Neutron reflection from fluorinated nanodiamonds for N-Nbar

- Introduction to nano-diamond neutron reflectors
- The problem of hydrogen impurities
- The impact of hydrogen substitution by fluor
- Conclusions and prospects
Introduction to nano-diamond reflectors (broader than particle physics)

Complementarity of neutron and synchrotron radiation.

Neutron radiation: particularly light elements and magnetic structures; the object of research in particle physics – in this sense, complementary to high-energy particle accelerators; mostly sensitive to nuclei in atoms.

Synchrotron radiation: mostly sensitive to electrons in atoms.
Slow neutrons are traditionally subdivided into several groups as a function of their energy/velocity:

- **Cold neutrons (CNs):** a typical velocity 1000 m/s; you have a lot of CNs from all typical neutron sources (nuclear reactors and spallation neutron sources), if they are equipped, for instance, with a cold liquid-deuterium or liquid-hydrogen source;

- **Ultracold neutrons (UCNs):** a typical velocity 5 m/s; in spite of all worldwide efforts, extremely low densities available for experiments, however a unique property of total reflection from material and magnetic walls thus storage of UCNs in traps;

- **Very cold neutrons (VCNs):** a typical velocity 100 m/s; limited fluxes and no efficient reflectors ... until recently
Worldwide trend to increase the range of useful neutrons towards smaller energies (larger wavelengths), driven in particular by large-scale-structure diffractometers, reflectometers, time-of-flight and spin-echo techniques, by particle physics.

The progress is limited by low fluxes of slow neutrons (the wavelength larger than 0.5 nm, or the energy smaller than 3 meV).

The drop of flux is due to a fundamental reason: independently of the choice of materials for neutron reflectors, they are composed of atoms, thus a finite interatomic distance, thus diffraction and thus simply mean neutron-nuclei optical potential.

The solution of this problem: “Mimicking” conventional reflectors with nanoparticles.
**Introduction to nano-diamond reflectors**

**Neutron-atom:** the neutron-electron interaction is usually a minor correction compared to the neutron-nuclei interaction; **Neutron-nucleus:** as the wavelength of a slow neutron is larger than the size of a nucleus, we always deal with isotropic s-scattering and can characterize it with a single parameter: a scattering length; **Neutron-matter:** as the wavelength of a slow neutron is also larger than a typical inter-atomic distance, we deal with coherent scattering of neutrons at many nuclei simultaneously; **Optical potential:** as a result, any medium can be represented as a uniform effective optical potential; **Potential strength:** a typical value of the optical neutron-nuclei potential is $\sim 10^{-7}$ eV (could be thought of as a typical nuclear potential of $\sim 10$ MeV diluted over volume).

**Two contradicting tendencies:**

1) Cross-section increases rapidly as a function of the nanoparticle size; 2) Angular divergence and cross-section drop down rapidly, if the size is large.

1) The optimum neutron wavelength is approximately equal to the nanoparticle size; 2) The cross-section is then measured in square nanometers; 3) The best material is diamond.
The (elastic) reflection of VCNs from powder of diamond nanoparticles, the storage of VCNs in closed volumes with nano-powder walls, and quasi-specular reflection of cold neutrons (CNs) from diamond nano-powder have been proven.
The danger of hydrogen impurities

An important limitation for further improving the reflectivity consisted of the presence of hydrogen in the amorphous shells of diamond nanoparticles.

\[ \sigma_{abs}^{C} = 3.5 \text{ mb} \quad \sigma_{abs}^{H} = 333 \text{ mb} \quad \sigma_{abs}^{F} = 9.6 \text{ mb} \]

\[ b^{C} = 6.65 \text{ fm} \quad b^{H} = -3.74 \text{ fm} \quad b^{F} = 5.65 \text{ fm} \]

1% of mass but !! \[ \sigma_{in.sc.}^{H} = 108(3) \text{ b} \]

We have explored three methods to remove hydrogen:
- Thermal treatment;
- Isotopic substitution;
- Chemical treatment.
Fluorination of nanodiamonds

An important limitation for further improving the reflectivity consisted of the presence of hydrogen in the amorphous shells of diamond nanoparticles.

As-prepared (detonation technology)

\[ C_{7.4 \pm 0.15} H \]

After thermal treatment

\[ C_{12.4 \pm 0.2} H \]

After fluorination

\[ C_{430 \pm 30} H \]

Energy dependence of neutron inelastic scattering showed that C-H bond is responsible for neutron losses.

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Fluorination of nanodiamonds

X-ray diffraction patterns of raw and fluorinated nanodiamond powder:
- Diamond sp\(^3\) cores remain unaffected;
- Destruction of sp\(^2\) carbon shells.

Destruction of sp\(^2\) carbon will lead to significantly higher efficiency of neutron scattering!
Fluorination of nanodiamonds

A) Raman spectra (inelastic scattering of monochromatic light) of raw and fluorinated nanodiamond;
B) FTIR (Fourier-transform infrared spectroscopy) spectra of raw and fluorinated nanodiamond.

Disappearance of sp² carbon, C-H and O-H.
Fluorination of nanodiamonds

$^{13}$C (a), $^1$H (b) and $^{19}$F (c) MAS NMR spectra of raw and fluorinated nano-diamonds

- The departure of -OH groups and their replacement by -F groups;
- Minor residual H content upon fluorination;
- C-F bonds with sp$^3$ carbons, very low amount of C-F bonds with sp$^2$ carbons.
Chemical cleaning from isotopes posing the neutron activation danger

Fluorination does not affect most disturbing radioactive chemical elements (isotopes).

As revealed by neutron activation analysis of raw and fluorinated nano-diamond samples, most disturbing isotopes are $^{64}$Cu, $^{24}$Na, $^{51}$Cr. A chemical treatment reduces their amount by factors of 12, 6 and 2, respectively.

Wet chemical treatment in concentrated hydrochloric acid at the temperature of 140 °C for 18 hours (+ washing, centrifugation, air annealing at the temperature of 600 °C for 5 hours).

The amount of $^{38}$Cl increases by an order of magnitude due to the chemical treatment, however, due to a relatively short lifetime of this radioactive isotope, it is not particularly disturbing (but contributes to absorption!).
0.5 kg fluorinated nano-diamonds were produced in 2-cycle fluorination of thin (2 mm) layers of raw nano-diamond powder with 99.9 % clean F₂ gas at the pressure of 0.6 bar, at the temperature of 450 °C for 12 hours.
The impact of removal of hydrogen from diamond nanoparticles
Quasi-specular reflection
Quasi-specular reflection

The intensity of neutron scattering (within the angular acceptance of the D17 position-sensitive detector in the vertical direction) as a function of neutron wavelength and scattering angle, for the incidence angle of 1 deg.

On the left - non-fluorinated nanodiamond; on the right - fluorinated nanodiamond
The total probability of neutron scattering (within the angular acceptance of the D17 position-sensitive detector) as a function of the neutron wavelength, for the incidence angles of 1deg., 2deg., 3deg.

**Graph Description:**
- **Red color** – fluorinated nanodiamond
- **Black color** – non-fluorinated nanodiamond
Quasi-specular reflection

The probability of neutron scattering as a function of the neutron wavelength, for the incidence angle of 1deg.
Quasi-specular reflection

Mean angle of reflection as a function of the neutron wavelength, for incident angles 1deg., 2deg., 3deg.

Half-width of the angle of reflection as a function of the neutron wavelength, for incident angles 1deg., 2deg., 3deg.
Quasi-specular reflection

The intensity of neutron scattering (within the angular acceptance of the D17 position-sensitive detector) as a function of neutron wavelength and scattering angle, for the incidence angle of 1deg.

On the left - 5 nm nanodiamond; on the right - 30 nm nanodiamond
Quasi-specular reflection

The total probability of neutron scattering (within the angular acceptance of the D17 position-sensitive detector) as a function of the neutron wavelength, for the incidence angles of 1deg., 2deg., 3deg.

Red color – 30 nm nanodiamond; Black color – 5 nm nanodiamond
Quasi-specular reflection

The probability of neutron scattering as a function of the neutron wavelength, for the incidence angle of 1 deg.

- Powder of diamond nanoparticles provided the first efficient reflectors for VCNs and efficient quasi-specular reflection of CNs;

- Such powders can provide a major gain in fluxes and densities of slow neutrons in various configurations;

- Losses of neutrons in raw diamond nano-powders are dominated by hydrogen impurities; the amount of hydrogen has been largely reduced by fluorination;

- Samples of diamond nanoparticles with “close-to-ideal” parameters have been produced and successfully studied. We explore a possibility of larger-scale production in order to provide their real applications in neutron science/technology.

- More powerful sources of slow neutrons (CNs, VCNs, UCNs)!
  - A new generation of general-purpose neutron sources!? 
  - More efficient nuclear reactors of the future?
UCNs versus VCNs

To remind advantages of VCNs:

- Longer observation times (compared to CNs and TNs) that is interesting for particle physics (nñ oscillations, neutron beta-decay etc);

- Larger absorption and fission cross-sections (compared to CNs and TNs) that is interesting for nuclear and particle physics;

- Relaxed geometrical constrains and higher sensitivity (compared to CNs and TNs) that is interesting for neutron reflectometers;

- Broader dynamical range for large-structure diffractometers, time-of-flight spectrometers and reflectometers (compared to CNs and TNs);

- Much higher sensitivity for spin-echo techniques (compared to CNs and TNs);

- Higher fluxes than UCNs etc...
However, huge disadvantages:

- Relatively low fluxes compared to CNs and TNs (as no efficient VCN reflectors have been available...), and

- Short observation times compared to UCNs (also ... as no efficient reflectors have been available).

Our method: Keep advantages and reduce disadvantages!

High fluxes and storage in closed traps

The list of possible applications is long
Directional extraction of VCNs

The gain factor is about 20-30 (preliminary, in progress)
References relevant to nano-diamond neutron reflectors: