Summary of Proposal 24095

Requested Access Route:	Standard		
Principal Investigator:	**Professor Richard Walton, University of Warwick**		
Alternate Contact(s):			
Co-Investigator(s):	Dr Reza Kashtiban, University of Warwick Dr. Jeremy Sloan, University of Warwick		
Title:	**The Local Structure of Inorganic Materials Confined in Carbon Nanotubes**		
Requested Instrument(s):	B18 (3 shifts)		
Total Shifts Requested:	3	**RCaH requested:**	No
Industry Involved:	No	**Industry Group Links:**	Yes
Science Area(s):	Chemistry, Materials, Physics		

Abstract: The aim of this experiment is to examine the local structure of extremely small crystals of matter confined inside carbon nanotubes. Such materials are just a few atoms in diameters so it is anticipated that the average coordination numbers are dramatically lower than bulk materials of the same compositions. The average oxidation states of the elements also needs to be considered into order to understand how charge is balanced. The reason for studying such unusual forms of matters is that their properties deviate dramatically from conventional samples of the same compositions: this includes electronic behaviour and the temperature at which phase changes occur. To understand these properties and how they might be exploited in future applications, quantitative information about the atomic-scale structure is needed. EXAFS is ideally suited to provide this information.

Grants:
Number: EP/R019428/1
Dates: 30/07/2018 - 29/07/2023
Sponsor: EPSRC
Title: CRYSTALLOGRAPHY AND FUNCTIONAL EVOLUTION OF ATOMICALLY THIN CONFINED NANOWIRES

B18 Instrument Questions

Question	Answer
Please confirm you have checked the B18 website for the current status and conditions	Yes
If you have discussed your proposal with a beamline staff member, please indicate the main points of the discussion and with whom.	Giannantonio Cibin
Have you any objections to this proposal being appraised for technical feasibility by the beamline staff?	No
Which element and absorption edge are you planning to study? (if more than one, please indicate all of them)	Sb, Te, Cs, Sn, I K-edges
Which monochromator crystal cut do you need for your experiment? Please refer to the B18 webpage for information about energy ranges covered by the crystals.	Si(311)
Is your sample...	solid
What is the concentration or total amount of the absorber in the sample (e.g Molarity, Molality, Mole fraction, Stoichiometric atomic fraction, Thin Film (Thickness) etc)?	The samples are concentrated and concentration be be adjusted using polyethylene powder to bring the absorption to within an acceptable range.
What is the density of the major component?	No measured
If your sample is air/moisture sensitive or needs special handling, please specify the requirements.	Not applicable
Which sample environment do you need for your experiment?	Room Temperature

Question	Answer
Specify temperature range or own equipment details.	Not applicable
If the experiment requires special synchronization of signals please specify requirements and discuss with beamline staff.	Not applicable
If you need to use gases in your experiment, please list them all.	Not applicable
Do you need cooling water for your experiment?	No
Do you plan to use B18 sample cells?	Yes
If not using B18 sample cells, please describe other specific specimen environments you are planning to use at the beamline and discuss with beamline staff.	Not applicable
Select spectroscopy laboratories, if required.	Wet Chemistry laboratory, Not applicable
If other Diamond lab required, please specify	Not applicable
Select the equipment from the instrumentation lab, if required.	Not applicable
Select the equipment from the chemistry lab, if required.	Fume Cupboard, Pellet Press
Select the equipment from the physics lab, if required.	Not applicable
If the equipment that you need for your experiment is not listed, please specify your needs and we will try to find if it is available at Diamond.	Not applicable
Which detector do you require?	Ionization chambers (transmission mode)

Samples:

Name	CAS No	Type	
caesium tin iodide	None	**ChemicalSubstance:**	powder
antimony telluride	1327-50-0	**ChemicalSubstance:**	powder

Experimental Method: Method

Sample Preparation: Diamond prep-lab required: Pressing pellets

Instrument Experiment and Environment: Description of experimental set-up and procedures: Solid samples will be weighed, mixed with polyethylene powder and pressed into pellets

The Local Structure of Inorganic Materials Confined in Carbon Nanotubes

1. Abstract The aim of this experiment is to examine the local structure of extremely small crystals of matter confined inside carbon nanotubes. Such materials are just a few atoms in diameters so it is anticipated that the average coordination numbers are dramatically lower than bulk materials of the same compositions. The average oxidation states of the elements also needs to be considered into order to understand how charge is balanced. The reason for studying such unusual forms of matters is that their properties deviate dramatically from conventional samples of the same compositions: this includes electronic behaviour and the temperature at which phase changes occur. To understand these properties and how they might be exploited in future applications, quantitative information about the atomic-scale structure is needed. EXAFS is ideally suited to provide this information from bundles of filled nanotubes and will complement high-resolution TEM results, which are naturally area-selective.

2. Scientific context The filling of carbon nanotubes is an innovative way of accessing novel states of matter on the nanoscale. Nanowires formed by filling the central pore of single walled carbon nanotubes (SWCNTs) with extremely small diameters can be constrained to as little as 1-3 atoms thick in cross section, equivalent to a single row of atoms or a partial unit cell or single unit cell of simple binary or ternary structures. Such encapsulation can enforce radical properties changes on the embedded materials resulting, for example, in the practical realisation of Peierls distortions for metallic 1D chains of tellurium [1] or dramatic enhancement of the Seebeck coefficient in the case of thermoelectric materials such as SnTe [2]. In Warwick, recent work in this area has been extended to more complex chemistry and we are uncovering new families of materials with unprecedented atomic-scale structure and properties. This proposal is concerned with such materials, including 'phase change materials' that show dramatically different behaviour compared to the bulk material, of relevance for application in high-density data storage materials [3], and the first examples of ternary materials being introduced into carbon nanotubes (unpublished results 2019). The applicant Jeremy Sloan has pioneered work in the area of filled nanotubes for more than 20 years [4,5] and his work is currently funded by an EPSRC Established Career Fellowship (2018-2023), which supports the postdoc Reza Kashtiban as microscopist. Richard Walton has collaborated with Sloan and Kashtiban at Warwick for more than 10 years on the study of various inorganic materials analysis and himself has used XAFS to study materials for almost 25 years: this collaborative approach will allow us to shed new insights into emerging materials that have fundamentally different properties than bulk crystals.

3. Experiment proposed We propose to study two sets of samples, one containing the binary Sb-Te, and the other ternary compositions in the Cs-Sn-I system. ***We can remove extraneous inorganic material from around the nanotubes to provide 10s of mgs of specimen that just contain carbon-filled tubes.*** As shown in the figures below, we have TEM data in-hand that shows a high proportion of filling of the nanotubes for each system. The Sb-Te system is important because of the potential use of phase change materials in data storage. Confinement within SWCNTs, Figure 1, maintains the phase change behaviour, but the temperature of glass transition is lowered significantly. As shown on Figure 1, we have been able to build an atomic-scale models for the material. We now wish to confirm this as being representative of the whole sample by measuring XAFS to determine bond distances, coordination numbers and valence states of both Sb and Te.

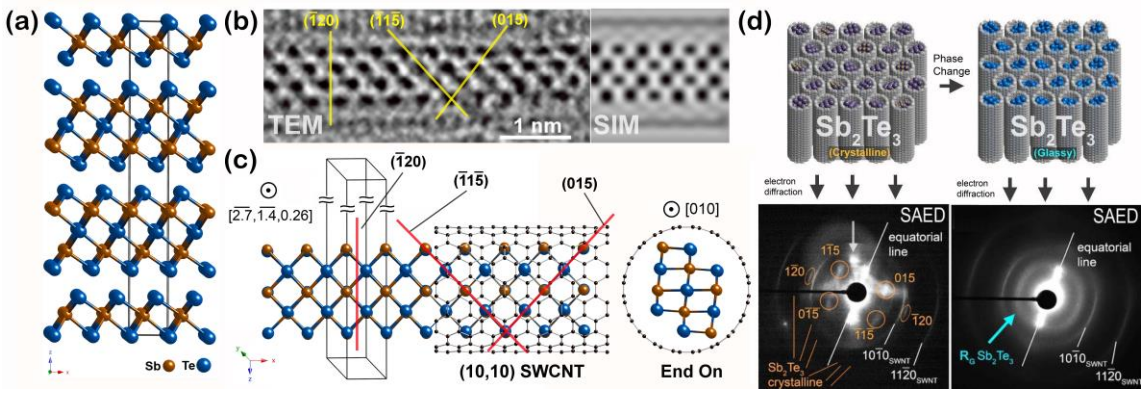
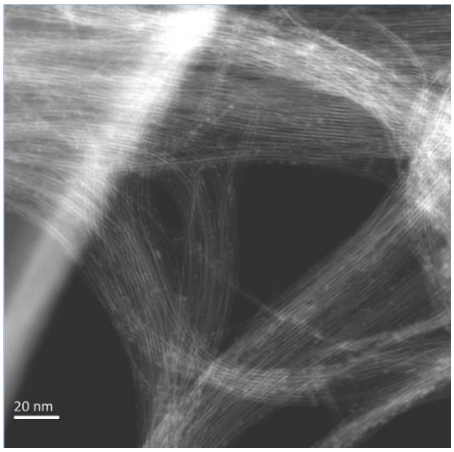


Fig. 1. (a) Bulk Sb_2Te_3; (b) TEM image of Sb_2Te_3@SWNTs and corresponding multislice simulation; (c) crystal structure for encapsulated nanowire from a single layer of Sb_2Te_3 with prominent scattering planes indicated; (d) The electron diffraction protocol (top) and electron diffraction patterns of the crystalline (bottom left) and amorphous (bottom right) with the SWNT diffraction contribution indicated. Six discrete reflections are clearly observed for crystalline Sb_2Te_3 (indexed) whereas only a single diffuse ring is observed for embedded amorphous Sb_2Te_3.

We will study two samples as-made (via different temperatures), and then the two samples that have been pre-heated and rapidly cooled to amorphise the nanotube contents (relevant for phase-change applications). Bulk Sb_2Te_3 in crystalline and amorphous states will provide reference materials. Measuring XANES/EXAFS at both the Sb (30.49 keV) and Te (31.81 keV) K-edges will provide the quantitative information that we require about local atomic structure and how the confinement in the tubes affects this.



The Cs-Sn-I system is of recent importance since a number of phases with useful electronic properties have been reported in the literature. This includes $CsSnI_3$ [6], and Cs_2SnI_6 [7], which are proposed for application in solar devices. Note that the former contains Sn(II) and the latter Sn(IV), and redox may take place during the melt filling of the tubes and so XANES spectroscopy at the Sn K-edge (29.2 keV) will be invaluable in determining bulk average oxidation state. Figure 2 illustrates the high level of SWCNT filling achieved in this system.

Figure 2: ADF STEM Images of bundles of 1.3 – 1.7 nm diameter SWNTs filled quantitatively with ternary Cs-Sn-I material.

We will have 6 Sb-Te samples to study (two filled nanotubes before/after amorphisation and two Sb_2Te_3 reference materials) at each of the Sb and Te K-edges. For the Cs-Sn-I system we will have 6 samples to study (filled nanotubes prepared at two different temperatures and the same after air exposure, and two reference materials), at each of the Cs, Sn and I K-edges (35.98, 29.20 and 33.17 keV, respectively). Note that although the Cs K-edge is towards the edge of the reflectivity of the B18 mirrors and intensity drops down quickly, Giannantonio Cibin has confirmed that transmission experiments are possible and have been successful before. Thus in total we will measure 30 EXAFS spectra. The data will all be collected in transmission mode at room temperature, with pellets pre-made using polyethylene as diluent where necessary. 1 day of beam-time will provide up to 45 minutes per spectrum to ensure good signal:noise ratio at high *k* to obtain the best possible EXAFS spectra, bearing in mind the initial setup at the beginning of the beamtime.

4. Results expected To our knowledge there have been only a few published XAFS studies of filled carbon nanotubes [8,9] since many specimens reported are not quantitatively filled nor free of excess bulk material, and so our study will yield highly publishable results. We will be able to verify that our new materials have the expected lowering of coordination numbers seen by selected area analysis using TEM. The Cs-Sn-I materials are the first example of a ternary phase within carbon nanotubes and the XAFS will be invaluable in determining the composition and chemistry of the phases present. We will combine the XAFS results with TEM data already measured at Warwick and at the SuperSTEM facility at Daresbury, to rationalise with property measurements in progress (optical and thermal behaviour) and would anticipate publishing the results in high-profile journals. If this first set of experiments is successful, in the future we will plan to apply for beamtime to follow structural changes within filled nanotubes *in situ* with heating.

5. References [1] V. C. Medeiros, S. R. Marks, J. M. Wynn, A. Vasylenko, Q. Ramasse, D. Quigley, J. Sloan, and A. J. Morris, *ACS Nano* **11**, 6178-6185 (2017) ; [2] A. Vasylenko, S, Marks, J. M. Wynn, P. V. C. Medeiros, Q. M. Ramasse, A. J. Morris, J. Sloan, and D. Quigley, *ACS Nano*, **12**, 6023–6031 (2018); [3] S.R. Marks, K. Morawiec, P. Dluzewski, S. Kret and J. Sloan, *Acta Phys. Polon. A* **131**, 1324-1327 (2017); [4] J. Sloan, A.I. Kirkland, J.L. Hutchison and M.L.H. Green, *J. Chem. Soc., Chem. Commun.*, 1319-1332 (2002); [5] J. Sloan, A. I. Kirkland, J. L. Hutchison and M. L. H. Green, *Comptes Rend. Phys.* **4**, 1063-1074 (2003); [6] K. P. Marshall, M. Walker, R. I. Walton, R. A. Hatton, *Nature Ener.* **1**, 1-9 (2016); [7] B. Lee, C.C. Stoumpos, N. Zhou, F. Hao, C. Malliakas, C.-Y. Yeh, T.J. Marks, M.G. Kanatzidis, and R.P.H. Chang, *J. Am. Chem. Soc.* **136**, 15379–15385 (2014); [8] A.A. Eliseev, L.V. Yashina, N.I. Verbitskiy, M.M. Brzhezinskay, M.V. Kharlamova, M.V. Chernysheva, A.V. Lukashin, N.A. Kiselev, A.S. Kumskov, B. Freitag, A.V. Generalov, A.S. Vinogradov, Y.V. Zubavichus, E. Kleimenov, M. Nachtegaal, *Carbon*, **50**, 4021-4039 (2012); [9] T. Michel, L. Alvarez, J-L. Sauvajol, R. Almairac, R. Aznar, J-L. Bantignies, and O. Mathon, *Phys. Rev. B* **73**, 195419 (2006).