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NANOMATERIALS, CERAMICS

Study of Bound Hydrogen in Powders of Diamond Nanoparticles

A. R. Krylov[a], E. V. Lychagin[a, b], A. Yu. Muzychka[a, b], V. V. Nesvizhevsky[c, b], G. V. Nekhaev[a, b], A. V. Strelkov[a, b], and A. S. Ivanov[c]

[a] *Joint Institute for Nuclear Research*
[b] *Research Institute of Materials Technology*
[c] *Institut Laue-Langevin*
e-mail: nesvizhevsky@ill.eu

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Abstract—In order to access feasibility of increasing albedo of very cold neutrons from powder of diamond nanoparticles, we studied hydrogen bound to surface of diamond nanoparticles, which causes unwanted losses of neutrons. We showed that one could decrease a fraction of hydrogen atoms from a ratio $C_{7.4 \pm 0.15}H$ to a ratio $C_{12.4 \pm 0.2}H$ by means of thermal treatment and outgasing of powder. Measurements of atomic excitation spectra of these samples, using a method of inelastic incoherent neutron scattering, indicate that residual hydrogen is chemically bound to carbon, while a removed fraction was composed of adsorbed water. The total cross section of scattering of neutrons with a wavelength of 4.4 Å on residual hydrogen atoms equals 108 ± 2 b; it weakly changes with temperature. Thus preliminary cleaning of powder from hydrogen and its moderate cooling do not improve considerably neutron albedo from powder of nano-diamonds. An alternative approach is isotopic replacement of hydrogen by deuterium.

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INTRODUCTION

Our interest to reflection of very cold neutrons (VCN) from nano-structures is motivated by an idea to develop sources of ultracold neutrons (UCN) with high density [1, 2], also by numerous methodical applications of nano-structured reflectors. Nano-dispersed diamonds [3] is a promising material for efficient VCN reflectors [4–13] due to fortunate combination of their physical parameters (their size is about the VCN wavelength, they provide high neutron-optical potential and low neutron absorption). Currently powders of diamond nanoparticles is the most efficient VCN reflector in the complete VCN energy range [5]. Presence of hydrogen atoms in powder of nano-diamonds causes extra inelastic scattering and absorption of neutrons. In order to explore methods and degree of increasing albedo of VCN from powder of diamond nano-particles, we studied hydrogen bound to nanoparticles surface. We were interested in the degree of cleaning the nano-diamond powders from hydrogen by means of their thermal treatment and outgasing, in the cross section of neutron scattering on residual hydrogen atoms, as well as in its behavior as a function of temperature that is important for practical applications. Besides, we measured atomic excitation spectra of the powder materials in order to judge on a type of hydrogen bond to nanoparticles. The measurements were performed with powder produced in RFNC-VNIITF (Snezhinsk).

MEASUREMENT OF HYDROGEN FRACTION

A fraction of hydrogen was measured using the method of γ-spectroscopy in a neutron beam of the high-flux ILL reactor, Grenoble, France (instrument ADAM [14]). A principal scheme of this measurement is shown if Fig. 1.

A sample (1) is placed in a monochromatic beam of neutrons with the wavelength 4.4 Å (2) behind a collimator (3). A germanium γ-quanta detector (4) is installed on a side of the sample; the detector is covered by the shielding against neutrons scattered in the sample, also against γ-quanta from the experimental hall (5), which would otherwise hit the detector. The

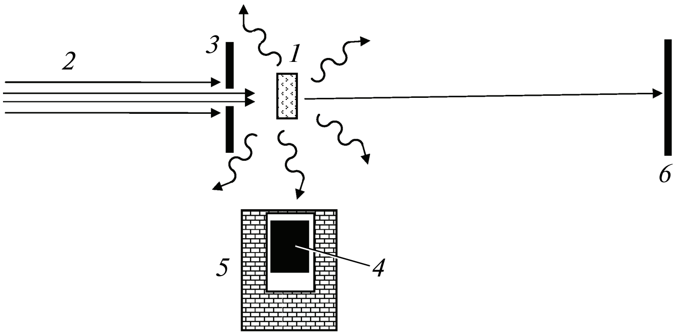

Fig. 1. A scheme of the measurement of a fraction of hydrogen in powder. 1—sample; 2—neutron beam; 3—collimator; 4—γ-detector; 5—detector shielding; 6—neutron detector.

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[1] The article was translated by the authors.

flux of neutrons passing through the sample is monitored in a neutron detector (6).

First, we measured the count rate in the γ-quanta peak of total absorption of the reaction $n(pd)\gamma$ (E_γ = 2.223 MeV); γ-quanta are emitted from powder samples as well as from samples with known number of hydrogen atoms (we used polyethylene for this calibration). Relative count rates in the peak indicate the amount of hydrogen in the samples. As powder samples were encapsulated in aluminum containers, we had to carry out an additional measurement with aluminum samples of equal thickness. Spectra of neutrons scattered on powder were calculated by means of subtracting the results of these two measurements.

Measured samples and their parameters are listed in Table 1. A part of γ-spectra (peak $E_\gamma = 2.223$ MeV) is shown in Fig. 2. The values of powder density in Table 1 are the results of division of the weight of power to its volume. These values were used to calculate fractions of hydrogen in the samples.

We simulated neutron transport using Monte-Carlo method and took into account the corrections in the experimental data for finite sample thickness, both for neutrons and γ-quanta, and got the following ratios for carbon and hydrogen in the samples:

– a sample cleaned from hydrogen by means of its heating in vacuum:

$$C_{12.4 \pm 0.2}H(n_C/n_H) = 12.4 \pm 0.2);$$

– a non-cleaned sample:

$$C_{7.4 \pm 0.15}H(n_C/n_H) = 7.4 \pm 0.15).$$

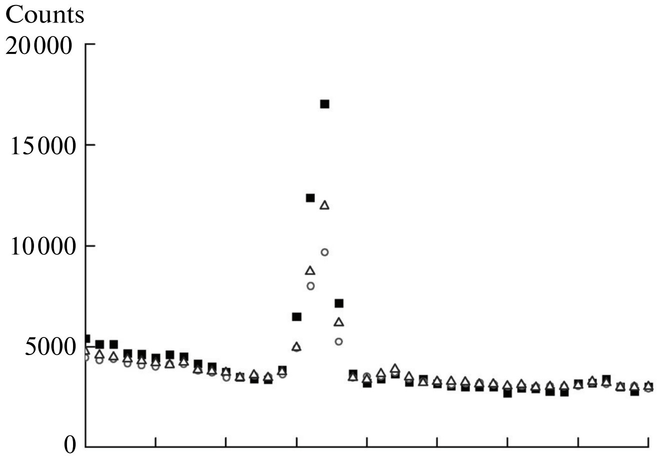

Fig. 2. The peak of total absorption in the reaction $n(pd)\gamma$ for polyethylene (■), for Sample no. 1 (○) and Sample no. 2 (△). Spectra from an aluminum sample with the thickness equal to that of the aluminum containers are subtracted from the spectra measured with nano-powders.

Table 1. Parameters of samples

Sample	Thickness, *d* mm	Density, ρ g/cm^3
Polyethylene	1.5	0.91
Sample no. 1 (powder of nano-diamonds after thermal treatment at the temperature 150°C and outgasing for 23 hours)	40	0.378
Sample no. 2 (powder of nano-diamonds with no treatment)	40	0.300

MEASUREMENT OF THE TOTAL CROSS SECTION OF NEUTRON SCATTERING ON HYDROGEN IMPURITIES

These measurements were also performed using the installation ADAM in ILL. We studied samples of nano-diamond powder presented in Table 1. A scheme of this measurement is shown in Fig. 3.

A monochromatic beam of neutrons (1) with the wavelength 4.4 Å and the diameter 11 mm is shaped by a diaphragm cut of boron rubber (2). The sample plane (3) is perpendicular to the beam axis. A position-sensitive detector (4) with a sensitive area of 25 × 25 cm^2 is installed at a distance of 26 cm from the sample front wall.

Here, a method consists of measuring the count rate of neutrons scattered out of the initial beam in such a direction that they cannot counted in the detector. We assume that neutrons are scattered on diamond nanoparticles to small angles, and they are scattered on hydrogen atoms isotropically. Therefore the distance between a sample and the detector is chosen so that all neutrons, passing a sample with no scattering or scattered on nanoparticles, are counted in the detector. In order to verify this statement, we mea-

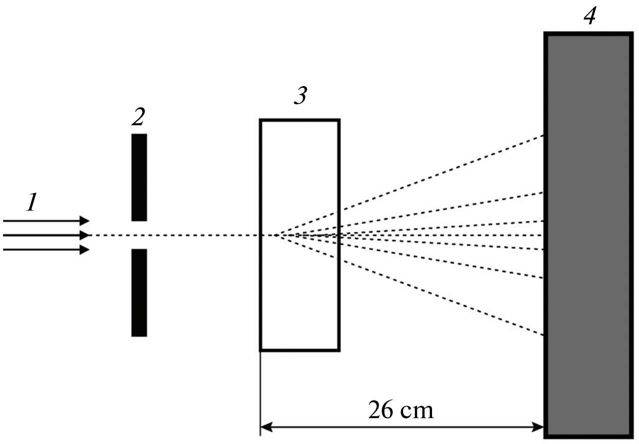

Fig. 3. A scheme of the measurement of the total cross-section of neutron scattering. 1—neutron beam; 2—diaphragm; 3—sample; 4—position-sensitive neutron detector.

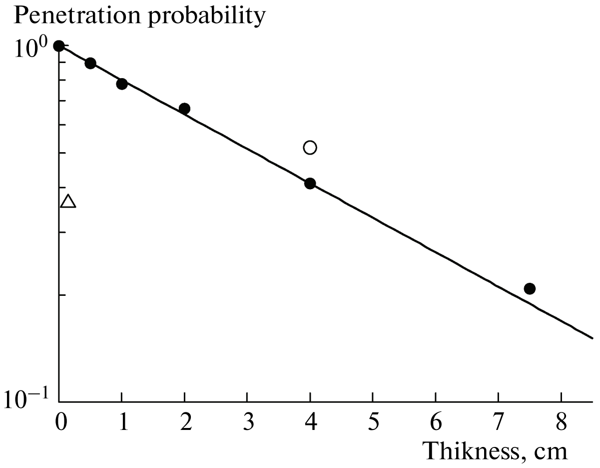

Fig. 4. The transmission though samples as a function of their thickness at ambient temperature: (●) correspond to the measurements with a non-cleaned sample of nano-diamonds; (○) indicates results for a sample of cleaned powder of nano-diamondsl; (△) shows the transmission through a sample of polyethylene with the thickness of 1.5 mm.

sured additionally with other distances between a sample and the detector. A fraction of isotropically scattered neutrons hits the detector as well; this effect is taken into account. Bragg scattering of neutrons (first order) in the diamond nano-crystals is absent as the neutron wavelength is larger than the double interplane distance of 4.119 Å (for reflection (111)) in diamond.

In order to verify the procedure of the experimental data treatment, we measured with non-cleaned nano-diamond powder of various thicknesses. The transmission probability as a function of the sample thickness is given in Fig. 4. The obtained results are approximated with an exponent, apart from the data for the thickest sample. This deviation is explained by a noticeable contribution of the detector background from isotropically-scattered neutrons. The results for a polyethylene sample and for a sample of nano-diamond cleaned from hydrogen are also shown in this figure.

Table 2. Measured cross-sections of neutron scattering on hydrogen

Sample	Scattering cross-section per hydrogen atom, bn
Polyethylene	172 ± 1.5*
Cleaned sample at the temperature 300 K	108 ± 2
Cleaned sample at the temperature 80 K	105 ± 2
Non-cleaned sample at the temperature 300 K	109 ± 2

* the cross-section is given for a molecule CH_2.

Measurements with Sample no. 1 (powder cleaned from hydrogen) were carried out at ambient temperature and at the liquid nitrogen temperature. The transmission through the sample was higher by ~3% in the second case. This sample was placed into an aluminum cryostat for these measurements; in order to take into account effect of aluminum cryostat walls and screens with the total thickness 7.2 mm, we measured additionally the transmission of neutrons through aluminum alone in the same geometrical configuration and temperature.

From measured experimental data, we calculated the total cross-section of neutron scattering on hydrogen atoms in the sample; the measured hydrogen fractions are taken into account. The results are given in Table 2. The given uncertainties are defined by precision of estimation of the absolute value of the measured hydrogen fraction; the accuracy of relative measurements at different temperatures with the same sample is much higher. The cross-section of absorption of neutrons with the wavelength of 4.4 Å in hydrogen is 0.81 b; it is taken into account in the data treatment.

The measured here cross-sections of neutron scattering in a test polyethylene sample agree well with results given in ENDF, in particular in [15].

MEASUREMENTS OF ATOMIC SPECTRA IN NANO-POWDER SAMPLES USING NEUTRON SPECTROSCOPY

In order to measure spectra of inelastic scattering of neutrons in nano-powders, we prepared two samples of equal mass in equivalent aluminum containers. One sample had not been treated (“non-cleaned from hydrogen”), while another sample (“cleaned from hydrogen”) had been heated in advance up to the temperature 140°C under permanent pumping during 12 hours (the average temperature during pumping was ~80°C).

These measurements were carried out using the spectrometer IN1-BeF [16] in ILL. Excitation spectra measured in powders are shown in Figs. 5, 6 for cleaned and non-cleaned powders respectively. Here, the energy of elementary excitation in a sample (or the neutron energy transferred to a sample) is plotted on the x-axis, the count rate in the detector (or the flux of neutrons scattered in a sample) is plotted on the y-axis; no data treatment is applied.

A background spectrum from the aluminum container does not exhibit an energy structure thus could be neglected if energy is higher than ~40 meV. The most important component of the experimental background in the IN1-BeF spectrometer, which depends weakly on the energy transferred, is related to non-complete filtering of neutrons elastically scattered in the beryllium filter; the intensity of this background

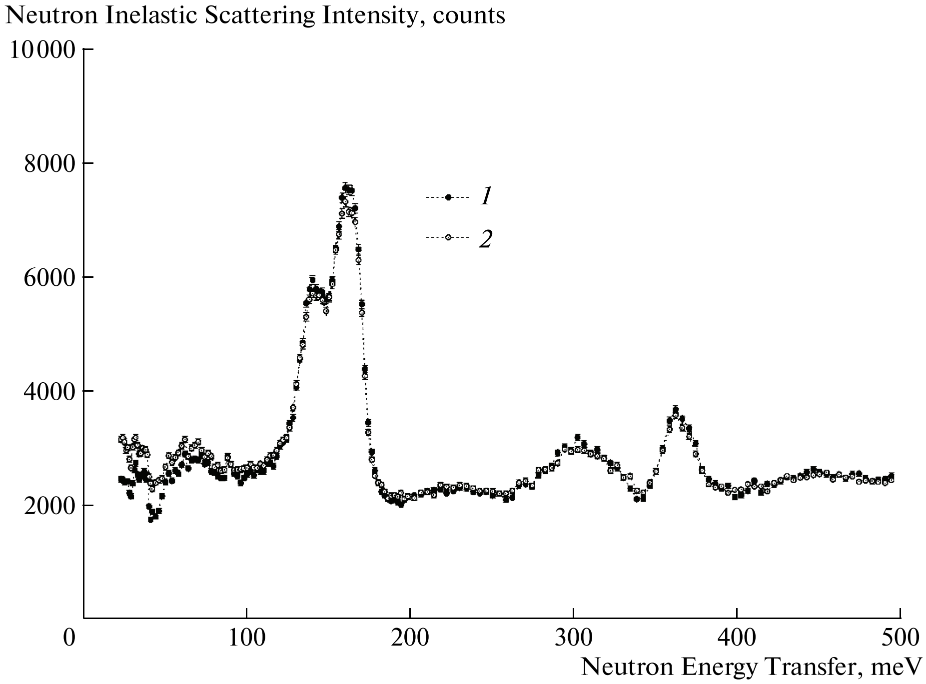

Fig. 5. The spectrum of excitation of cleaned nano-diamond powder in the energy range of 25–500 meV at the temperatures of 15 K (1) and 300 K (2).

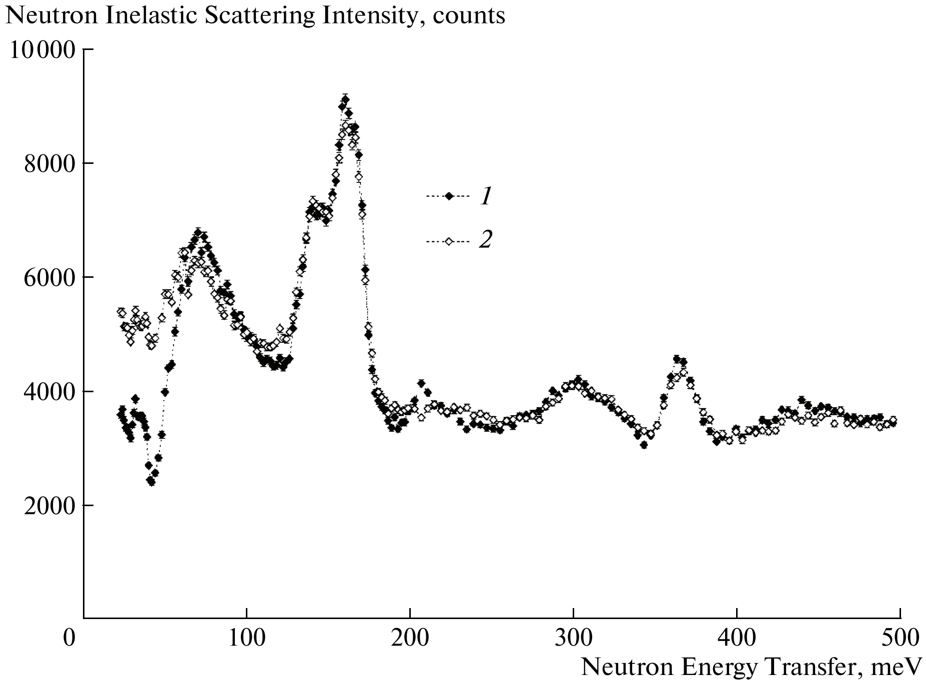

Fig. 6. The spectra of excitations of non-cleaned nano-diamond powder in the energy range of 25–500 meV at the temperature of 15 K (1) and 300 K (2).

components exceeds the inelastic scattering of interest by several orders of magnitude. Some measured decrease of this background for the cleaned sample corresponds qualitatively to a smaller fraction of hydrogen in it.

Inelastic component of neutron scattering is shown in Figs. 5, 6 mainly by the characteristic peaks in the energy dependence of the scattering intensity, which corresponds to enhanced density of excitations. As the intensity of this scattering is proportional to the ratio

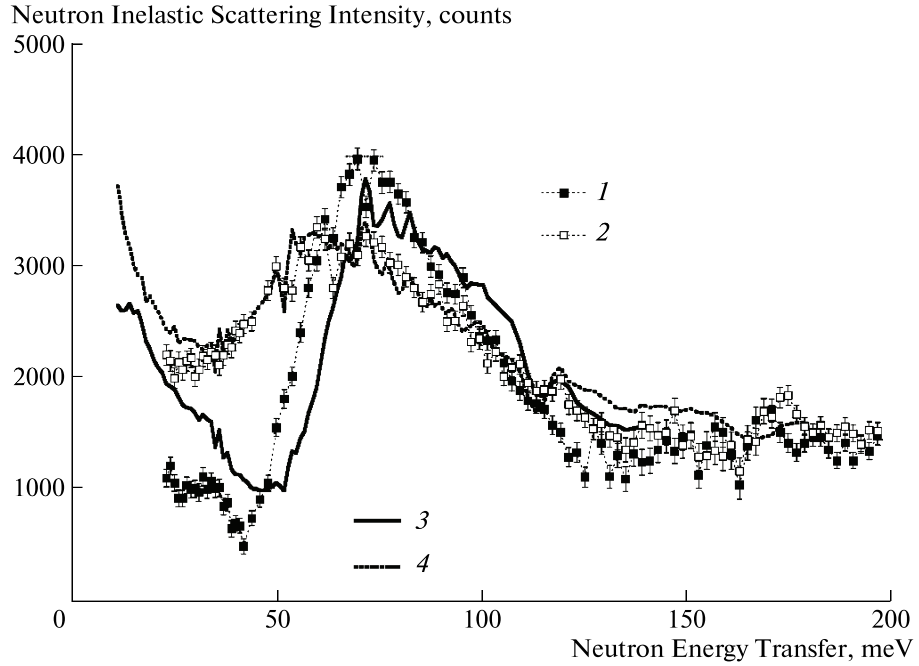

Fig. 7. Comparison of the spectra from "substances" and "bonds" removed from nano-powder due to thermal treatment and outgasing at the temperatures 15 K (1) and 300 K (2) to the spectra from ice (3) and water (4). For energies higher than 200 meV spectra 1 and 2 are nearly indistinguishable within statistical accuracy.

of the scattering cross-section to the mass of the scattering atom, the contribution of the hydrogen component exceeds, by more than an order of magnitude, the contribution of the carbon component for all energies in the studied range, in spite of relatively small ~10% atomic fraction of hydrogen.

One should note that the given spectra of inelastic scattering agree well quantitatively if energy is higher than ~100 meV. Following [17–20], and references therein on various systems with carbon-hydrogen bonds, the energy of the peak at ~360–365 meV corresponds to the excitation in the direction of the bond C–H (precise value depends on a type of sp^n hybridization), while the zone of the intensive peak between 125 and 180 meV corresponds to oscillations of the type "bending" of the C–H bond (the range 260–350 meV corresponds approximately to the contribution of multi-phonon processes from this "main" zone). This means that the number of C–H bonds in the cleaned and non-cleaned samples is nearly equal.

Main differences between the excitation spectra of cleaned and non-cleaned samples in Figs. 5, 6 are observed around the energy ~70 meV: the intense signal of inelastic scattering in a non-cleaned sample is largely suppressed in a cleaned sample. Some temperature changes in the spectra of a cleaned sample might be attributed to changes in the populations of excitations, while both quantitative and qualitative changes in the spectra of inelastic neutron scattering on a non-cleaned sample could be clearly noticed.

Differences between the spectra from cleaned and non-cleaned samples provide the excitation spectra of the substances removed by the sample thermal treatment and outgasing. Such energy dependencies measured at the temperatures of 300 K and 15 K are presented in Fig. 7 and compared to the excitation spectra measured earlier for ice and water under close experimental conditions. Comparison of the spectra indicates that thermal treatment and outgasing of nano-diamond samples eliminates hydrogen in a form of water adsorbed on nanoparticles surface.

In fact, the spectra 2 and 4 (for water) in Fig. 7 show good quantitative agreement. The spectra 1 and 3 (for ice) are close in shape, however, with some "softening" of the spectra of excitation of adsorbed molecules compared to the spectra of "usual" ice.

Evidently, more detailed study of the excitation spectra analogous to those presented in Figs. 5–7 would reveal the types of chemical bonds in diamond nano-powders; however, this subject is beyond the scope of the present study.

CONCLUSION

We showed that a fraction of hydrogen atoms in powder of nano-diamonds could be decreased by means of its thermal treatment and outgasing (or just by long outgasing) down to the ratio $C_{12.4}H$. This value corresponds to a mass fraction of hydrogen equal to 0.7%, which is about equal to the value 1% given in [21]. The initial ratio of carbon and hydrogen atoms in non-cleaned powder is $C_{7.4}H$. Measurements of excitation spectra in powder indicate that removed hydrogen has been in a form of water adsorbed to surface. The residual hydrogen is chemically bound to carbon. The total cross-section of neutron scattering on chemically bound hydrogen is 108 ± 2 bn; it decreases by no more than 3% when powder is cooled down to the nitrogen temperature. Thus preliminary thermal treatment and outgasing of powder from hydrogen does not improve considerably the reflecting properties of nano-diamond powder. Apparently, one should study an option of isotopic substitution of hydrogen by deuterium, with its much lower cross-sections of scattering and absorption.

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