Experimental report

07/09/2022

Proposal: 3-07-403 **Council:** 4/2021

Title: Study of graphite intercalated by fluor for neutron reflection

Research area: Nuclear and Particle Physics

This proposal is a new proposal

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Samples: Graphite

Instrument	Requested days	Allocated days	From	To
PF1B	21	21	11/05/2021	01/06/2021

Abstract:

The development of efficient neutron reflectors is important both for production of neutrons of different wavelengths as well as for their efficient use. Thus, we develop nano-diamond (ND) reflectors, which are particularly useful for the diffusive reflection of very cold neutrons and the quasi-specular reflection of cold neutrons. However, there is still a reflectivity gap in terms of neutron velocity (wavelength) corresponding to ND reflectors and standard reflectors of thermal and a harder fraction of cold neutrons. In order to bridge this gap we proposed a new type of reflector and developed it in the framework of NERF ANR project in the collaboration between Clermomt-Ferrand University and ILL. There are powders of graphite intercalated by flour. In analogy to the efficient F-ND reflectors, it contains only nuclei with small absorption cross section. The specific feature of this material is its huge interplanar distances. We plan to perform its detailed reflecting properties as a function of wavelength, outcoming angle, transport in the powder etc. There is no standard ILL instrument which allows this study. We have done a test at PF1B and showed that it is feasible here.

In the framework of this experiment, we performed a series of detailed studies of slow neutron reflectors based on fluorinated detonation nanodiamond (F-DND) powders and graphites intercalated with fluor (F-GIC). Some of the obtained results of this and the previous test experiment at PF1B are partly included in recent broader publications [1] in a high-impact journal (Nanomaterials), and the others are analyzed and would result to a few more publications of our whole team in the near future.

DND powders with different core diameter were fluorinated using elemental fluorine at high temperature (520°C) for long duration (at least 12 h) to remove H and sp^2 carbon shell from their surface. The synthesis of fluorine graphite intercalation compounds has been carried at the very beginning of the ANR NERF project and the parameters were partly optimized.

F-DND reflectors are particularly useful for the diffusive reflection of very cold neutrons (VCN) and quasi-specular reflection of cold neutrons (CN) [2]. F-GIC are developed to bridge the rest of the reflectivity gap left in terms of neutron velocity (wavelength) between the reflectivity of F-DND reflectors and the reflectivity of standard reflectors of thermal and cold neutrons. Both studies are done within the framework of NERF ANR project, where the new type of reflectors based on intercalated crystals was proposed for the first time. The technology of production of both F-DND and F-GIC is developed in the collaboration of Clermont-Ferrand University and ILL.

The principle of their operation is as follows. F-DND reflectors “mimic” standard neutron reflectors for thermal (and faster) neutrons, the problem of which consists of the fact that neutrons with wavelengths larger than a typical inter-atomic distance cannot “resolve” separate atoms and, therefore, cannot be efficiently scattered in the reflector material. The use of nanoparticles consisting of highly-scattering slightly-absorbing materials shifts the reflection cut-off towards larger wavelengths. In analogy to efficient F-DND reflectors, F-GIC contain only nuclei with small absorption and large scattering cross sections, like carbon and fluor. In contrast to F-DND, they do not use the enhancement of coherent elastic scattering of neutrons on nuclei in nanoparticle. Instead, they are based on the intense Bragg scattering of neutrons in a special parameter range. The very specific feature of these materials is their huge interlayer distances. They provide intense scattering of neutrons with significantly larger wavelengths than those corresponding to standard neutron reflectors. Figure 1 illustrates these arguments (copied from the ANR NERF application). It is also useful for the estimation of characteristic wavelengths, velocities and absolute probabilities.

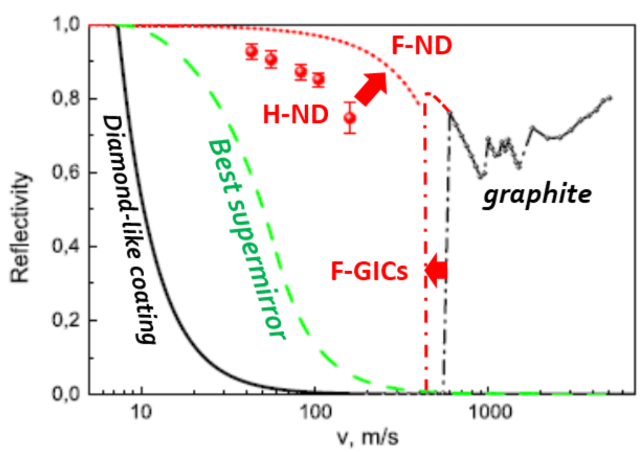

Fig. 1. *The elastic reflection probability for isotropic neutron flux is shown as a function of the neutron velocity for various carbon-based reflectors: Diamond-like coating (DLC), the best supermirror, Hydrogen-free ultra-diamond powder with the infinite thickness (F-DND dotted red line) - calculation), VCN reflection from 3 cm-thick diamond nanopowders at ambient temperature (ND red points), with significant hydrogen contamination – experiment, MCNP calculation for reactor graphite reflector with the infinite thickness at ambient temperature (dash-dotted black line). f) Objective for F-GICs reflectors (dash-dotted red line).*

In order to perform this series of detailed studies of F-GIC and F-DND, we built at PF1B a special setup which includes the capabilities of several standard neutron instruments (diffractometers, reflectometers, small-angle scattering instruments), but also includes the capabilities which are missing at standard neutron scattering instruments. These extra features include those of principal importance for the study of low-energy neutron reflectors. In particular, the diffraction can be measured as a function of the incoming neutron wavelength including the longest wavelengths, and the scattering angles cover nearly the full range of scattering angles. The reflection can be measured to all scattering angles. The small-angle scattering can be measured for a very broad range of incoming neutron wavelengths. Moreover, all these options are available in the same setup simultaneously. With these options available, we can 1) Measure directly all process for the neutron wavelengths of interest, in particular, small-angle scattering, diffraction and reflection of VCN. This information cannot be extracted from measurements at standard neutron instruments. 2) Measure scattering to all final angles. This information is not accessible for all the processes of interest simultaneously at any standard neutron instrument. 3) Measure directly the total and differential cross sections. In order to extract this information, one should measure all the process simultaneously in the full parameter range that is not accessible at standard neutron instruments. The "price to pay" is a limited spatial and wavelength resolution of each particular measurement which is not a problem for this particular study (low-energy neutron reflectors).

The first main result is that the chosen experimental configuration appeared to be very close to the optimum from the first attempt, and we succeeded to cover the full range of parameters of interest. Thus, this, or similar configuration can be used for the future experiments at PF1B. However, after the analysis of the measured results, we found a few systematic effects which might be improved in the future. In particular, 1) Standard quartz sample holders that are used at most standard neutron instruments are not optimal for our tasks. They produce a significant neutron scattering at short wavelength below the Bragg cut-off. This is of minor importance for measurements with neutron wavelength above the Bragg cut-off but of high importance for us as we are interested in the full parameter range (including short wavelengths of the incident neutrons). Thus, special holders with significantly thinner walls and well-defined thickness have to be developed. 2) A minor fraction of the initial neutron beam passed through the neutron chopper in the state "closed". This is of minor importance for measurements with short wavelengths of incident neutrons, however, produces an important systematic effect for measurements with large neutron wavelengths. The range of interest for F-GIC studies is 6-10 A. The flux of neutrons is rapidly falling down with increasing the wavelength. This means that the flux of the slowest neutrons is low, while the systematic effect caused by the false chopper transmission stays the same. Thus, good tightness of the chopper for all wavelengths should be provided in the future. 3) To avoid overload of the position-sensitive detector when counting the incident beam, we should build a system of masking the initial beam on the face of the detector as it is typically done at other neutron scattering instruments. 4) During the data analysis, we developed software which allows full data treatment (nearly) in real time during the measurement. It has to be used for the future experiments in order to better control the parameters of experiment in real time. 5) The collimation system can be improved to optimize the fluxes of the slowest neutrons, without scarifying the range of angles of scattered neutrons. This means that a special optimized collimation system has to be built and used. 6) Some mechanical modifications of the setup would allow smoother translations of the detector with higher positioning accuracy and more precise installation and control of the samples.

The second main result consists of the first ever evidence of the efficiency of F-GIC reflectors and their capability to cover completely the rest of the neutron reflectors "reflectivity gap". This is the main expected "deliverable" of the ANR NERF project. Prior to the experiment, we had developed a few modifications of graphite with different flour intercalation, however, their neutron scattering properties are hard to calculate from the first principles and they were not optimized for the neutron reflectivity. Such F-GICs are biphasic with either residual graphite and (C2F)n phase or (C2F)n and (CF)n phase. With these samples, we performed the first measurements. The preliminary results evidence that the inter-planar spacing can be established, i.e. 0.86 nm, 0.73 nm or 0.6 nm, according to both the fluorine content and the C-F bonding. For the case of non-fluorinated graphite, the peak 0.337 nm is observed. This peak disappears completely for the F-GIC with the highest fluorine content and partially for the sample with less F content. Results are normalized to sample density. The absolute values of the effective scattering cross sections are averaged over the whole neutron spectrum. If calculated for the neutron velocities corresponding to the main peaks, the effective cross-section will increase significantly for the peaks of the lowest velocity.

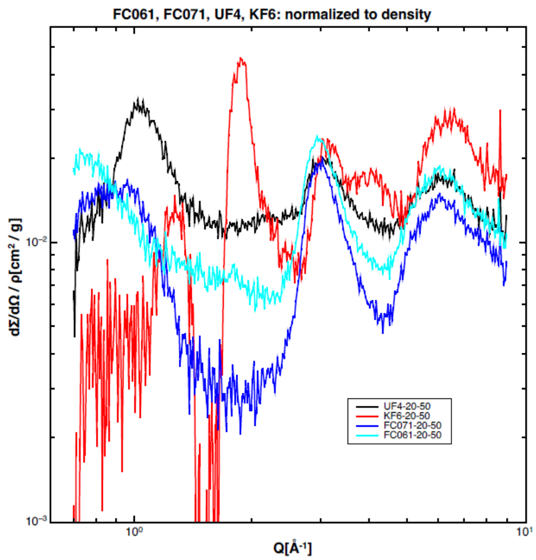

Fig. 1. *The differential cross section of neutron scattering as a function of neutron transferred momentum for the following samples: KF6-20-50 used as a precursor (before intercalation), FC061-20-50, FC071-20-50, UF4-20-50 – intercalated graphites with different degree and temperature of intercalation. The result demonstrates both 1) the large inter-plane distances (0.86 nm, 0.73 nm, 0.6 nm, respectively, compared with 0.34 nm for the precursor), 2) the large probability of scattering for the F-GIC samples (taking into account that the absolute values of the effective scattering cross sections are averaged here over the whole neutron spectrum, and the fraction of 0.86 nm, 0.73 nm, 0.6 nm neutrons in the initial spectrum are much lower than that of 0.34 nm neutrons. Full treatment of the data and the simulation of neutron transport are still in progress.*

The third main result is the demonstration that other experiments of our interest have been performed in close-to-optimum conditions. They include the feasibility of studies of: 1) All absolute differential cross-sections for all samples in the full dynamic range, 2) Total neutron transmission through all samples as a function of the neutron wavelength in the full dynamic range, 3) Main corrections can be quantified in calibration measurements for all samples of interest, 4) Inelastic scattering cross sections are small and would be measured at other instruments, 5) With a sufficiently thick sample and at a sufficiently large wavelength, the back reflection of neutrons from the sample can be measured directly, 6) A whole set of promising measurements with different F-GIC and F-DND samples was performed successfully, and their analysis is in progress.

In addition to the expected further outcome of these already performed experiments, we are confident that the new experimental setup and method can become a standard tool for the studies of slow neutron reflectors at PF1B by our and other collaborating groups. In particular, a series of different measurements with the same experimental setup is more efficient than separate measurements because this arrangement would allow saving time and resources on mounting, optimizing, calibrating and dismounting of the experimental setup.

References:

1. **Aleksenskii, A., *et al*,** *Clustering of diamond nanoparticles, fluorination and efficiency of slow neutron reflectors*, **Nanomaterials 11** (2021) 1945; **Aleksenskii, A., *et al*,** *Effect of particle sizes on the efficiency of fluorinated nanodiamond neutron reflectors*, **Nanomaterials 11** (2021) 3067;
2. **Nesvizhevsky, V.V.,** *Interaction of neutrons with nanoparticles*, **Phys. At. Nucl. 65** (2002) 400; **Nesvizhevsky, V.V., *et al*,** *The reflection of very slow neutrons from diamond powder nanoparticles*, **Nucl. Instr. Meth. A 595** (2008) 631; **Lychagin, E.V., *et al*,** *Storage of very cold neutrons in a trap with nano-structured walls*, **Phys. Lett. B** (2009) 186; **Nesvizhevsky, V.V., *et al*,** *Application of diamond nanoparticles in low energy neutron physics*, **Materials 3** (2010) 1768; **Cubitt, R, *et al*,** *Quasi-specular reflection of cold neutrons from nano-dispersed media at above critical angles*, **Nucl. Instr. Meth. A 622** (2010) 182; **Krylov, A.R., *et al*,** *Study of bound hydrogen in powders of diamond nanoparticles*, **Crystal. Rep. 56** (2011) 1186; **Nesvizhevsky, V.V., *et al*,** *Fluorinated nanodiamonds as unique neutron reflector*, **Carbon 130** (2018) 799; **Nesvizhevsky, V.V., *et al*,** *Effect of nanodiamond fluorination on the efficiency of quasispecular reflection of cold neutrons*, **Phys. Rev. A 97** (2018) 023629; **Ersez, T., *et al*,** *Small angle and inelastic scattering investigation of nanodiamonds*, **Phys. B 551** (2018) 278; **Batsanov, S.S., *et al*,** *Novel synthesis and properties of hydrogen-free detonation nanodiamond*, **Mater. Chem. Phys. 216** (2018) 120; **Teshigawara, M., *et al*,** *Measurement of neutron scattering cross section of nano-diamond with particle diameter of approximately 5 nm in energy range of 0.2 meV to 100 meV*, **Nucl. Instr. Meth. A 929** (2019) 113; **Bosak, A., *et al*,** *Fluorination of diamond nanoparticles in slow neutron reflectors does not destroy their crystalline cores and clustering while decreasing neutron losses*, **Materials 113** (2020) 3337; **Herraiz, M., *et al*,** *A multitechnique study of fluorinated nanodiamonds for low-energy neutron physics applications*, **J. Phys. Chem. C 124** (2020) 14229; **Grammer, K.B., *et al*,** *The small-angle neutron scattering extension in MCNPX and the SANS cross section for nanodiamonds*, **Nucl. Instr. Meth. A 953** (2020) 163226; **Granada, J.R., *et al*,** *Studies of reflector materials for cold neutrons*, **Eur. Phys. J. Web Conf. 231** (2020) 04002; **Jamalipour, M., *et al*,** *Directional reflection of cold neutrons using nanodiamond particles for compact neutron sources*, **Eur. Phys. J. Web Conf. 231** (2020) 04003;