Experimental report

21/09/2016

Proposal: **7-01-410**   **Council:** 10/2014

Title: Experimental measurement of DOS for nanocarbons: applications to isotopic fractionation processes and interstellar dust behaviour

Research area: Physics

This proposal is a new proposal

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Samples: graphite
diamond

Instrument	Requested days	Allocated days	From	To
IN4	5	5	17/09/2015	22/09/2015
IN1 LAG	5	0		

Abstract:

The project is aimed at experimental investigation of phonon density of states (PDOS) in several types of nanocarbons with emphasis on nanodiamonds and on various types of nanographites. The data obtained in our work will be used to study size effect on carbon reduced isotopic partition function ratio, to calculate thermal capacity of nanocarbons, and to investigate eventual influence of a confinement effect of nanocarbons properties.

Two applications of the obtained PDOS are of principal interest:

1) Geosciences: calculation of carbon isotope fractionation factors for nanoparticles and its comparison with results for macroscopic materials (the confinement effect on equilibrium stable isotope fractionation); and

2) Astrophysics: to put constrains on degree of heating of isolated carbonaceous particles in stellar environment by so-called stochastic heating.

In addition thermal capacity of nanocarbons will be calculated. This is important for construction of nanostructured plasma-facing blankets in ITER-type reactors.

This project will provide unique and pioneering information on size effect on isotopic fractionation.

Experimental measurement of DOS for nanocarbons: applications to isotopic fractionation processes and interstellar dust behavior

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The aim of the project was to measure experimentally phonon densities of states (PDOS) for several types of well-characterised nanocarbons with emphasis on nanodiamonds and on various types of nanographites. The data obtained in our work will be used to study size effect on carbon reduced isotopic partition function ratio, to calculate heat capacity of nanocarbons, and to investigate influence of a confinement effect of nanocarbons properties.

Two applications of the obtained PDOS are of principal interest:

1) Geosciences: calculation of carbon isotope fractionation factors for nanoparticles and its comparison with results for macroscopic materials (the confinement effect on equilibrium stable isotope fractionation); and

2) Astrophysics: to put constrains on degree of heating of isolated carbonaceous particles in stellar environment by so-called stochastic heating.

In addition, knowledge of thermal capacity of nanocarbons is important for construction of nanostructured plasma-facing blankets in ITER-type reactors.

Heat capacity of nanocarbon powder is difficult to measure reliably using direct methods such as calorimetry since they are prone to adsorption of water and other molecules from atmosphere and due to poorly controlled thermal contact of the powder. Many of these problems could be solved by using phonon density of states measured by Inelastic Neutron Scattering.

Samples and experimental details

Though DOS for macroscopic diamond and graphite are measured with considerable precision, the PDOS for nanodiamonds remain unknown. In this project synthetic nanodiamonds with well-known sizes were studied: 4-5 nm, 40 nm and 170 nm. Note that the method of production of these materials is very different: detonation of explosives for the smallest grains (4-5 nm) and mechanical crushing of macroscopic crystals. These differences introduce different types of defects into the grains, which apparently influence obtained results.

In addition to nanodiamonds several types of sp^2-bonded nanocarbons (nanographites) with variable degree of crystalline perfection were studied.

The measurements were performed in vacuum at several temperatures. To remove adsorbed water the first data point was at 500 K.

Results

Representative data for nanodiamonds of different sizes are shown in Fig. 1. The heat treatment effectively removed adsorbed water. The PDOS curves for nanodiamonds with sizes 40 and 170 nm are similar to the bulk diamond, though minor differences are present. We are currently investigating these variations in detail in order to clarify whether the variations are related to defect population in the grains.

The smallest nanodiamond grains are characterized by rather strong contribution of surface-bound C-H vibrations (breathing modes) which is not unexpected, since dehydrogenation of nanodiamonds requires much higher temperatures (e.g., Maturilli et al., 2014). The pDOS curve shows expected decreased intensity of the high energy peak. Nevertheless, even at sizes of 4-5 nm the DOD of diamond is generally similar to that of macroscopic crystal. This indicates that isotopic fractionation factors of nano- and macrodiamonds are close.

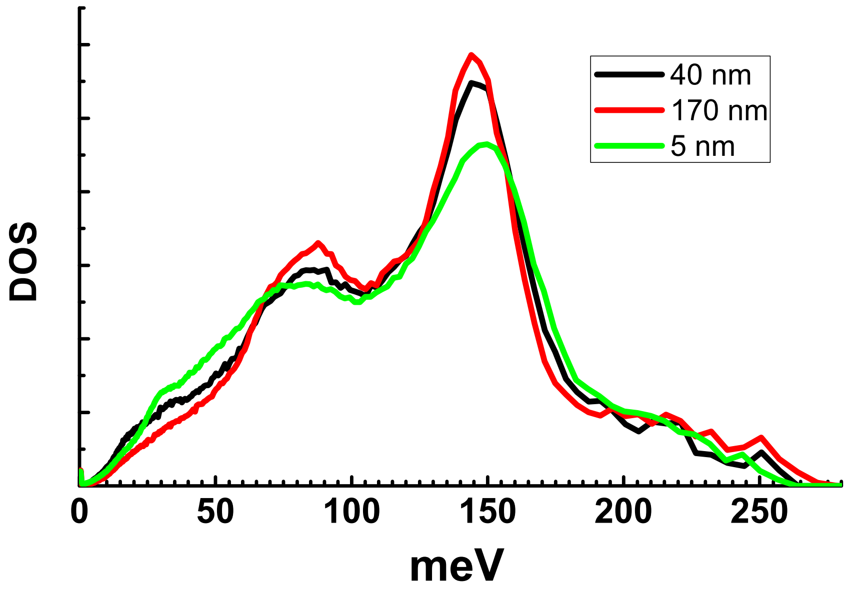

Figure 1. Experimental area normalized g(ω) curves for nanodiamonds of different sizes at 500 K.

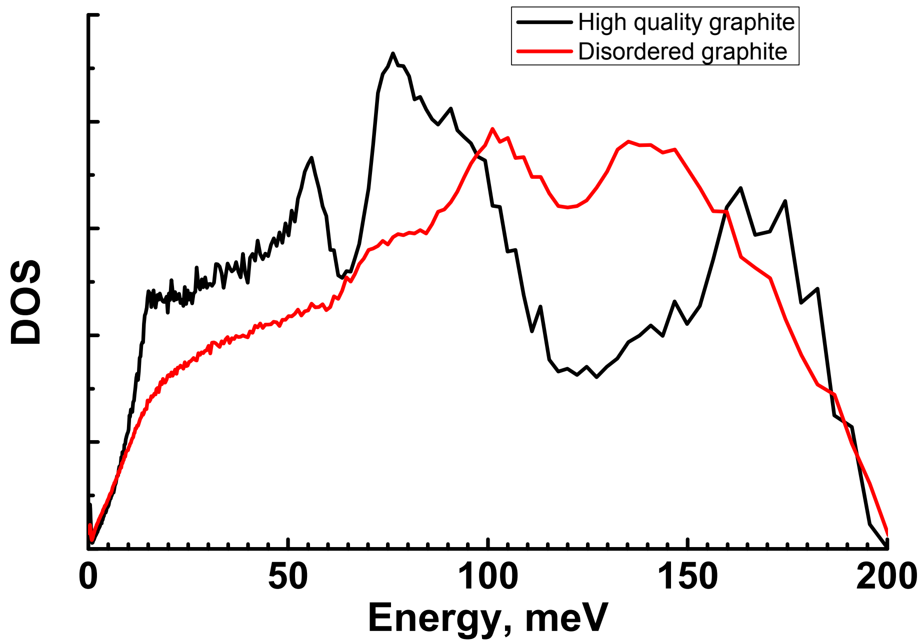

Figure 1. Experimental area normalized g(ω) curves for two types of graphite different sizes at 500 K

Data for nanographites are shown on Fig. 2. The curves are influenced by adsorbed H-containing functional groups and are being evaluated at present.

References

Maturilli et al., Infra-Red Reflectance and Emissivity Spectra of Nanodiamonds, Spectroscopy Letters, 47(6), 446-450 (2014)