13–Defects, Microstructures and Textures

13.01 – Electron Microscopy of Defects, Microstructures and Textures

MS–13.01.01 Structural Study of Carbon Nanotubes
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This talk covers an introduction of carbon nanotubes which we discovered (Iijima,Nature,**354**,56(1991)), and some latest developments in nanotube studies. The materials draw much attentions among many solid state scientists in physics, chemistry and materials science in various aspects because of their unusual size dependent properties. The tubules, studied by HREM and electron microdiffraction, are only a less than few nanometers in diameter, and each needle consists of a few nesting cylinders of graphitic carbon sheets. On each graphitic tubule the carbon atom hexagons form in a helical fashion about the needle axis. Electron diffraction patterns taken from individual nano-scale tubules are a main technique available for the structural studies. The technique was extended to observe single cylinder tubes with a diameter of around one nanometer. It emphasizes that we deal with electron scattering from a single atomic sheet with a nano-scale size.

Tubule morphologies were affected by occurrence of pentagons and heptagons in the hexagon sheet tubes (Iijima et al., Nature,**356**,776(1992)). The latter introduces negative gaussian curvature into a hexagon sheet network and causes various graphitic structures (Mackay & Terrones, Nature,**352**,762(1991)). Non-hexagon rings play an important role in tubule growth and lead us to propose an open-end growth mechanism (Iijima,et al. Phys.Rev.Lett. **69**,3100(1992)).

Other subjects include oxidation and capillarity of the nanotubes (Ajayan & Iijima, Nature,**361**,333(1993)) which provide interesting crystallographic problems occurring specifically in a nanospace.

MS–13.01.02 "GRAPHENE TEXTURES : TUBULES AND WHISKERS RELATED TO FULLERENE CRYSTALLOGRAPHY"
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Since the discovery of the fullerenes with their "master" molecules C60 and C70 , a wealth of scientific research has been devoted to these pure carbon molecules, structures, and textures, so much different from the well-known graphite and diamond-based structures and materials.
The present review will report crystallographic aspects derived by electron microscopy , electron diffraction and also HREM of the growth and structure of graphite tubules and of conical graphite whiskers in relation with the fullerenes.

Crystallography and electron diffraction study of tubules.
During the preparation of C60 and C70 sometimes the soot contains other carbon based products such as graphitic tubules, spheres, onions with possibly fullerene related structural features or textures. S.Iijima [Nature 354 (1991) 56] reported the existence and a study by electron microscopy and high resolution imaging of the tubules which he interpreted as coaxial seamless cylindrical tubes . D. Ugarte [Nature 359 (1992) 707] also reported a HREM-study and growth considerations of tubules and onion textures.

A thorough study by electron diffraction of these tubules enabled further interpretation on the construction and growth characteristics. [X.F. Zhang, X.B. Zhang et al. to appear in J.Crystal Growth (1993)]. From reciprocal space considerations of the tubule texture, diffraction features are predicted and compared with the diffraction patterns obtained under various orientations of the tubule axis with respect to the incident beam. It is found that the tubules consist of a complex succession of concentric tubes of cylindrically bent graphene layers with various but discrete helicities containing also non-helical members. The helicity can be related with the seamless closure of the graphene layers into tubes and a growth mechanism could be proposed. The image features in high resolution in particular concerning the nonhelical tubules could be confirmed by simulation of suitably modeled texture proposals.

Helical graphite whiskers
Conically structured graphite whiskers found under similar conditions of formation as those for fullerene containing soot present unusual features in the electron diffraction patterns taken along the whisker axis. [S.Amelinckx et al. J.Crystal Growth 121 (1992) 543] The fragments of the easily cleaved whiskers have conically shaped ends with an obtuse top and reentrant bottom angle of about 140°. The electron diffraction patterns of disc shaped thin fragments exhibit circular rings of equispaced spots. The spacing is variable but discrete, depending on the type of whisker. A growth mechanism is proposed whereby the initial graphene layer adopts a slitted dome configuration obtained by inserting a fivefold carbon ring in the sixfold network. Successive sheets are rotated with respect to the previous ones over a constant angle, thus realising a helical cone around a "disclination" with a fivefold carbon ring core. This model explains the morphology and the diffraction effects of these columnar graphite crystals. The growth mechanism has a direct relationship to the formation of the "bucky ball" molecules.

MS–13.01.03 HRTEM STUDY OF APERIODIC SOLIDS RELATED TO THE ARCHIMEDIAN SPIRAL
by L.A. Bursill, Peng JuLin and Fan XuDong School of Physics, University of Melbourne Parkville, VIC 3052, Australia.

The concept of spiral lattice was applied to some known mineral structures by Bursill, Inter. J. Mod. Phys. B4, 2197-2216, 1990. These include clino-asbestos, halloysite (a clay) and cylindrite (a sulphide). Further examples of synthetic curved structures, related to normal crystals via conformal transformations, are found in sulphide catalyst particles as well as some derivatives of graphitized carbon, including nanotube variants.

Some recent results of high resolution electron microscopic studies of this family of aperiodic solids are presented.

MS–13.01.04 STRUCTURAL ANALYSIS BY ELECTRON DIFFUSE SCATTERING.
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$YBa_2Cu_3O_{7-\delta}$ superconductors undergo a structural transition (from twin to tweed) when oxygen levels are sufficient depleted or a small fraction of the Cu atoms is replaced by certain tri-

valent cations. The three-dimensional tweedy modulation, with components along the <110> and [001] directions, has been systematically studied by transmission electron microscopy in $YBa_2(Cu_{1-x}M_x)_3O_{7-\delta}$ (M=Fe, Co or Al; x>0.025). We observed the streaking and splitting of both fundamental and satellite diffraction spots in selected-area diffraction mode and nano-diffraction mode, respectively. Careful analysis of the diffuse scattering suggests that the <110> modulation can be attributed to pseudo-periodic domains with <110> twinning displacement, while the [001] modulation reflects the stacking of such domains on top each other along the c-axis. The size of the domain (or the period of the modulation) decreases with increasing dopant concentration. Intensity calculations of the tweed image and diffuse scattering using a displacement wave model and Monte Carlo simulation show good agreement with the observations. The presence of off-stoichiometric oxygen, or variation in local orthorhombicity, was found to be responsible for such structural modulation.

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MS-13.01.05 COHERENT CONVERGENT-BEAM ELECTRON DIFFRACTION

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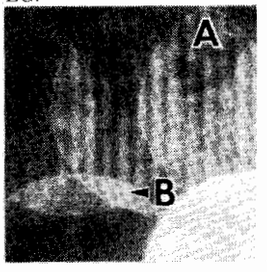
Convergent-Beam Electron Diffraction (CBED) is a powerful technique to identify the symmetries of crystals and the characters of lattice defects. The explanations of the experimental results in these cases are based on the assumption that incident electrons falling on a specimen are incoherent. When a high coherent electron source (i.e. Field-Emission Gun; FEG) is used, interference fringes are produced in the overlapping regions of CBED disks. Lin and Cowley (Ultramicroscopy, 19(1986)31) observed the interference fringes using a STEM microscope, though the fringes were distorted by the aberration of the probe forming lens. Bristol group (Ultramicroscopy, 41(1992)423) obtained the interference fringes of a lattice spacing 15Å of 6H-SiC without the distortion using a new TEM microscope. The interference fringes showed a shift of a half period due to a glide plane. The resolution of the fringes 15Å is rather large for applying this technique to other materials. We have obtained similar interference fringes of smaller lattice spacings of FeS_2, $Sr_2Nb_2O_7$, $Sr_2Ta_2O_7$, $La_2Ti_2O_7$, Mo_8O_{23} and TiO_2(Brookite) using electron microscopes JEM2010F and JEM100CX-FEG equipped with a FEG.

The minimum lattice spacing, from which we could obtain the interference fringes (right figure), is 2.7Å or the lattice spacing of the 200 reflection of FeS_2. The vertical fringes *A* corresponding to the spacing 5.4Å are produced by the interference between the 021 and the 020 reflections. The horizontal fringes *B* corresponding to the spacing 2.7Å are due to the interference between the 002 and the 022 reflections.



MS-13.01.06 HIGH SPATIAL RESOLUTION OF DIFFRACTION INFORMATION IN LARGE-ANGLE CONVERGENT-BEAM ELECTRON DIFFRACTION PATTERNS FROM CROSS-SECTIONAL SPECIMENS OF Ge_xSi_{1-x}/Si STRAINED-LAYER SUPERLATTICES

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Fine diffraction lines in large-angle convergent-beam electron diffraction (LACBED) patterns can be used to investigate the strain in a lattice misfit system because they are sensitively dependent on small changes of the spacing between lattice planes. Since the probe is slightly defocussed, equivalent to imaging the specimen with a convergent spherical wave, a LACBED pattern formed in the diffraction plane of the microscope is superimposed on a high spacial resolution shadow-image of the specimen. In the case of cross-sectional specimens of Ge_xSi_{1-x}/Si strained-layer superlattices (SLS) LACBED can give much information on local strain and misfit stress relaxation. It is important that the probe size, which defines the spatial resolution of the shadow-image, should be as small as possible. The elastic relaxation of strain in the very thin samples used for cross-sectional transmission electron microscopy (XTEM) must be taken into account. The diffraction lines in the GeSi layers are shifted from their position in the Si layers by amount determined by the misfit strain and the subsequent relaxation. We shall demonstrate that the line shifts in XTEM specimen caused by the effects of misfit strain and stress relaxation can be separated. This technique can therefore be used to profile strain and misfit stress relaxation in SLS.

PS-13.01.07 THEORY OF SPIRAL CRYSTALLOGRAPHY

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Spiral structures exist widely in nature; in both biological and inorganical materials. One of the most perfect examples occurs in botanical species where the structures exhibit alternating visible spirals known as parastichies. The latter always have numbers given by a Fibonacci series. Apart from their present day genetic origin, these types of spiral lattices were also obtained by close packing of growing discs, just as the hexagonal pattern can be obtained by close packing of equal size discs (see Bursill and Fan, Mod. Phys. Letts. B2, 1245-1252(1988).

In this paper a generalized abstract model is developed, based on the mechanism of the close-packing model, to enable the critical role played by the initial conditions and the growth law to be analyzed. This model describes the growing disc by a one-dimensional single peak centro-symmetrical function f(x). The spiral lattice aggregates are thus generalized as a multi-peak function $F_n(x)$ obtained by adding f(x) at the global minimum of the existing aggregate $F_{n-1}(x)$. Both functions f(x) and F(x) have the same periodicity, reflecting the angular divergence parameter of the spiral lattice. The periodicity may be taken as 1, with no loss of generality. The divergence interval, defined as the distance between successive global minima, may then be renormalized into the interval (0,1).

Similar to the divergence angle of a spiral lattice aggregate, the generalized divergence interval converges to a constant, simply related to the golden mean. This result agrees of course with our earlier graphical computer simulations.

A kinematic approach is attempted and its corresponding initial conditions investigated. A kinematic process of this model is where there is always a self-similar configuration of the aggregate functions for each stage so that the global minima are predictable and the consequent divergence intervals can be expressed with recurrence formulae. Using the latter, the properties of the divergence sequence are easily analyzed and found to converge, with limits simply related to the golden mean.

Much effort was devoted to search analytically for a functional form appropriate for representing the initial conditions in as general a way as possible. At this stage, the initial conditions, required for convergence, have been found within certain limits.