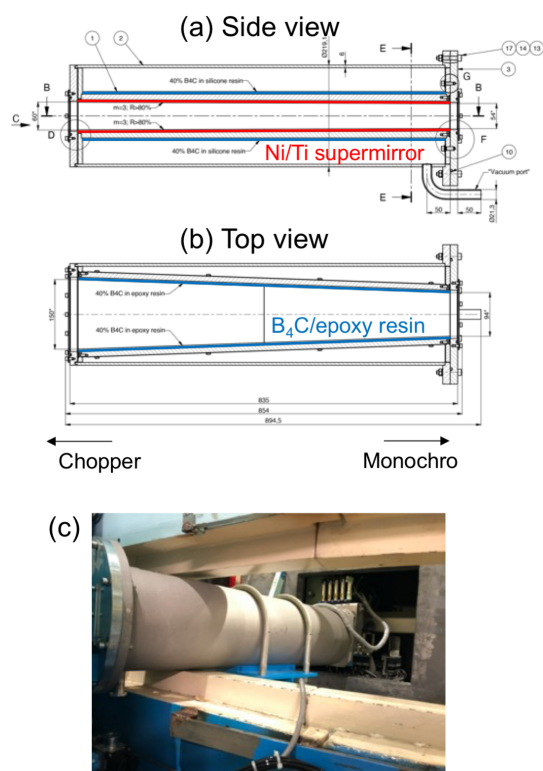


Fig. 3. (Color online) Schematic drawing [(a) side view, (b) top view] and photo of supermirror collimator.

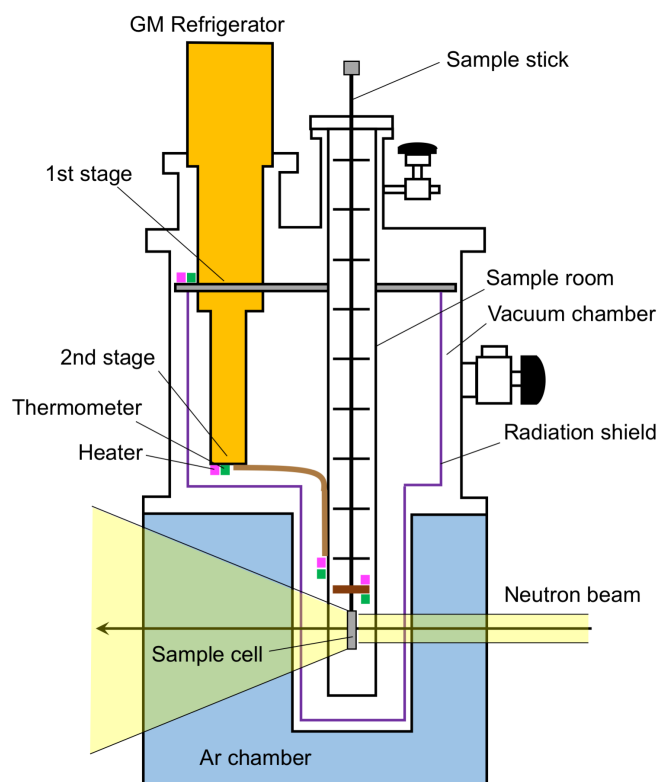


Fig. 5. (Color online) Schematic sectional drawing of the new cryo-furnace with a sample stick for the low-temperature mode.

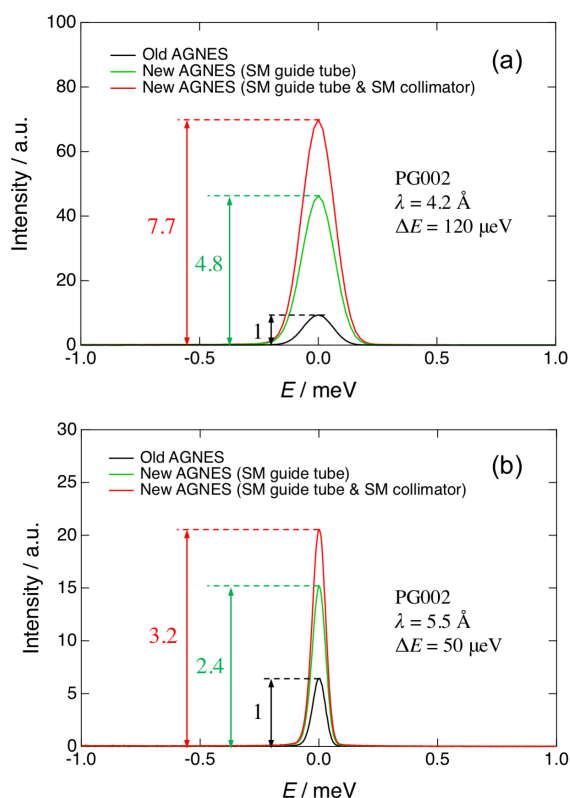


Fig. 4. (Color online) Elastic scattering data from a vanadium rod before and after the installation of supermirror guide tube and supermirror collimator for (a) standard mode and (b) high-resolution mode. The data from all the detectors from 20 to 120° are summed up.

The depicted data are summation of the intensities of all the detectors located between $2\theta = 20$ and 120° . As a result of installation of the both the supermirror-coated neutron guide tubes and collimator, the neutron intensity increased by 7.7 times in the standard mode and by 3.2 times in the high-resolution mode. This is consistent with the result of the simulation described in the Sect. 3.1.

3.3 Structure and performance of new cryo-furnace

Figure 5 shows the schematic drawing of the cryo-furnace installed at the restarting of JRR-3 in 2021; this is the setup in the low-temperature mode. The temperature range is 2.5 to 800 K. In the low-temperature mode ($2.5 \text{ K} < T < 370 \text{ K}$), the sample room is filled with ca. 10 kPa of helium gas. Then the temperature of sample room is controlled. The temperature difference between the sample room and a block holding the sample cell is smaller than 1 K. In the high-temperature mode ($10 \text{ K} < T < 800 \text{ K}$), the sample room is evacuated and the temperature of the block holding the sample cell is controlled. The Al radiation shield is attached surrounding the sample cell (not shown in Fig. 5) in the high-temperature mode. There is temperature difference between the block and the sample cell (40 K at maximum), but the sample temperature is corrected according to calibration curve which was made by measuring the melting points of several standard materials. To avoid neutron scattering from the air and to reduce the measurement background, the Ar chamber located outside the sample room is filled with Ar gas at 0.1 MPa. The total neutron scattering cross section of Ar is 0.683 barn while that of air is 10.05 barn (1 barn = 10^{-24} cm^2).

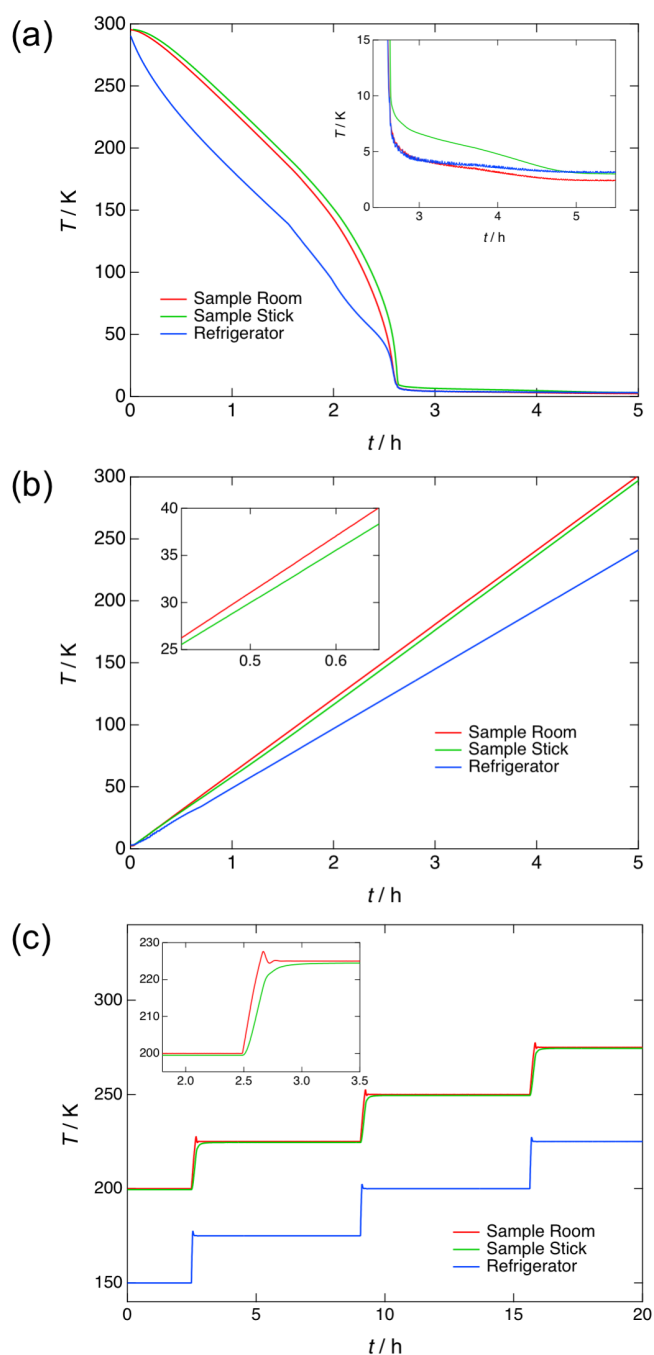


Fig. 6. (Color online) Temperatures of the sample room, sample stick, and refrigerator as functions of time for the low-temperature mode. (a) Cooling from room temperature, (b) during fixed-window scan, (c) during QENS/INS measurement as functions of temperature (every 25 K).

Figure 6 shows the temperatures of the sample room, sample stick, and refrigerator as functions of time for the low-temperature mode. Figure 6(a) indicates that the sample is cooled down to below 5 K in 3 h and 3 K (lowest temperature) in 4 h (5–6 h in regular cryostats). Figure 6(b) is the temperature change during the fixed-window scan (low temperature mode, heating direction, 1 K min^{-1}) which is usually conducted to investigate overall feature of relaxation. It is noteworthy that the temperature difference between the sample room and sample stick (sample cell holding block) is smaller than 3 K even for the continuous heating process. Figure 6(c) demonstrates the quickness and stability of the temperature change of the sample stick during the QENS or

INS measurements. After starting heating, the temperature of the sample stick reaches a target temperature (25 K higher in this case) within 10 min and stabilized within 10 min (20–30 min in regular cryostats).

As shown above, the performance of the new top-loading cryo-furnace is quite high and greatly facilitated the total performance of the measurements. This is mainly owing to the compact design of the present cryostat; the diameter of the sample room of the present cryostat is 60 mm but those of regular cryostats are 80–100 mm. Another reason is the use of the world's most powerful level GM refrigerator (Sumitomo Heavy Industries, SRDK-415D-F50L; 1.5 W at 4.2 K).

4. Overview of QENS and INS Studies Using Improved AGNES

Since the restart of JRR-3 in 2021, approximately 40 experiments have been performed. And some works have already been published.^{7–9)} The research on AGNES is classified into three categories. The first one is the dynamics of molecular and ionic liquids in bulk, on surfaces, and in porous materials. Major research examples are diffusions of waters bound by proteins and polymer networks (gels). These waters are hindered by polymers and conversely plasticize the polymers. Electrolyte polymer membranes containing water are another well-known target of QENS. Of course, these are applied to proton conductors utilized in fuel cells. The second category is novel and high-performance polymer solids. A recent topic is the dynamics of ultra-tough polymers which are utilized to bulletproof glass. A rare archaeological material, amber, was also measured. In the studies on solid polymers, it is important to investigate the relation between QENS and low-energy excitations which are usually called boson peaks. The third category is diffusion and rotation in solids. We are focusing attention on the dynamics of H atoms and Li ions in crystals. The scattering cross sections of a ^7Li atom ($\sigma_{\text{coh}} = 0.62 \text{ barn}$, $\sigma_{\text{inc}} = 0.78 \text{ barn}$) are very small, but its motion can be detected by the improved AGNES.

The following is a summary of two preliminary data measured in our laboratory. The first example, acetonitrile/MgTFSI solution, belongs to category 1, while the second example, methane solid, belongs to category 3.

Figure 7 shows the QENS spectra of AN/MgTFSI solution [AN: acetonitrile, TFSI: bis(trifluoromethanesulfonyl)imide], an encouraging candidate for electrolyte in the magnesium secondary battery.¹⁰⁾ For comparison, the QENS spectra of pure AN solution are also shown. For both samples, the QENS spectra become broader as the temperature increases, indicating that the motions of AN molecules are faster at higher temperatures. Furthermore, the AN motion in AN/MgTFSI solution slows down prominently more than in pure AN solution. These results suggest the formation of clusters where AN molecules are coordinated to Mg ion, and provide a crucial insight into the Mg ion transport mechanism.

Figure 8 shows the QENS and INS data of solid methane CH_4 obtained by the vapor deposition method. The thickness of the deposited sample was approximately 0.1 mm. These data were collected for 2 h at each temperature. It is known that CH_4 solid exhibits a phase transition from I to II at $T_c = 20.4 \text{ K}$.¹¹⁾ In the phase I ($Fm3m$), where all CH_4 molecules are orientationally disordered, the solid methane

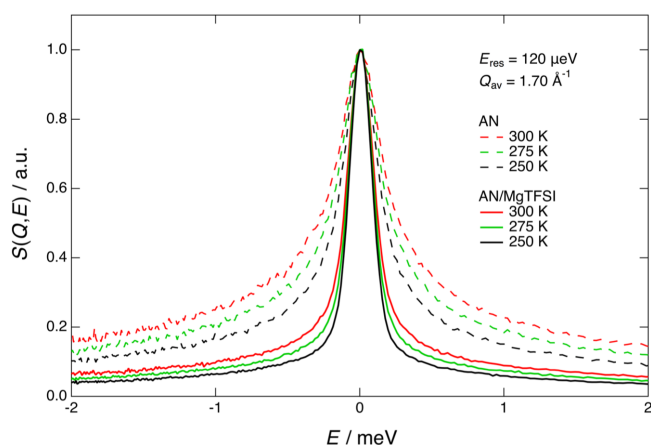


Fig. 7. (Color online) QENS spectra of pure AN and AN/MgTFSI solutions at different temperatures for standard mode. The maximum of these data is normalized to 1.

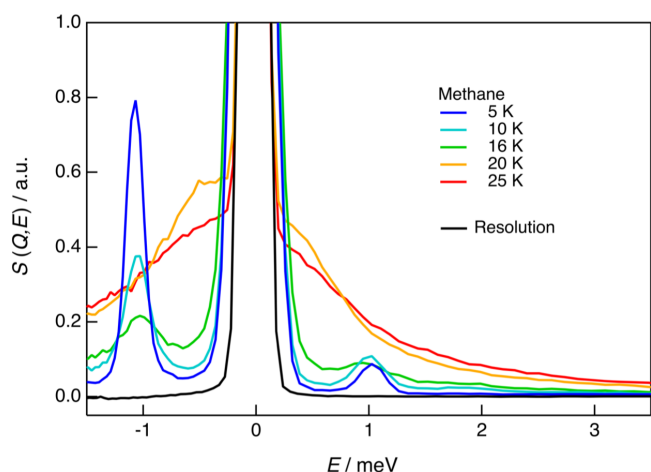


Fig. 8. (Color online) QENS and INS spectra of phase I and II for CH_4 solid at different temperatures obtained using the standard mode. The data from all the detectors from 20 to 120° are summed up. The average Q_{av} value is $1.7 \text{ \AA}^{-1}$. The transition temperature between phase I and II is 20.4 K .¹¹⁾

exhibits usual QENS broadening, corresponding to the rotational relaxations over potential energy barriers (hindered rotations). On the other hand, in the phase II ($Fm3c$) below T_c , 25% of CH_4 molecules are disordered (free rotor) and 75% of methane molecules are orientationally ordered.^{12–14)} A clear INS peaks observed at $\pm 1 \text{ meV}$ correspond to the rotational excitations between the rotational quantum number of $J = 0$ and 1 states for the free rotor. The apparent broadening of the elastic peak originates from the tunneling excitations that occurs due to wavefunction overlap between adjacent deep potential minima for the ordered molecules.¹⁵⁾ It should be noted that with the improved AGNES, complete QENS and INS data from a small sample with 0.1 mm thickness can be obtained in a few hours if the sample contains relatively abundant hydrogen.

5. Concluding Remarks

The most important aspect of the AGNES future plan is its complementary use with J-PARC. On AGNES, we can study dynamics in a 0.1 to 50 ps time region by changing the energy resolution of 120 , 50 , and $15 \mu\text{eV}$. Therefore, it is ideal to combine AGNES with DNA or VIN-ROSE at J-PARC, which has an energy resolution higher than $10 \mu\text{eV}$ (corresponding to a time scale longer than 10 ps). The time domain of AGNES overlaps considerably with that of AMATERAS. However, AMATERAS is mainly focused on inelastic scattering studies, especially for solid-state physics targets, and is a highly competitive instrument. It is indeed reasonable to use AGNES for quasi-elastic scattering, especially for liquid, soft matter, and powder solid samples. There are many research targets where the dynamics from 1 to 100 ps is decisive. For more information on AGNES, please visit the following website. <http://www.issp.u-tokyo.ac.jp/labs/neutron/inst/AGNES/index-j.html>

Acknowledgment The authors thank Mr. Toshio Asami, Mr. Ryosuke Sugiura, and Dr. Daichi Kawana. They are technicians of Neutron Science Laboratory, Institute for Solid State Physics, University of Tokyo, and have greatly contributed to the improvement of AGNES and experiments using AGNES. The authors are grateful for Dr. Itaru Tamura who calculated neutron intensity in Fig. 2(c) using McStas software. Thanks are extended to all of AGNES users who conducted interesting neutron research using AGNES. This work was carried out by the JRR-3 general user program managed by Institute for Solid State Physics, University of Tokyo (Proposal Nos. 21406, 22406, 23406, 24406).

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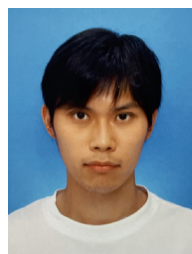


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porous material including small molecules, hydrogen and ionic conducting solids. They are investigated by neutron scattering, x-ray diffraction, heat capacity, dielectric and rheometric measurements.