Introduction to crystallography

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Crystallography is the versatile and rapidly developing area of natural science. While holding its intrinsic cross-disciplinary appeal, it supplies invaluable characterization tools for broad communities of solid state physicists, materials scientists, chemists and biologist. The goal of a crystallographer is to describe and measure long-ranged ordered atomic structures of crystals and connect them to the physical properties of the corresponding crystalline materials. Crystallographers implement many experimental facilities, ranging from table-top X-ray diffractometers, transmission electron microscopes, large synchrotron radiation facilities and, quite recently, free-electron lasers. Mathematical methods of crystallography embrace vector and matrix algebra, tensor analysis, group theory, the theory of Fourier transforms and mathematical statistics. 100 years of X-ray crystallography are celebrated by 29 Nobel Prizes and the International Year of Crystallography 2014.

This lecture is the compact introduction to the subject. We will start by discussing the ancient and contemporary definitions of a crystal. After that we will highlight the major breakthroughs and discoveries, which shaped the understanding of crystal structures. The lecture will present such key concepts of fundamental crystallography as periodicity, natural faces of crystals, symmetry and space groups of atomic structures. We will also discuss the key concepts, underpinning diffraction experiments and the meaning of the terms “structure factor” and “systematic extinction”. Finally, we will briefly discuss the concept of a Fourier synthesis and the phase problem of X-ray crystallography.
Electron channelling contrast imaging
(Electron Microscopy of Thick Crystals)

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Dislocation patterning is of importance in understanding growth processes in semiconductors and deformation processes in structural metallics. In all cases the spatial distribution of the dislocations has significant consequences for the material properties. The transmission electron microscope is generally the 'go to' tool for imaging lattice defects in crystals but over the years there have been many attempts at diffraction contrast imaging in the scanning electron microscope (SEM). The current generation of SEMs makes it possible to routinely characterise dislocations near the surface of bulk samples using electron channelling contrast imaging (ECCI) – see example image below. The history, theory and practice of generating electron channelling patterns and electron channelling contrast images will be outlined. The method will be illustrated with key examples from the literature and some recent applications.

![ECCI Image](image)

Threading dislocations in a GaN film on sapphire viewed 'end-on' using ECCI
Probing Local Crystal Structure in Liquids and Gases

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The transmission electron microscope (TEM) provides an invaluable tool for atomic scale characterisation. Traditionally high resolution TEM characterisation has required an ultra high vacuum enviroment which reduces the applicability of the technique especially for biological systems and for nanocatalysts. Enviromental imaging of nanomaterials in liquids and gases can now been acheived by trapping the specimen between electron transparent silicon nitride windows. In this talk I will outline several examples of imaging materials without exposing them to the TEM vacuum. I will show the structural evolution of nanoparticle catalysts in gaseous environments with the aim of understanding and optimising catalytic performance.[1] I will also demonstrate imaging of \textit{geobacter sulfurreducens} in a liquid cell to study their synthesis of metal nanoparticles [2]. In the second part of this talk I will demonstrate how graphene nanocapillaries are allowing new studies of the behaviour of water and aqueous salts in confined spaces [3,4] and how a new generation of graphene liquid cells are allowing higher resolution structural and elemental imaging [5].

Electron Diffraction in The TEM and Related Imaging Modes - A Brief Introduction and Overview

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Acquisition of electron diffraction patterns using the transmission electron microscope (TEM) is a powerful method for characterizing the structure of materials, including perfect crystals and defect structures. The main advantages of electron diffraction over other methods, e.g., x-ray or neutron scattering, arise from the extremely short wavelength (≈2 pm), the strong interaction of electrons with atoms (atomic scattering), and the ability to examine very small volumes of matter down to the subnano-scale.

Another great advantage of the transmission electron microscope is in the capability to observe, by adjusting the electron lenses, both electron microscope images (information in real space) and diffraction patterns (information in reciprocal space) for the same region. Moreover, one can obtain diffraction contrast images which contain very rich structural crystallographic information.

In this tutorial the different modes of operation of the TEM will be presented and practical aspects of the various options will be addressed for the characterization of single, poly and nano-crystalline materials.
Electron Crystallography as a Tool for Structure Solution of Nanosized Materials

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Solving the structure of periodic crystals at atomic resolution is essential for understanding material properties. If materials of an interest are on nano-size, this structural information usually cannot be attained using traditional X-ray diffraction methods, limited by the small volume and size of the nano-materials. Electron diffraction (ED) is in these cases the most suitable method. The interaction of electrons with matter is much stronger than that of X-rays, thus ED pattern can be obtained from a single nano-sized crystal. The advantages of the electron-matter interaction are twofold. First, the ED pattern is that of a single crystal, so there is no reflection overlap. Secondly, the interaction is stronger than that of X-rays, so the resolution is much higher. However, this strong interaction of electrons with matter is responsible for many beam dynamical diffraction and secondary scattering effects (dynamical effects), which cause strong deviations of the diffraction intensities from their kinematical, hampering their use for structure solution purpose. One of the discoveries responsible for tremendous leap forward of ED as a tool for structure solution is Precession Electron Diffraction$^1$ which allows obtaining quasi-kinematical data which can be used for structure solution of novel materials. The specific path of structure solution using ED methods can vary, depending on the structure studied and type of the sample used. In general, it consists of several steps: 1) estimation of the geometry of the unit cell (indexing), 2) evaluation of the symmetry (space group determination), 3) proposal of initial atomic model (solution), and, 4) completion and verification of the model (refinement).  

Current lecture will summarize theory on this subject - briefly going through the each step of the solution path and providing examples from the research performed by my group. 

References:  

Materials Science Track (including plenary)  
UK-Israel Workshop on Nano-Scale Crystallography for Bio and Materials Research
Electrons can be accelerated to high energies (100s of keV) resulting in a short wavelength and so they can be scattered from objects separated by only a few picometres. Additionally the ability to deflect electrons using magnetic fields (via the Lorentz force) means that electrons can be focussed, allowing electron beams with a diameter of less than 1nm to be readily formed. The combination of resolving power of the radiation and spatial resolution of the electron microscope allows for nearly unparalleled ability to study the atomic structure of nanoscale materials.

However the same electrostatic interactions can also lead to difficulties, primarily from dynamical scattering, where an elastically scattered electron can be scattered repeatedly as it traverses the sample. This makes direct comparison of scattered intensities with the underlying structure factors (as with X-ray or neutron scattering) difficult or impossible. However the information dynamical scattering introduces about the sample into the diffraction pattern can be predicted, accessed and even overcome through careful experiment and simulation.

One such approach is precession electron diffraction (see Figure 1 below) which will be discussed in both conventional and scanning modes of microscope operation.

![Figure 1. Simplified ray path for precession electron diffraction and experimental PED patterns (with a kinematical simulation for comparison)](image-url)
Precession Electron Diffraction and orientation imaging/phase mapping at nm scale in TEM material science applications

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The tremendous impact of SEM based EBSD techniques over the past 20 years demonstrates the value of mapped crystallographic information, which provides insight on processing history, structure-property relationships, interfaces and phase structure with resolution range from 50-10 nm. The development of TEM based-automated crystallographic mapping techniques (ASTAR) in combination with precession electron diffraction (PED) [1,2] has pushed the resolution limit at 1 nm scale. Combination of ASTAR 4D scanning orientation/phase map technique with advanced TEM Cs corrected /FEG instruments over the last 10 years allowed study of various materials such as metals /alloys, minerals, semiconductors and even organic materials. The combination of PED with scanning nanodiffraction enables to measure accurately strain (precision up to 0.01%) with 1-3 nm resolution at semiconductor devices.

The recent application of e-PDF (electron Pair Distribution Function) techniques [3] allows to analyse at local scale Electron Diffraction (ED) patterns even from amorphous materials. e-PDF technique allows to analyse interatomic distances, bonding and possible short/large scale order of nanocrystalline/amorphous materials at nm scale, enabling to monitor in situ solid state reactions, structure of glassy materials, layered thin films quality and amorphous/re-crystallization studies in semiconductor devices.

The combination of ASTAR 4D scanning orientation/phase map technique with e-PDF allows to characterize various nanostructures at nm scale and PED application on e-PDF may allow reliable atomic coordination number calculation on nanostructures.

Kikuchi Pattern Simulations for EBSD Data Analysis

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Kikuchi patterns carry the essential crystallographic information in the method of Electron Backscatter Diffraction. Simulations based on the scattering physics of electrons in crystals can improve our understanding of the Kikuchi pattern formation process itself, and they also provide a powerful tool for EBSD data analysis. In this contribution, we provide a short overview about several approaches that can be used to simulate Kikuchi patterns for applications pushing the limits of orientation measurements and structure analysis in the SEM [1].

Fig.1 Kikuchi Patterns observed from a Gallium Nitride sample [2] compared to a simulation using dynamical electron diffraction theory as implemented in ESPRIT DynamicS (Bruker Nano)


Materials Science Track (including plenary)

UK-Israel Workshop on Nano-Scale Crystallography for Bio and Materials Research
Introduction of CMOS technology in EBSD – Super speed and sensitivity in a single EBSD detector
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The CCD (Charge Coupled Device) commonly used as the image sensor in EBSD detectors is a serial device – the pixels are read out sequentially. Pixel 'binning' is used to increase frame rates, and to boost the signal level in each read pixel. A high-resolution, high-sensitivity detector may have a full resolution of 1344x1024 pixels; operated at 8x8 binning, it may achieve a max. solve rate of ~100pps at >100pA.

High-speed EBSD detectors use VGA format CCD sensors (640x480 pixels, at max. ~200Hz). Again, binning increases frame rates, whilst also improving the low electron dose detection limit (because the read-out noise decreases relative to the signal in the binned 'super pixel'). To achieve the highest solve rates (~1600pps at >12nA), 16x16 binning is required which has two very significant disadvantages: reduction of the EBSP resolution to 40x30 pixels; and reduction of the maximum signal to noise ratio (SNR) before image saturation (owing to the limited charge capacity of the CCD's output node). At such extreme binning levels, accurate band detection and indexing is compromised, and angular precision of orientation measurements is reduced.

With the ‘massively parallel’ device architecture of a CMOS (Complementary Metal Oxide Semiconductor) image sensor, many outputs are read simultaneously, greatly increasing frame rates without the need for pixel binning. Thus CMOS can offer significant advantages over CCD for EBSD detectors – higher speed at higher resolution, and with higher SNR.

Compared to the best high-speed CCD detector, the new AZtec 'Symmetry' CMOS achieves twice the speed for the same electron dose, with four times the resolution: >3000pps at >12nA and 156x128 pixels. 'Symmetry' offers high speed with high indexing rates and high angular precision, even with low-contrast EBSPs where the low SNR of CCD fails. Symmetry also out-performs high-resolution, high-sensitivity CCDs: 250pps at >250pA and 1244x1024 pixels. With Symmetry CMOS, a single EBSD detector can now encompass all applications, exceeding the performance of both high-resolution and high-speed CCD detectors, and with higher sensitivity.
Innovative and non-conventional STEM diffractive imaging using patented Integrated Differential Phase Contrast (iDPC) and new generation of hybrid pixelated detectors

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STEM is widely used for imaging materials, and can provide excellent contrast and high resolution. Typical STEM detectors are round or ring-shaped and open access to a wide range of contrasts by adjusting camera length. Annular devices can be physically divided into segments showing exactly the same size and shape, typically 4, but can be any other even number, each of them being exposed to exactly the same amount of illumination. From there Differential Phase Contrast (DPC) can easily be extracted to highlight electrical or magnetic field distribution in the sample.

Illustrations and applications of the newly developed and patented integrated DPC (so-called iDPC) live STEM imaging technique [1] will also be shown, where low- and high-Z atoms will simultaneously be imaged at very high S/N ratio, single defocus value, and without any contrast reversal. Moreover, iDPC, due to high S/N ratio, will be shown to be an ideal imaging method for very low dose STEM studies on beam sensitive specimens: 2D materials, zeolites, polymers, cryo-sections...

There is a common agreement in the EM community that most of the contrast information available from a thin sample shows up in the diffraction pattern (DP), if an effective method to record and extract it can be found. 4D-STEM, or diffractive imaging, attempts to measure all this information by acquiring and post-processing a DP from every point in the sample. Latest results will show up here from a new Electron Microscopy Pixel Array Detector (EMPAD) developed at the Kavli Institute of Cornell University and Thermo Fisher Scientific MSD Division [2].

The very high dynamic range (1,000,000:1 primary electron dynamic range) shown by the unique sensor technology enables the acquisition of a complete diffraction pattern including the central spot, without any detector saturation. Single electron sensitivity (typical 1/140 e- SNR) means that the detector will also be effective for low dose applications and beam sensitive samples, while the detector stands radiation hard and maintains high sensitivity over a wide range of microscope high tensions (30 to 300kV typically).

Pixelated detectors clearly open opportunities not only to acquire fully quantified DPs and to highlight magnetic and/or electric field information through differential phase contrast techniques (DPC and/or iDPC), but also to perform phase determination and mapping, as shown in Figure 2.

Multivariate Statistical Analysis of EBSD Data

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Multivariate statistical analysis (MSA) is widely used across science disciplines including microscopy. It is surprising that application to electron backscattered diffraction (EBSD) data has been limited to the work of Brewer et al [1]. MSA methods are typically used for data reduction, identifying inter-related variables, and clusters in datasets. In applying MSA to EBSD and microstructural analysis the key benefits to pursue are its use in (i) segmenting the spatial domain into distinct similar regions (i.e. grains or sub-grains), and (ii) producing representative lower noise patterns associated with these domains to aid pattern indexing. The presentation will explore use of principal component analysis (PCA) with the Varimax rotation and k-means clustering. MSA is unlikely to ever replace Hough-based analysis of EBSD patterns but may augment it by improving analysis of low quality data sets, or differentiating finer details not routinely detected though the Hough/Radon transform.

Transmission Kikuchi Diffraction (TKD)

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Transmission Kikuchi Diffraction (TKD) method in the Scanning Electron Microscope (SEM) provides similar information to Electron Backscattered Diffraction (EBSD). The TKD advantages over EBSD include an order of magnitude improved spatial resolution and narrower energy distribution of detected Kikuchi patterns. Pioneering papers in the field refer to Trimby [1] and Keller & Geiss [2].

The TKD method enables phase mapping (image below) and crystallographic orientation mapping of nanostructured materials including metals, alloys, semiconductors, and bio-minerals of various applications [3-5]. The TKD analysis is applied to electron-transparent samples in similarly to the Transmission Electron Microscope (TEM).

The current talk describes: (i) TKD relative to EBSD in terms of improved lateral/energy resolution, (ii) on-axis and off-axis TKD configurations, (iii) methods for preparation of electron transparent samples and related TKD research. Furthermore, we discuss issues such as dependence of TKD resolution on sample thickness, sample thickness bottom limit for Kikuchi pattern acquisition and the special effect of contrast inversion.

mapping of fcc/bcc phases in stainless steel (blue/red)


Materials Science Track (including plenary)
UK-Israel Workshop on Nano-Scale Crystallography for Bio and Materials Research
Nano-scale characterization of short-range-order in amorphous materials by electron scattering

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Amorphous materials do possess short range order, which can be described by distribution functions, in particular, the radial distribution function (RDF). The RDF quantifies the number of atoms as a function of distance from a reference atom, which then enables to construct structural models of the material (Fig 1).

A structural description of amorphous materials is important for understanding their mechanical and electrical properties and indeed has been studied extensively using X-ray and Neutron diffraction. However, these methods are not applicable when characterizing amorphous materials in small volumes. Such cases are of scientific and technological importance, for example barrier layers in magnetic and electronic devices, thin films and intergranular regions.

For nano-scale volumes, the use of electron diffraction is advantageous because of the ability to form a small beam of electrons and their large scattering cross section with atoms. In this talk, I will review briefly the use of electron diffraction to characterize short range order in nanoscale volumes of materials.

![Graph](image1)

Fig.1, *Phys. Rev. B* 79, 014203 (2009): (top) Example of a reduced density function, $G(r)$, of an amorphous ferromagnetic Co$_{40}$Fe$_{40}$B$_{20}$ thin film. The peak positions correspond to characteristic bond lengths in the material.

(bottom) Short range order structures as calculated by fitting to the $G(r)$ measurement. Transition metal atoms are light gray and Boron atoms are dark gray.
Strain and deformation in 2D materials

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2D crystals can be layered together to create new van der Waals crystals with bespoke properties. However, the performance of such materials is strongly dependent on the quality of the crystals and the interfaces at the atomic scale. Transmission electron microscopy (TEM) is the only technique able to characterize the nature of buried interfaces in these engineered van der Waals crystals and hence to provide insights into the local strain and deformation which control the optical, electronic and mechanical properties. I will report the use of TEM imaging technique to aid the development of 2D heterostructures. We have performed mechanical exfoliation of air sensitive 2D materials in an inert argon atmosphere and used hBN or graphene encapsulation to allow the novel electrical properties of air sensitive 2D crystals to be realized [1]. However we find that even when fabricated in an inert atmosphere, NbSe\textsubscript{2} monolayers contain point defects that can be observed by strain mapping from high resolution TEM data [2]. Furthermore, cross sectional scanning TEM imaging reveals that even comparatively stable materials like MoSe\textsubscript{2} and WSe\textsubscript{2} have different interlayer separation when exfoliated in a glove box compared to fabrication in air [3].

2D diffraction by low and high energy electrons for studying surface crystallography and defects

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3D electron diffraction in transmission electron microscopy (TEM) is an important and well-established tool, capable of acquiring multitude of useful structural data, from basic crystallography to complex defect analysis. Though low energy electron diffraction (LEED) was demonstrated by Davisson & Germer as early as 1927, to date 2D electron diffraction methods such as LEED, and reflection high energy electron diffraction (RHEED), have been mostly used for qualitative surface analysis. While more sophisticated set-ups, with energy filters and computerized surface structure determination programs exist, they are quite scarce. Basic RHEED and LEED systems, bolted on the vast majority of standard surface science chambers, are mostly employed in a fast “on screen” mode, for an instant assessment of surface quality, symmetry, and periodicity.

In this talk, brief introduction to the basic concepts of 2D electron diffraction will be followed by examples of deeper and more interesting RHEED and LEED surface analyses, including the use of diffuse scattering for defect studies.
In my talk I will present application of diffraction techniques to estimation of crystal size in ensembles of nanoscale crystals. Applicability of XRD-based size measurements will be discussed based on the results obtained for specific size ranges within a nanoscale (from a few to 100 nm) and for specific morphology of nanoparticles. Examples of typical diffracted intensity distribution in electron diffraction patterns acquired at ensembles of nanocrystals will be discussed in relation to the size range within nano-interval, statistical distribution of sizes, morphological features and phase composition of an ensemble. To conclude I will present a practical approach to realistic characterization of crystalline nanoscale materials based on combination of diffraction and imaging in an escalation manner.

Exploring the underlying structure in TEM diffraction data

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Data science approaches have been successfully applied to a variety of electron microscopy measurements, resulting in highly detailed analysis of composition, electronic structure, crystallography and atomic structure of complex systems. The goal in all of these approaches is to take a large set of measurements from a sample and to utilise the redundancy in the data to recover a model, or set of significant components that accurately describe the real system.

Statistical decompositions are one widely used method for this, broadly using matrix factorisation methods to isolate those particular signals that describe the whole of the data as efficiently as possible. However, one major issue is in determining how many significant components are needed to produce the most robust model of the measured data. To achieve this, the idea of data-clustering has been developed alongside decomposition. This uses the structure of the data to guide the correct number of components needed in the model, and under some circumstances can even provide physical insight into the structure and crystallography of the sample. For example, the nature of a low angle grain boundary (a dislocation cluster) in a wrought nickel alloy can be seen in Figure 1.

Figure 1. Clustering results from a nickel alloy studied by scanning electron diffraction.