EUROPEAN SYNCHROTRON RADIATION FACILITY
INSTALLATION EUROPÉENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Application for XMaS-BM28 CRG Beam Time

Proposal Title (175 chars maximum.)

XAFS and XRD of Inorganic Materials Confined in Carbon Nanotubes

Keywords

#1: nanomaterials #2: semiconductor #3: EXAFS #4:

- **This proposal is:**
  - A new proposal ☑
  - A resubmission of ...
  - A continuation of : ...

Societal Themes

- ○ Earth and Environment
- ○ Energy
- ○ Health
- ○ Fundamental Science
- ○ Information and Communication Technology (ICT)
- ○ Other
- ◉ Other Functional Materials

Scientific Area of the proposal

- ◉ HC - Hard Condensed Matter Science
- ○ SC - Soft Condensed Matter Science
- ○ ES - Earth Sciences
- ○ MA - Applied Materials Science
- ○ LS - Life Sciences
- ○ EV - Environment
- ○ ME - Engineering
- ○ MD - Medicine
- ○ HG - Cultural Heritage
- ○ CH - Chemistry
- ○ MI - Methods and Instrumentation

Number of shifts required *(1 shift is 8 hours)* 12

Preferred starting time: *Please select the period* October/November *Unacceptable dates*

Beam Requirements

☐ 16 Bunch Mode ☐ 4 x 10mA Mode ☑ Multi Bunch

☐ Circular polarization ☐ White beam ☑ Monochromatic beam

☐ Fixed energy [keV]: ☑ Tunable energy [keV] from: 29 to: 40

Beam energy resolution [meV]: Spot size on sample [µm]:

Other:

Main proposer (to whom correspondence will be addressed):

Laboratory University of Warwick Department of Chemistry West Midlands GB - CV4 7AL COVENTRY

Name Professor **WALTON** **Richard Ian** Phone 44 24 7652 3241 Fax 44 24 7652 4112
Email r.i.walton@warwick.ac.uk

Co-Proposers (Laboratory if different from main proposer)

Laboratory Warwick University Department of Physics Gibbet Hill road West Midlands GB - CV4 7AL COVENTRY

Name Dr **KASHTIBAN** **Reza** Email R.kashtiban@warwick.ac.uk

Name Dr **SLOAN** **Jeremy** Phone +44 (0)2476 523392 Fax NA Email j.sloan@warwick.ac.uk

Laboratory Support Facility

- ☐ Biology Lab
- ☐ Central Chemistry Lab (Science Building)
- ☐ PSCM Labs (Science Building)

Sample Environment

Items Supplied by the ESRF

☐ Furnace ☐ Magnet ☐ Cryostat ☐ Cryogenic gas stream ☐ Refrigerator

Société Civile
RCS Grenoble D 338 723 919
N° Siret 338 723 919 00027 - APE 7219 Z

Postal Address: ESRF User Office - CS 40220 - 38043 Grenoble Cedex 9 - France
Location: Polygone Scientifique Louis Néel - 71, avenue des Martyrs - 38000 Grenoble - France
Telephone (Switchboard): 33-(0)4 76 88 20 00 - Telefax: 33-(0)4 76 88 20 20

☐ Laser Class ... Wavelength [nm] ☐

☐ High pressure Pressure range [GPa] from ☐ to ☐

☐ Fixed temperature Temperature range [K] from ☐ to ☐
Temperature [K] ☐

Detector system

Other equipment

Items Not Supplied by the ESRF
List all equipment that you will insert into the instrument

☐ Laser Class Wavelength [nm] ☐

☐ Other equipment

Please indicate requirements for special equipment or facilities

Sample Description

Substance and formula

Carbon nanotubes filled with Sb2Te3, CsSnI3 and Cs2SnI6, plus bulks samples of the inorganics. Up to 50 mg of each sample. Note that they will already be sealed in Kapton film before the experiment.

☐ Single crystal ☐ Powder ☑ Polycrystalline ☐ Multilayer ☐ Liquid ☐ Gas

☐ Nanoparticles ☐ Prepared at ESRF ☐ Other ?

Average size [mm] Volume [mm³] Surface area [mm²]

Mass [mg] Matrix or solvent Conc.of absorb.[mmol]

Space group Cell dimensions at T= K:

a= Å b= Å c= Å alpha= Â° beta= Â° gamma= Â°

Container (capillary, flat plate, type of pressure cell, etc.)

Extra information required for Macromolecular Crystallography:

Origin and expression system

Previously observed diffraction (resolution, X-ray source, exposure/Â°)

Safety

Is the sample:

☐ Radioactive? ☐ Contaminant? ☐ Corrosive? ☐ Oxidizing?

☐ Explosive? ☐ Biologic? ☑ None of those

Is there any danger associated with the proposed sample, with any preparation at ESRF, or with sample equipment?

○ Yes ○ Uncertain ◉ No

If you have ticked Yes or Uncertain, you must give details of the associated risks in the box below:

Will you use live animals *on site for your experiment* ***(all kinds of animals are concerned)?*** ○ Yes ◉ No

After the experiment *, will the sample be:* ◉ Removed by user? ○ Stored at ESRF?

To be filled by ESRF	***Comments by safety Officer:***
Sample environment code:	

Experience with Synchrotron Radiation

What are the technical reasons which make ESRF necessary for your experiment?Why are other synchrotron radiation sources not appropriate?

The ESRF provides high flux at the high energy absorption edges that will be studied

Have you used synchrotron radiation at the ESRF? ○ No ◉ Yes

Have you used synchrotron radiation at other sources? ○ No ◉ Yes, at: Daresbury SRS, Diamond Light Source, HASYLAB

Have you already used synchrotron radiation for this project? ○ No ◉ Yes

Publications

Please give the references of papers published by the proposers during the past 3 years as a result of experiments done at the ESRF.

Origin (1): if from data from ESRF beamlines ONLY, (2) : if from data from more than one source

	Description	**Origin**

New ESRF User

New ESRF users may list below up to 10 publications not involving any data taken at ESRF. (Do NOT list any ESRF publications here, this MUST be done in the section above).

	Description	
[1]		

EUROPEAN SYNCHROTRON RADIATION FACILITY

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Application for beam time at ESRF – Experimental Method

Proposal Summary (should state the aims and scientific basis of the proposal): 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 diameter so it is anticipated that the average coordination numbers are dramatically lower than bulk materials of the same compositions. The reason for studying such unusual forms of matter is that their properties deviate 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 applications, quantitative atomic-scale structure is needed. XAFS + XRD is ideally suited to provide this information from bundles of filled nanotubes and will complement high-resolution TEM results, which are naturally area-selective.

Scientific background: 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, this 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 worked with Sloan and Kashtiban at Warwick for more than 10 years on the study of various inorganic materials and their structural analysis.

Experimental technique(s), required set-up(s), measurement strategy, sample details (quantity...etc): 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 filled carbon nanotubes.*** As shown in the figures below, we have TEM data in-hand that shows a high proportion of filling of the nanotubes. The Sb-Te system is important because of the potential use of phase change materials in data storage.

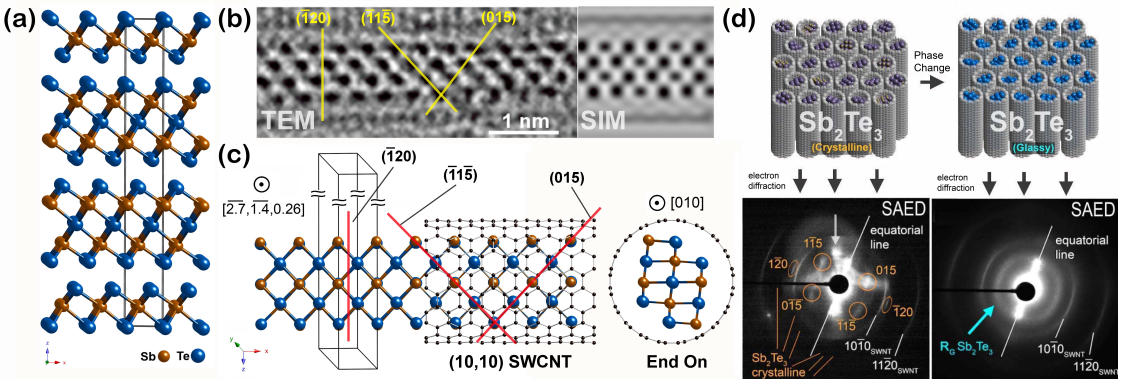

Fig. 1. (a) Bulk Sb_2Te_3; (b) TEM image of Sb_2Te_3@SWNTs and corresponding multislice simulation; (c) crystal structure for encapsulated nanowire from a single layer of Sb_2Te_3 with prominent scattering planes indicated; (d) The electron diffraction protocol (top) and electron diffraction patterns 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 now wish to measure XAFS to determine bond distances, coordination numbers and valence states of both Sb and Te. We will study two samples as-made (via different temperatures), and then the 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 and Te K-edges will provide quantitative information about local atomic structure and how the confinement in the tubes affects this. XRD will confirm the degree of crystallinity.

The Cs-Sn-I system is of recent importance: this includes $CsSnI_3$[6], and Cs_2SnI_6[7], which are studied 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 will be invaluable in determining bulk average oxidation state. Figure 2a illustrates the high level of SWCNT filling achieved in this system. We already measured some preliminary XANES data at Diamond on B18, Figure 2b, that indicate that the filled tubes contain Sn(IV), consistent with composition Cs_2SnI_6. We need to now make further measurements to confirm this using XRD, and on new samples to rule out aerial oxidation during handling.

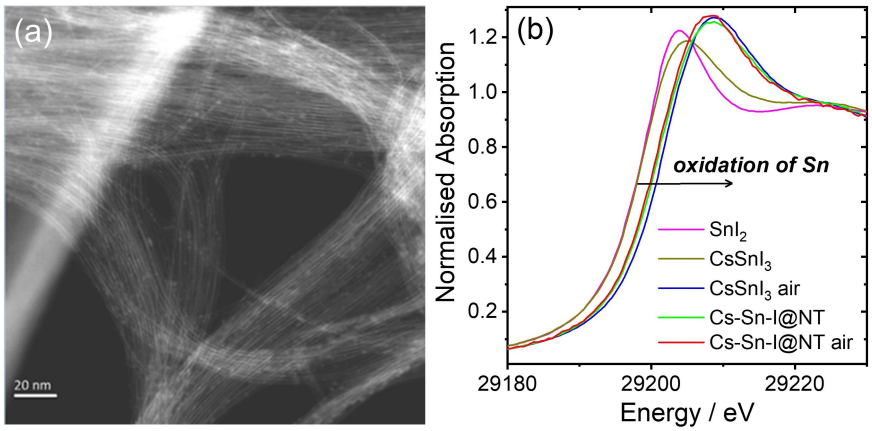

Figure 2: (a) ADF STEM Images of bundles of 1.3 – 1.7 nm diameter SWNTs filled quantitatively with ternary Cs-Sn-I material (b) Sn K-edge XANES measured on B18 at Diamond.

Beamline(s) and beam time requested with justification: We have 6 Sb-Te samples (two filled nanotubes each before/after amorphisation and two Sb_2Te_3 references) at each of the Sb (30.49 keV) and Te (31.81 keV) 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). Samples will be prepared in a glove box prior to the beamtime and sealed between pieces of Kapton tape. XMaS is ideally suited for this work as it will provide high flux at these energies, using a Ge detector for fluorescence XAFS, and we can also measure powder XRD patterns using a 2D detector attached to the 2θ arm. In total we will measure 30 EXAFS spectra and 30 XRD patterns. After discussion with Paul Thompson, we estimate that 4 days of beam-time will provide up to 1.5 hours per spectrum/pattern to ensure good signal:noise ratio at high k to obtain the best possible EXAFS spectra, and quantitative powder XRD, allowing also time for initial setup.

Results expected and their significance in the respective field of research: 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 their composition and chemistry. We will combine the XAFS results with TEM already measured to rationalise property measurements in progress (optical and thermal) and anticipate publishing the results in high-profile journals. If this first set of experiments is successful, we will plan for future beamtime to follow changes *in situ* with heating.

[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).