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1-D CRYSTAL GROWTH WITHIN SINGLE-WALL CARBON NANOTUBES

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At Oxford we have devised techniques for selectively opening single-wall carbon nanotubes (SWNTs) and filling them with a wide range of guest materials. In this paper we will present an overview of the project, outlining the methods that have been used successfully to open SWNTs and then fill them with crystalline structures. SWNTs are the smallest known discrete cylindrical structures, with internal diameters down to ~1 nm or less. They thus offer a unique environment for spatially confined crystal growth experiments, with the possibility of new structures being formed as a result of the confinement.

It is well known that in order to achieve wetting of carbon nanotubes by a molten salt, its surface tension should be 200mN/m. Also, the melting temperature is important, as the SWNTs may be destroyed at elevated temperatures in excess of 900 °C. With these factors in mind, we have focussed our efforts into crystallizing a wide range of metal halides, with structures ranging from simple cubic (KI) through layered ($CdCl_2$), chain ($ZrCl_4$) to molecular (SnI_4) compounds. In some cases mixtures of halides were also chosen in order to lower melting points, achieve higher filling yields and also to introduce ternary halide mixtures into SWNT capillaries. SWNTs prepared by arc vaporization were heated with molten salts for periods of 2-3 hrs and then characterised in a JEOL 3000F HREM operating at 300 kV. The point resolution of this instrument has been shown to 0.16 nm. Surprisingly, the filled nanotubes were fairly stable to electron irradiation (compared with exposed halide crystallites on a carbon-coated grid, for example), and allowed us to obtain HREM images and EDX spectra. This appears to be due to the confining walls of the SWNT acting as barriers to loss of halogen atoms.

A general point to note in considering the 1-D crystals and the interpretation of their images is that they are no longer "bulk" structures – the proportion of "surface" atoms is now significant – in the case of a cylindrical crystal only 2 x 2 atoms in cross-section, ALL the imaged atoms are surface atoms, with coordination that is substantially reduced from that in the bulk.

We will discuss examples from each class of structure, and in the case of KI (a close-packed cubic, rock-salt structure) show how we used through-focal series image reconstruction methods (with A I Kirkland & R R Meyer, Cambridge) to produce images showing ALL atomic sites in a 3x3 section. We were able to measure accurately local lattice distortions which arise as a result of the tight confinement.