

X-RAY ABSORPTION NEAR EDGE STRUCTURE SPECTROSCOPY OF NANODIAMONDS FROM THE ALLENDE METEORITE. G.J. Flynn¹, L. P. Keller², H. Hill³, C. Jacobsen⁴, and S. Wirick⁴, ¹ Dept. of Physics, SUNY-Plattsburgh, Plattsburgh, NY 12901 (george.flynn@plattsburgh.edu), ²MVA Inc., 5500 Oakbrook Pkwy., Suite 200, Norcross, GA 30093, ³Laboratory for Extraterrestrial Physics - Code 691, NASA Goddard Space Flight Center, Greenbelt MD 20771, ⁴Dept. of Physics, SUNY-Stony Brook, Stony Brook, NY 11794.

Introduction: Diamonds, a few nanometers in size, have been extracted from some meteorites by a sequence of severe acid dissolution and oxidization steps described by Lewis et al. [1]. These diamonds appear to carry nitrogen depleted in N¹⁵ compared to the solar system [2] and Xe distinct in isotopic composition from solar Xe, reflecting the addition of r- and p-process Xe in different proportions than in our Solar System [3]. These meteoritic nanodiamonds are believed to have originated in the atmospheric envelope of a star other than our Sun [3].

Bernatowicz et al. [4] performed Electron Energy Loss Spectroscopy (EELS), with an energy resolution of about 1.2 eV, on nanodiamonds extracted from the Allende and Murray meteorites and compared them to terrestrial nanodiamonds.

Using a Scanning Transmission X-Ray Microscope (STXM) installed on beamline X1A of the National Synchrotron Light Source at Brookhaven National Laboratory, we have performed Carbon-X-ray Absorption Near Edge Structure (C-XANES) spectroscopy, with an energy resolution better than 0.25 eV, on three nano-diamond samples:

- 1) Allende (from "Allende DM" residue preparation) nanodiamonds (provided by T. Bernatowicz),
- 2) detonation nanodiamonds (prepared by H. Hill), and,
- 3) terrestrial nanodiamonds (provided by T. Bernatowicz).

Transmission electron microscope examination indicates most diamonds in the first two samples are <4 nm in size, while the terrestrial nanodiamonds are somewhat larger, described as <0.2 μm by Bernatowicz et al. [4].

The objectives of our measurements were to examine the absorption spectrum of Allende nanodiamonds near the carbon edge with significantly better energy resolution than was available to Bernatowicz et al. [4] and to compare the absorption of Allende nanodiamonds with measurements on diamond thin films with crystallite sizes as small as 3.6 nm, recently published by Chang et al. [5].

Pre-edge Features: Bernatowicz et al. [4] observed a broad pre-edge absorption, at about 284 eV, in the Allende and Murray nano-diamonds but not in the terrestrial nano-diamonds. They attributed this feature to a 1s to π^* transition, resulting from sp² (graphite-like) terminations of the surface bonds.

Our C-XANES examination of the Allende DM nanodiamonds separates that absorption into two distinct peaks, at approximately 285 eV and 286.6 eV. (see Figure 1) These pre-edge absorptions could result from incomplete removal of meteoritic organic matter from the diamond-rich residue. However, our C-XANES examination of organic-rich, acid-insoluble residues from other meteorites (particularly Murray and Murchison) indicate that these organic residues show an additional strong absorption in the 288 to 289 eV range, most likely from C-O bonds. This feature is absent in the Allende diamond residue, suggesting that meteoritic organics were relatively completely removed, and that *the two pre-edge absorptions are associated with the Allende diamonds themselves.*

Both of these pre-edge absorptions have also been reported in x-ray absorption spectroscopy of nanodiamond thin-films by Chang et al. [5]. They reported that the two pre-edge absorptions show a general trend of increasing in strength with decreasing diamond crystallite size, but they observed the pre-edge absorption in films with diamonds crystallites as large as 5 μm in size [5]. The pre-edge absorption at 285 eV is attributed to the 1s to π^* transition, consistent with the interpretation of Bernatowicz et al. [4]. The absorption at 286.6 eV is consistent with C-H surface bonding [5] or with "dangling bonds" reported in thin polycrystalline diamond films [6].

Diamond Exciton: The high energy resolution of the STXM allows us to examine the diamond exciton absorption, previously reported in Type IIa and IIb diamonds by Ma et al. [6]. This absorption is attributed to transitions from the symmetrical ground state to an excitonic state resulting from the creation of an electron-hole pair [6]. We detected a prominent diamond exciton, a strong, sharp absorption just above 289 eV (see Figure 2), in the terrestrial diamond sample provided by Bernatowicz. The spectra of the terrestrial diamond published by Bernatowicz et al. [4] do not show the exciton, demonstrating that the energy resolution of their EELS instrument was insufficient to resolve this peak. The diamond exciton feature is absent in our spectra of the Allende nanodiamonds (see Figure 1) taken under the same analysis conditions as were used for the terrestrial diamond.

The diamond core exciton results from relatively long range order in the crystal. Chang et al. [5] have shown that the exciton absorption is essentially identical to that in bulk diamond in thin films with crystal-

lite sizes as small as $1\ \mu\text{m}$. For smaller crystallite sizes they report that the excitation becomes weaker and moves to progressively higher energies. However, they observed the exciton in samples with crystallite sizes as small as 3.6 nm in diameter [5], the smallest sample they measured.

We also examined detonation diamonds, which are similar in size to the Allende nanodiamonds. The detonation nanodiamonds are similar to the Allende nanodiamonds in that they show the same two pre-edge absorptions and they do not have the diamond exciton absorption (see Figure 3). However, the detonation diamonds are distinctly different from the Allende nano-diamonds in that the onset of the absorption edge appears to be shifted to an energy $\sim 0.5\ \text{eV}$ lower than in either the Allende or the terrestrial diamond samples.

Conclusions: The Allende nanodiamonds are similar to other ~ 4 nanometer diamond samples in that they show two prominent pre-edge absorptions, one attributable to $1s$ to π^* transitions and the other to C-H bond or dangling bonds. The Allende nanodiamonds are distinctly different from the larger terrestrial nanodiamonds and from the 3.8 nanometer crystallite size thin-film diamonds [described in 5] in that the Allende nanodiamonds do not show a prominent diamond exciton absorption.

This absence of the diamond core exciton in these Allende nano-diamond sample may simply result from the small size of the Allende nano-diamonds. However, Chang et al. [5] detected the diamond exciton in thin films with diamond crystallite sizes as small as 3.6 nm.

Alternatively, the absence of the exciton may indicate disorder of the structure of the Allende diamonds, resulting in an asymmetric ground state. This disorder might be produced by ion implantation, a proposed mechanism for trapping of the non-solar Xe in these nano-diamonds, or by the trapping of atoms other than carbon (e.g. nitrogen) in the diamond structure. Further study of these interstellar diamonds may allow us to infer some of the conditions in the environment where they formed.

References: 1) Lewis R. S. et al. (1987) *Nature*, 326, 160-163. 2) Virag A. et al. (1989) *Lunar & Planet. Sci.* XX, 1158-1159. 3) Anders, E. (1988) in *Meteorites and the Early Solar System*, U. of Arizona Press, 927. 4) Bernatowicz, T. J. et al. (1990) *Astrophys. J.*, 359, 246-255. 5) Chang, Y. K. et al. (1999), *Phys. Rev. Lett.*, 26, 5377-5380. 6) Y. Ma, et al. (1993) *Phys. Rev. Lett.*, 71, 3725-3728.

Figure 1: X-ray absorption of Allende DM diamond extract near the carbon edge.

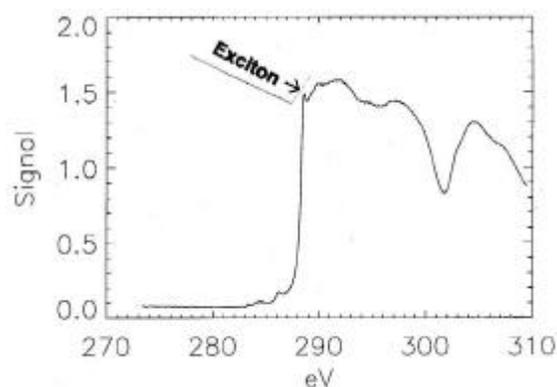


Figure 2: X-ray absorption of terrestrial diamond near the carbon edge. Note the diamond exciton.

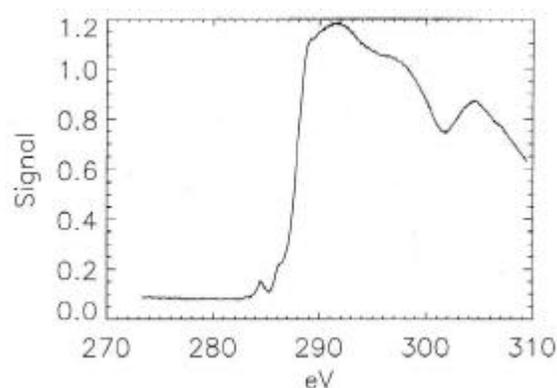


Figure 3: X-ray absorption of detonation diamond near the carbon edge.

