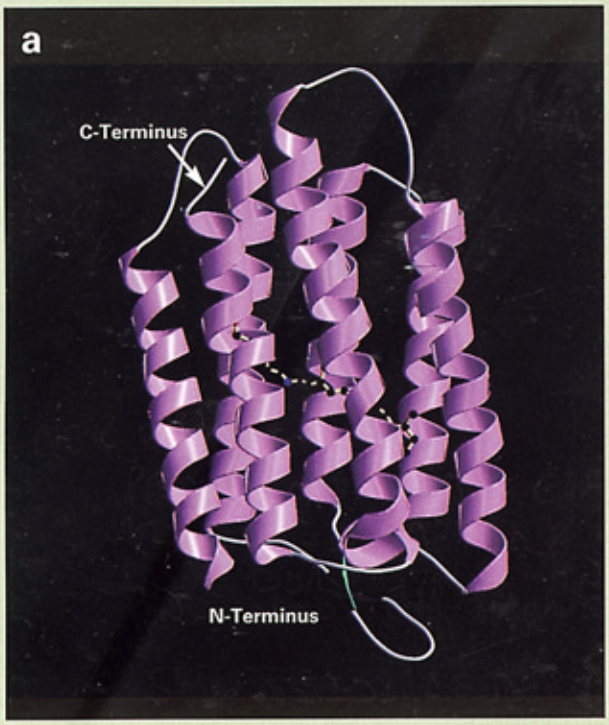
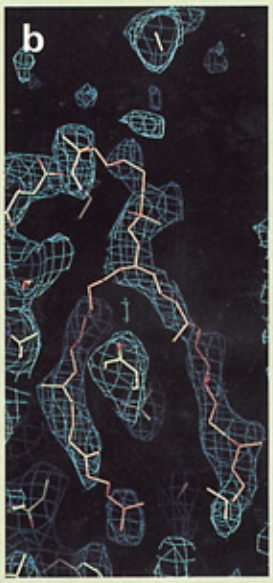
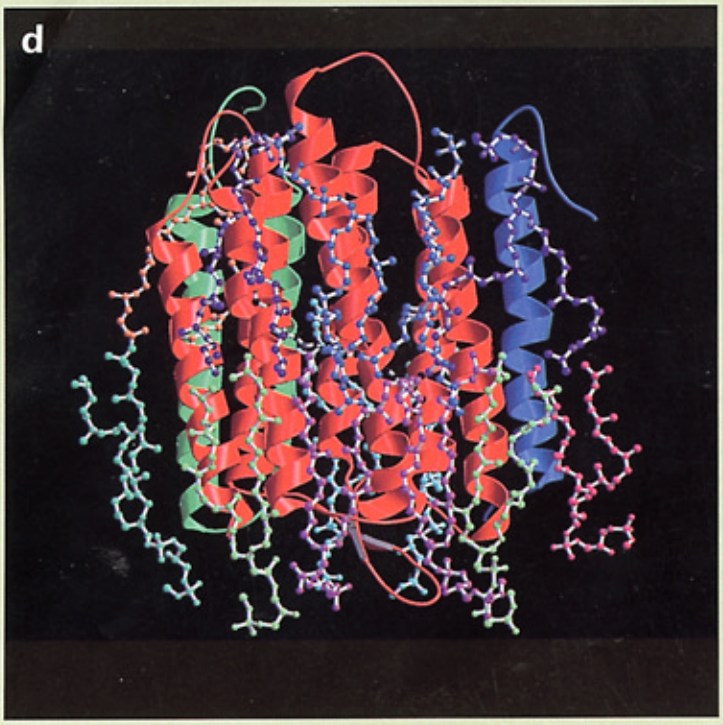
JEOL news
Volume 34E number 1, 1999
ISSN 0385-4426
electron optics instrumentation

JEOL 50th Anniversary Issue







The Development and Assessment of a High Performance Field-Emission-Gun Analytical HREM for Materials Science Applications

John L. Hutchison†, Ron C. Doole†, Rafal E. Dunin-Borkowski†, Jeremy Sloan†† and Malcolm L. H. Green††

†Department of Materials, University of Oxford
††Inorganic Chemistry Laboratory, University of Oxford

A new 300 kilovolt field-emission-gun analytical electron microscope has recently been installed in the Department of Materials at Oxford University. In this communication we first outline the materials developments for which we required a very high performance in all operating modes of the microscope. We then present the main features of this instrument, a JEM-3000F equipped with comprehensive analytical facilities, which is the first to be constructed in this particular configuration. Finally we show preliminary experimental results which confirm its performance, and also give examples of its applications to some novel nanostructured materials.

Development of novel nanostructured materials

An important area of materials research at Oxford concerns the fabrication and characterisation of advanced materials based on nanostructures. Our nanostructure development programme includes fullerenes and carbon nanotubes, novel nanocomposites, optoelectronic materials and information storage media. In order to understand and control the fabrication of these materials, it is essential that they be characterised at very close to the atomic scale. For this it became evident that our existing HREM facilities, based on JEM-4000EX(II) and JEM-2010 instruments, while routinely capable of atomic scale spatial imaging, could not provide a sufficiently high-current, sub-nanometre sized probe for both the high spatial resolution *and* chemical characterisation which was also required. The development of the new generation of high-resolution field-emission-gun (FEG) HREM instruments has provided such a tool, and when funding was made available for this project by the U.K.'s Engineering and Physical Sciences Research Council, we started working with JEOL (UK) and JEOL Ltd. to achieve an optimum instrument for our particular needs.

†Parks Road, Oxford OX1 3PH, UK.
††South Parks Road, Oxford OX1 3QR, UK
E-mail: john.hutchison@materials.ox.ac.uk

Performance criteria for the success of this project

In setting up this Advanced Microanalytical HREM Facility, it was necessary to take account of a number of factors which ultimately affected our choice of instrument. These included the following:

1. Good spatial resolution, better that 0.2 nm. This is essential for structure imaging of metallic particles.
2. Good specimen tilt capability, at least 20°, with the possibility of accommodating heating or cooling, double-tilt specimen holders.
3. A small probe capability, with a round probe smaller than 0.5 nm in diameter, with high beam current.
4. A high sensitivity EDX system, with good capability for light element analysis, and very low background X-ray counts.
5. A high performance digital image acquisition and analysis system.
6. PEELS analysis and energy filtered imaging.
7. As this would be a multi-user facility, ease of use and reliability were both additional, but important factors to consider.

The instrument

The installation is based around the JEM-3000F instrument, a 300 kilovolt microscope equipped with a thermally assisted, Schottky emitter type field emission electron source. The instrument is in the ultra-high resolution configuration, with a low-aberration objective lens. The additional analytical facilities are: an Oxford Instruments ISIS 300™ EDX system with an ultra-thin-window Si(Li) detector, a Gatan (1k×1k) CCD camera, and a Gatan GIF 2000™ PEELS and imaging filter, with a (2k×2k) CCD detector. An electron Biprism is also fitted for holographic studies. An overview of the facility is shown in **Figure 1**.

Assessing the performance

The specification included a newly designed objective lens polepiece which combines a C_s value of 0.6 mm with >20° double tilt capability. At the operating voltage of 300 kV, this C_s indicated a Scherzer (point) resolution better than 0.17 nm. The point resolution was initially measured on a thin film of amorphous germanium, as shown in **Fig. 2**. Fourier transforms were obtained using Gatan's Digital Micrograph™

software. Fig. 2 shows an FFT (rotationally averaged to reduce noise) obtained from an image of amorphous Ge, together with a line profile of its intensity distribution. The image was obtained at a defocus of – 42 nm, the Scherzer focus of this instrument. The position of the "first zero" in the plot is clearly seen, corresponding to a resolution of 0.16 nm. Additional contrast rings are visible, out to 0.12nm, indicating an extremely good chromatic damping envelope effect on the contrast transfer function.

As a further test of resolution, a thin <110> foil of natural diamond was investigated. The unit cell of diamond is small, with $a_o = 0.356$ nm. Thus in a <110> lattice image the largest spacings (d_{111}) are 0.206 nm, with smaller spacings also present. A typical <110> image of diamond is presented in **Fig. 3.** A much more stringent test using the same diamond specimen is to rotate the specimen around the 220-axis, to produce a systematic row of 220-type reflections, corresponding to a lattice spacing of d_{220} = 0.126 nm. Since these reflections *cannot* arise from multiple diffraction effects, they cannot be regarded as "half-spacings"; they represent "real" resolution. **Fig. 4** illustrates such an image; the 220 fringes with spacing 0.126 nm, are seen clearly, and verified in the accompanying FFT.

Progressing beyond this, we can then tilt the diamond into a 311- systematic orientation. In this case *only* 311-type reflections could contribute to the image contrast, with a spacing of d_{311} = 0.107 nm. Again, this is clearly shown in **Fig. 5**, with verification in the accompanying FFT.

Performance of the electron optical system

Since we are concerned with assessing the overall performance of the instrument, it is also necessary to quantify other electron optical parameters such as ultimate probe size, probe current, etc. This was done in the following tests.

The smallest probe size was recorded and measured by the CCD camera, measuring the

Fig.1. JEM-3000F analytical microscope at Oxford.

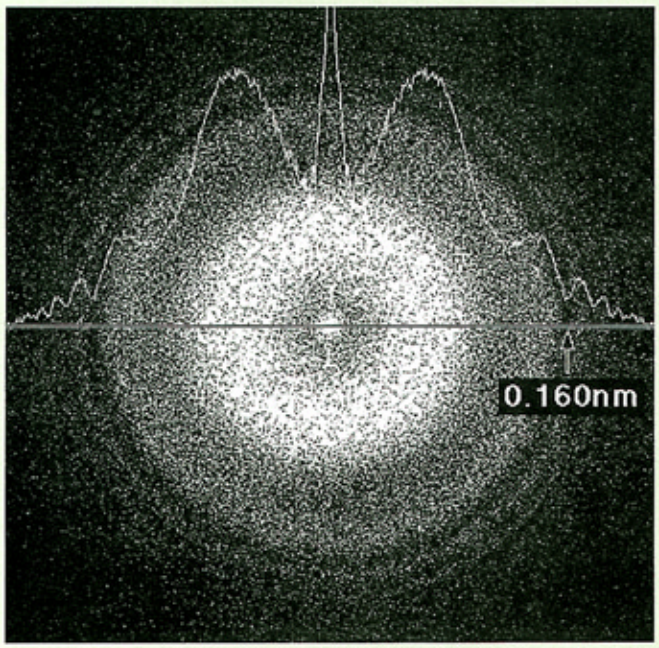


Fig.2. Fourier Transform from amorphous Ge film, at – 42 nm defocus indicating point resolution of 0.16 nm. Primary magnification of image: ×6000,000.

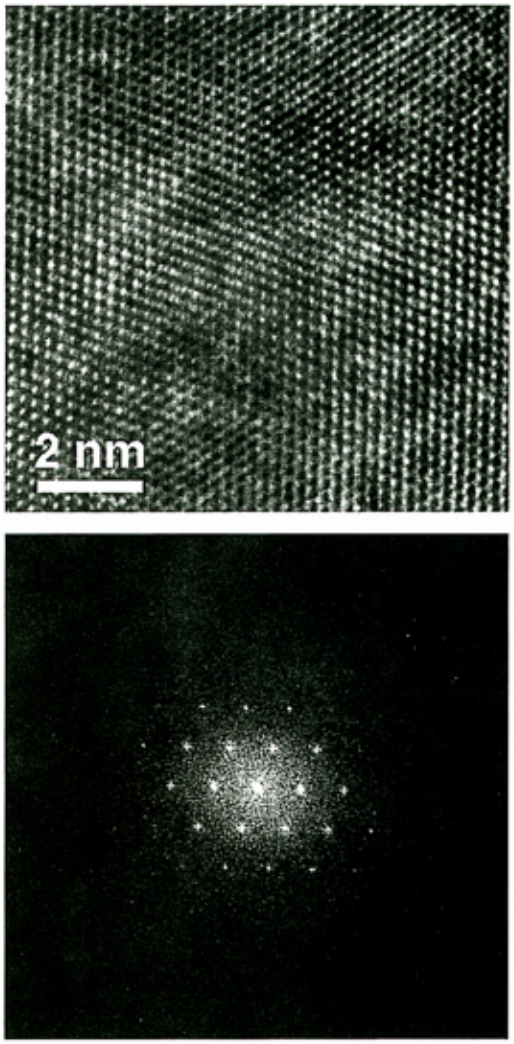


Fig.3. Lattice image of <110> diamond foil, with corresponding FFT, showing contrast transfer to <0.1 nm.

FWHM at various settings. **Fig. 6** shows the probe at the settings selected to produce the smallest nominal probe diameter of 0.4 nm. The diameter was measured at FWHM from an intensity profile, and confirmed to be better than 0.4 nm. A probe with a nominal diameter, measured by the same method, of 0.8 nm, produced a probe current of 550 pA.

Probe drift was estimated by comparing a series of images of the focussed small probe (1 nm diameter), over a ten minute period. The combined images are shown in **Fig. 7 a.** This was measured as 0.15 nm/min^{-1}, indicating an extremely stable illumination system. **Fig. 7 b** illustrates our analysis of the probe drift, with movement plotted as a function of time. From this it can be seen that most of the drift occurs wthin the first few minutes of switching to nano-beam conditions, after which the probe position remains essentially stable.

Energy spread in the electron beam was measured using the PEELS system. This is presented as a zero-loss EELS spectrum, shown in **Fig. 8**, and corresponds to a ΔE of 0.65 eV.

Accuracy of the objective lens alignment was estimated from a beam tilt tableau, where the electron beam incident on a thin amorphous carbon film was progressively tilted by up to 30 mrad around the coma-free axis. This is shown in **Fig. 9**, and again indicates an excellent alignment of the objective lens system.

Initial applications to new materials

Since their discovery almost ten years ago [1] carbon nanotubes have been widely studied by electron microscopy; in particular, the special case of "single wall tubes" (SWTs) have excited much interest on account of their unique structures and properties. The challenge for the materials scientist has been to devise methods of opening their capped ends and filling them with guest materials. At Oxford many systems have successfully been inserted into opened multi-wall carbon nanotubes [2, 3]. More recently attention has been focussed on SWTs, and one of the key projects that will exploit the full capabilities of the new microscope involves complete characterisation of filled SWTs. Methods have been successfully developed at Oxford [4] to fill SWTs with a range of materials; we provide some preliminary examples here. **Fig. 10 a** shows a SWT, of diameter 1.5 nm, which has been filled along its length with CdI_2.The guest material here is effectively a one-dimensional crystal, being completely constrained in its morphology by the enclosing carbon walls. The single atoms in this material are clearly visible. An EDX spectrum obtained from such a nanotube is also shown (**Fig. 10 b**). This confirms the chemical composition as being cadmium iodide.

A second example is a SWT filled with cadmium chloride, shown in **Fig. 11**. In this case the $CdCl_2$ appears as a double chain, which appears to be helically twisted at certain points along its length (arrows). Again, the composition is verified by EDX, obtained from the single SWT.

Finally, $ThCl_4$ is also shown inside a SWT —**Fig. 12 a**. In this structure the thorium chlo-

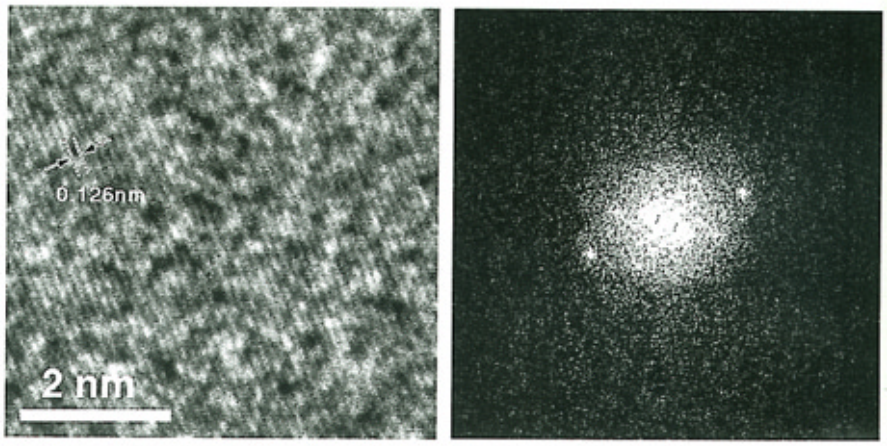


Fig.4. 220 lattice fringe image of diamond, with FFT showing 0.126 nm resolution.

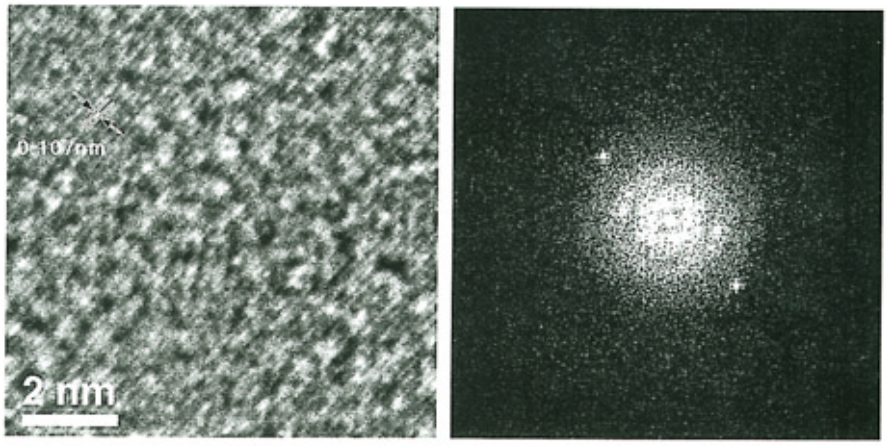


Fig.5. 311 lattice fringe image of diamond, with FFT showing 0.107 nm resolution.

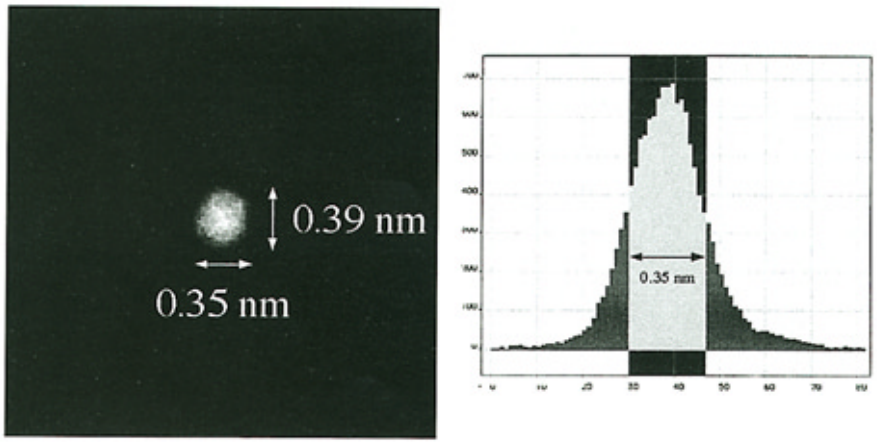
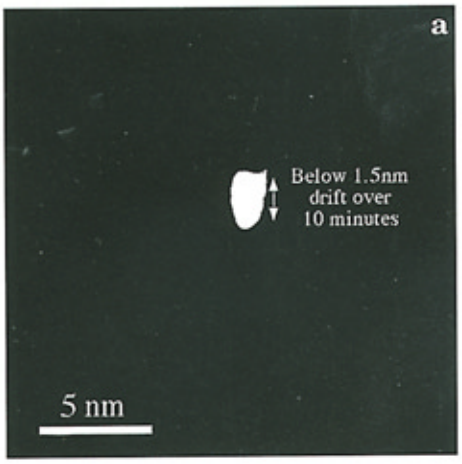


Fig.6. Image of focussed probe, with nominal diameter 0.4 nm.



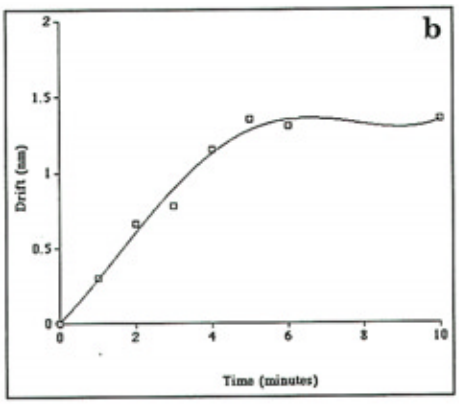


Fig.7. a). Composite image of 0.5 nm probe acquired over 10 mins.
b). Plot of probe movement versus time.

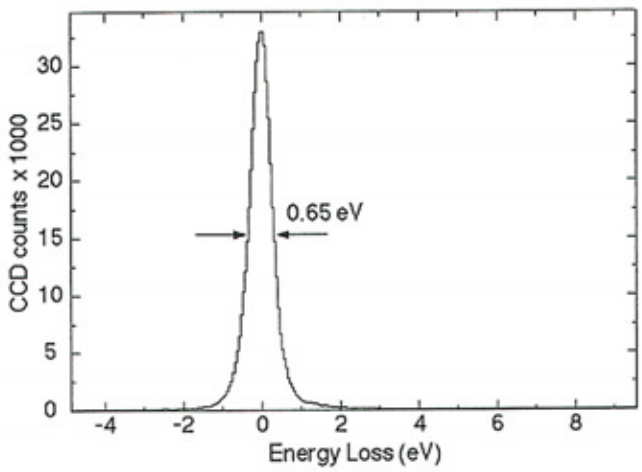


Fig.8. Zero-loss EELS spectrum, showing 0.65 eV energy spread. Conditions: 0.05 eV/channel dispersion, 0.6 mm entrance aperture, 0.1 s acqusition time.

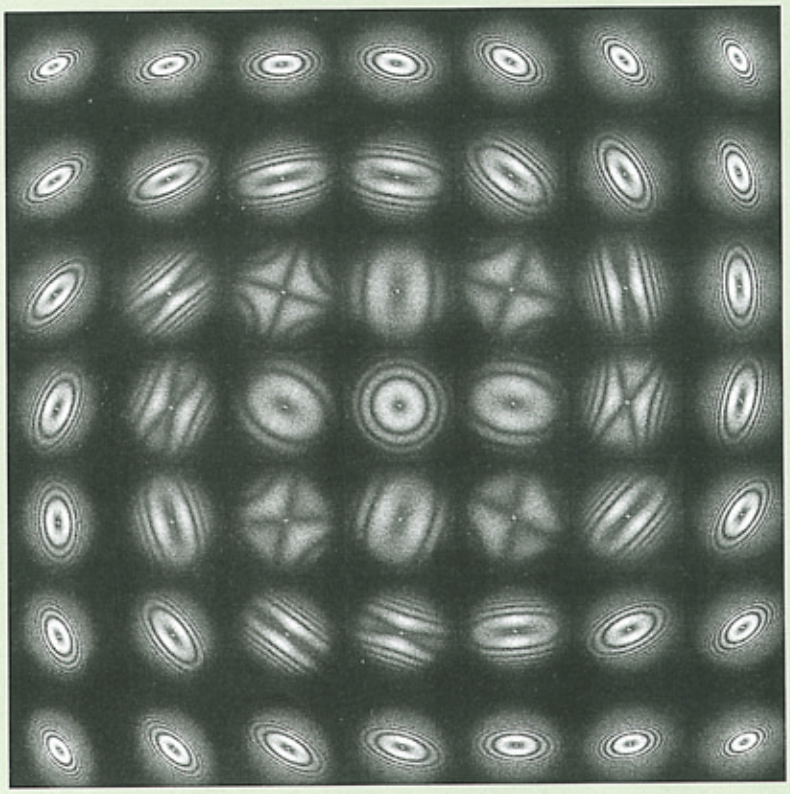
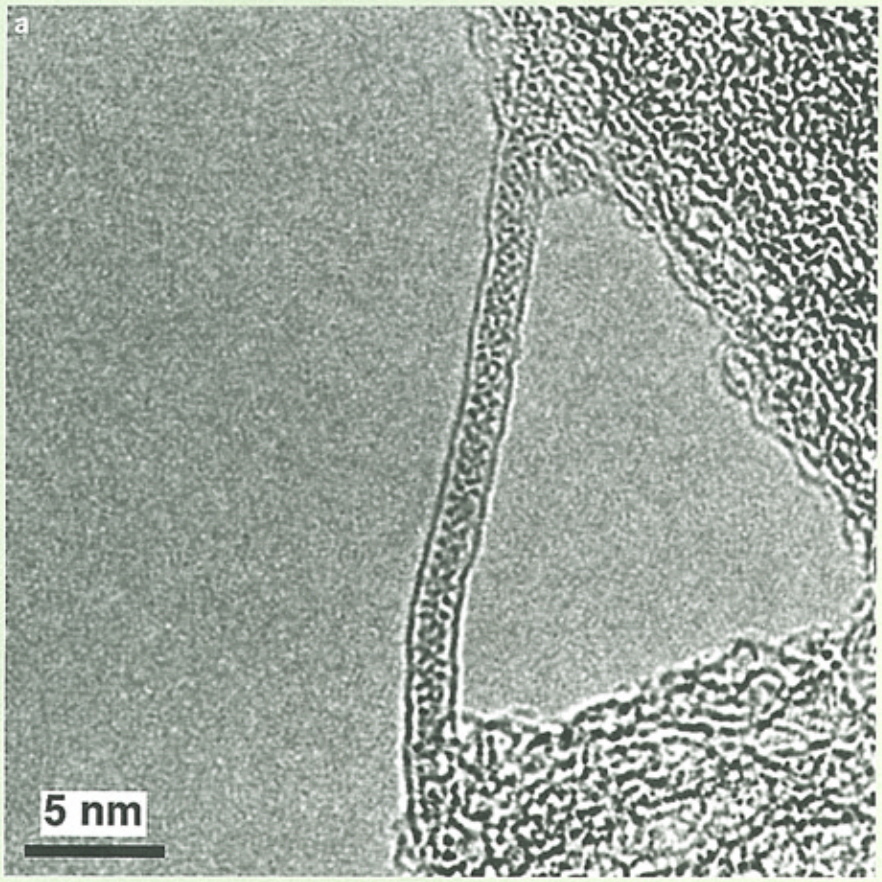


Fig.9. Beam tilt tableau, with up to +/− 30 mrad tilt in steps of 10 mrad. Defocus: – 210 nm.



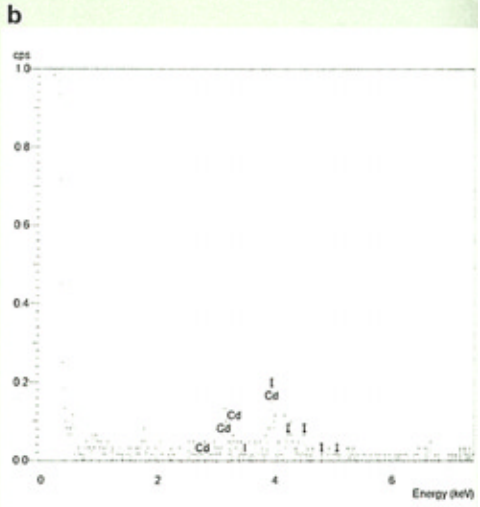


Fig.10.a) Single walled carbon nanotube filled with crystalline CdI_2.
b) EDX spectrum from sub-nm area of tube.

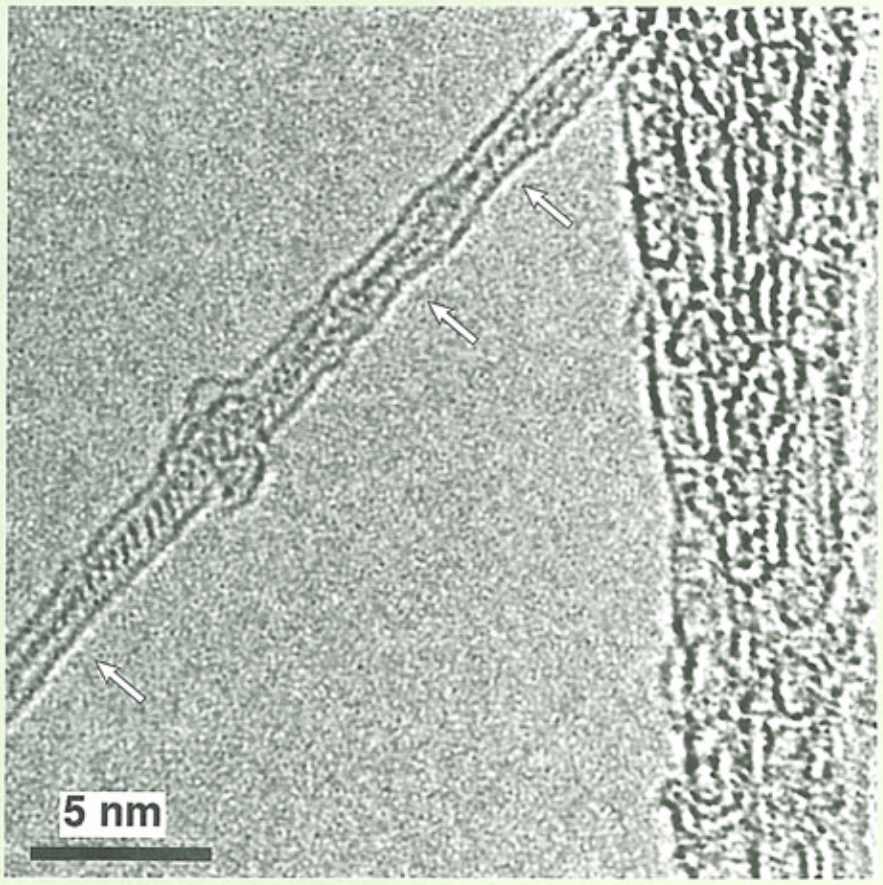
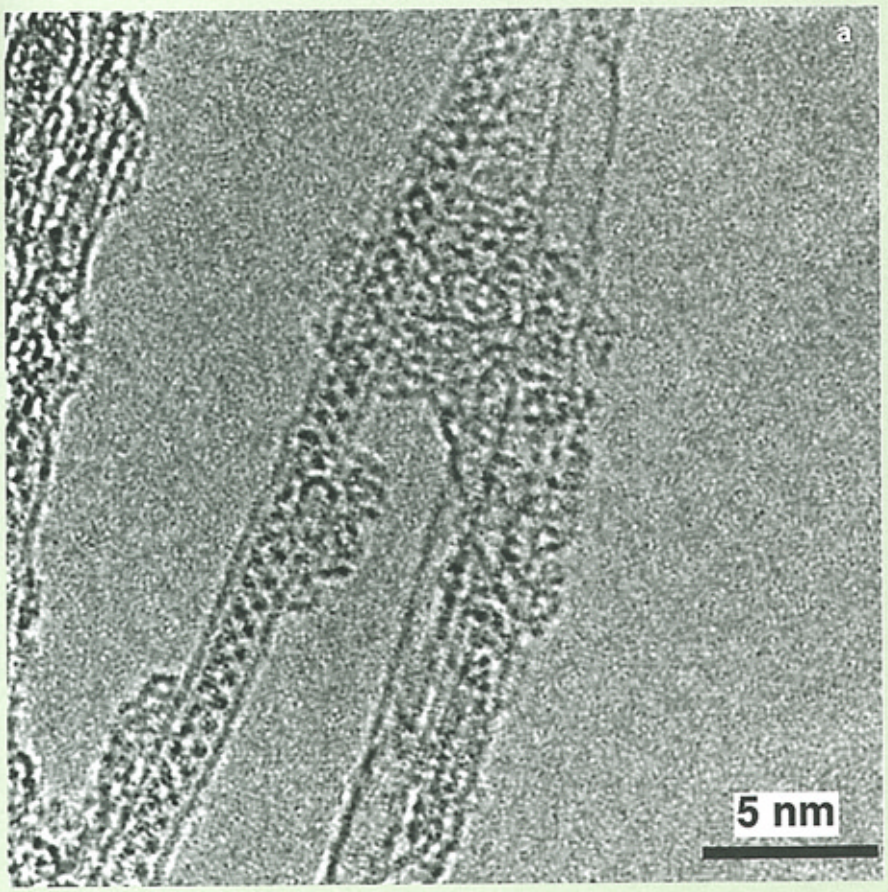


Fig.11. Single walled carbon nanotube filled with crystalline $CdCl_2$.



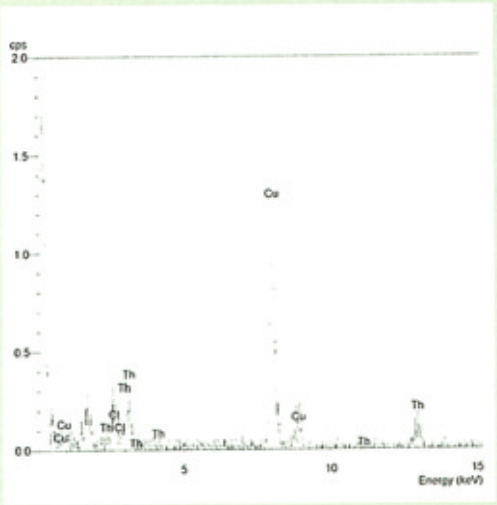


Fig.12.a) Single walled carbon nanotube filled with ordered chains of $ThCl_4$.
b) EDX spectrum from sub-nm area of tube.

ride is present as a linked chain of edge-sharing $ThCl_8$ units, in a zigzag configuration. This is clearly shown in the image; with confirmation of the composition obtained in the accompanying EDX spectrum (**Fig. 12 b**).

Conclusion

We have estimated the experimental performance of a JEM-3000F analytical electron microscope, showing that its point resolution to be 0.16 nm, with a capability of producing a small, stable probe down to less than 0.4 nm diameter. The energy spread of the electron beam was measured at 0.65 eV under appropriate conditions. Our initial applications of this instrument have exploited both its high spatial resolution for obtaining atomic images of filled carbon nanotubes, and its high sensitivity EDX capability for analyzing individual nanotubes.

Acknowledgements

This work is supported by the Engineering & Physical Science Research Council. We are also grateful to JEOL Ltd. for its ongoing support. We would also like to thank the following members of the Inorganic Chemistry Laboratory at Oxford for their assistance in the filled SWT synthesis: Kari Coleman, Andrew York, Sam Bailey, Gareth Brown, Cagang Xu and David Wright.

References

1. Iijima S.: *Nature*, **354**, 56 (1991).
2. Cook J., Sloan J., Chu A., Heeson R., Green M. L. H., Hutchison J. L. and Kawasaki M.: *JEOL News*, **32E**, 2-5 (1996).
3. Sloan J., Cook J., Chu A., Zweifka-Sibley M., Green M. L. H. and Hutchison J. L.: *J.Solid State Chemistry*, **140**, 83-90 (1998).
4. Sloan J., Wright D. M., Woo H.-G., Bailey S., Brown G., York A. P. E., Coleman K. S., Hutchison J. L. and Green M. L. H.: *Chem. Comm.* **1999**, 699-700(1999).