CSEM's
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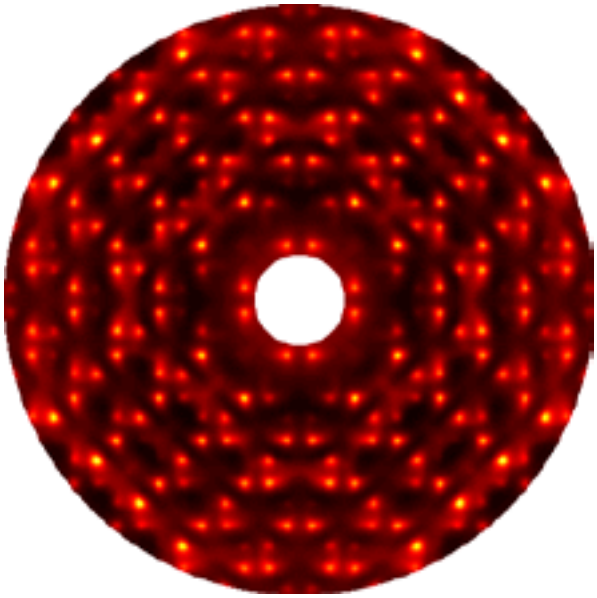
The Devil's in the (diffuse) detail

Modelling nano-scale disorder in crystals

X-ray crystallography is an important workhorse in the world of solid-state chemistry. However, while it's a powerful tool in determining the average structure in a crystal lattice, conventional crystallography is very limited when it comes to understanding nano-scale disorder within that crystal structure. And when it comes to understanding the properties of many important materials, the devil is in the detail. X-ray diffraction is still one of the keys to understanding this finer scale structure but using it requires a capacity to read between the lines – to understand the diffuse diffraction that most crystallography ignores. Scientists at the Research School of Chemistry are leading the world in this field. Their work on modelling nano-scaled disorder using diffuse diffraction is opening up new possibilities in understanding and modifying many of our most important materials.

Professor Richard Welberry has been working on methods to understand the arrangement of atoms and molecules in disordered crystals for many years. He's the head of the Disordered Materials Research Group at the Research School of Chemistry (RSC), and his main tools of trade are X-rays and computers. The X-rays are used to probe the atomic structure of the material being studied. The computers are used to construct models based on the information from these X-ray studies.



The X-ray pattern of the diffuse scattering that occurs between the Bragg peaks for calcia-stabilised cubic zirconia (an advanced ceramic). Information contained in this diffuse diffraction is the key to understanding the nano-scale structure of this material.

This field is known as X-ray crystallography, and it involves passing X-rays through the crystal lattice of the material being studied. The atoms in the lattice cause the X-rays to scatter and by measuring the pattern of the emerging X-rays – the diffraction pattern – it's possible to calculate the arrangement of the atoms in the material.

In most types of crystallography you're calculating a model of an ideal crystal, a structure in which every unit cell of the lattice contains identical atoms in identical positions, which scatter beams to identical points in the diffraction pattern. These patterns are known as Bragg reflections, named after the father-and-son team of William Henry Bragg and William Lawrence Bragg, the pair who pioneered the science.

It's been almost 100 years since the Braggs first used X-ray diffraction patterns to determine the crystal structure of common salt – sodium chloride. Since then X-ray crystallography has developed to the point where the structures of complex materials and huge molecules such as proteins can often be determined in a matter of hours by fully automated systems. However, this progress overshadows the fact

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Professor Richard Welberry (pointing at the screen) with the Disordered Materials Research Group at RSC. Seated is Mr Andrew Beasley, Dr Darren Goossens is on the right and Dr Aidan Heerdegen stands at the back.

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Devil in the detail

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that conventional crystallography is a limited technique that is only sensitive to the average structure within a crystal.

Working with diffuse diffraction

Real materials are never perfect. Individual atoms all deviate to some extent from their ideal positions in the average unit cell, and disorder within the crystal structure is often what gives a material its desirable properties. Many important materials such as ceramics, superconductors, catalysts, electro-optical materials and minerals owe their special properties to the disorder in their structure.

And this is where conventional X-ray crystallography has limitations because these variations from the ideal simply aren't picked up. To understand them you have to 'read between the lines' of the diffraction pattern, you need to interpret all the other information in the pattern.

This is known as working with diffuse diffraction and it's where Professor Welberry and his team come into their own. Professor Welberry has been working on diffuse scattering for decades and believes a better understanding of diffuse scattering will greatly enhance our understanding of the relationships between nano-scaled structure and properties in a wide range of materials.

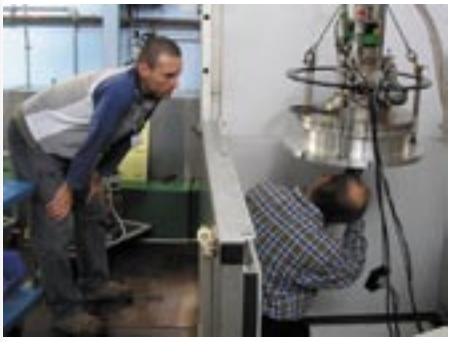
The dedicated diffuse-scattering diffractometer system used by the group. "This has been my workhorse for a number of years," says Professor Welberry.

"Because it's difficult to collect and to interpret, only a few specialist groups around the world practise the analysis of diffuse scattering," says Professor Welberry. "The vast majority of crystallographers neglect or simply don't notice the diffuse scattering that is always present in their experiments.

Building models

"My science is all about building models using the information contained in the diffuse diffraction," he says. "First, you observe things with real materials and X-rays, and then you try to build a model that will give the same diffraction pattern as the one observed.

"It's an iterative process. A model is set-up in terms of basic inter-atomic or inter-molecular interactions. Then you build a computer simulation of this model and calculate what diffraction pattern this model would produce. If that computer-generated diffraction pattern is the same as the observed X-ray diffraction pattern then we know we've created a valid model. However, if the computer model produces something different from the observed pattern then you need to go back and adjust your model



Andrew Beasley helps set up a neutron experiment at ISIS.

Understanding functional oxide materials

An example that underlies the value of working with diffuse diffraction can be found in the research being carried out by the Disordered Materials Research Group on functional oxide materials.

Local deviations from the average crystal structure are a common feature of oxide materials that exhibit exceptional phenomena such as colossal magneto-resistance (they show changes in electrical resistivity of up to 7 orders of magnitude in the presence of an applied magnetic field), relaxor ferroelectricity (which are ideal candidates for the next generation of solid-state transducers and actuators for telecommunications and medical imaging), and multiferroicity (they exhibit at least two of the three polar properties – ferroelectricity, ferromagnetism, and ferroelasticity). This is because these phenomena arise out of competing interactions within their crystal structure.

While most conventional and widely exploited oxides – semiconductors, ferroelectrics, ferromagnets, magnetoresistors, piezoelectrics – can be understood in terms of a simple relationship between the structure of a crystal and its physical properties, these exceptional oxides involve multiple structure-property relationships that compete with one another within a crystal. This means that close to the crossover between competing ground states, where exceptional properties are most pronounced, a crystal will always contain regions whose local structure deviates from the average.

Local structural deviations, and more particularly the relationships among them on length scales of 0.1-100 nm (the nanoscale), are therefore the key to exceptional phenomena in oxides. The Disordered Materials Research Group is seeking to determine the nanoscale structure of these exceptional oxides and the only effective way this can be done is by applying their methods of diffuse scattering analysis. A thorough understanding of nanoscale structure will provide a bridge between chemical composition and physical properties, allowing for the optimisation of these properties by tuning synthetic conditions.

"These exceptional oxides are potentially high-tech, billion dollar materials used in a wide variety of optoelectronic devices and so on," says Professor Welberry. "We're at the fundamental end of this trying to understand the basic reason why these things have the properties that they do and if you know that then you can do something about trying to improve those properties."

until it's produces a diffraction pattern that agrees with the observed pattern."

Using this approach Professor Welberry's group has produced numerous insights on a wide range of materials including flexible organic molecules, advanced functional oxides and quasicrystals. The group uses dedicated diffuse-scattering diffractometer systems based on curved position-sensitive wire detectors. These allow high quality diffuse scattering data to be efficiently recorded over large regions of diffraction space and provide a unique facility for tackling a whole range of complex structural problems.

"This equipment is of a quality unsurpassed worldwide," says Professor Welberry. "And, it's about to get even better with the acquisition of a specialised position-sensitive detector with the extremely high dynamic range needed to measure weak diffuse scattering in the presence of strong Bragg reflections. We should be installing this new detector later this year."

And while X-rays have been at the core of this research in the past, neutron diffraction is now also playing an increasingly important and complementary role in studies on diffuse diffraction.

Working with neutrons

"X-ray diffraction has been the tool that I've used most in my life but more recently I've been involved in neutron diffraction," comments Professor Welberry. "This is largely due to Dr Darren Goossens joining the group in recent years. Darren has brought with him considerable experience working with neutron beams, and we have had an ongoing collaboration with scientists at the ISIS centre in the UK where they specialise in neutron beams.

"And, of course, Australia is getting a new reactor in Sydney which will be an excellent neutron source for research so from next year we should be able to do similar work with ANSTO at Lucas Heights.

"Neutrons offer a number of advantages, one of which is that it's good for some atoms with which X-rays are difficult. With X-rays, the bigger the atom the more that it scatters so if you want to look at hydrogen atoms, for example, they can be very difficult to see, especially if they're associated with large heavy metals.

"With neutrons the amount of scattering is not dependent on the size of the atom at all. Indeed, hydrogen atoms are strong scatterers of neutrons so you can see hydrogen in the presence of platinum or palladium or any of the heavy metals.

"The other big advantage is that the diffraction patterns with X-rays tend to fall off with angle so you get a strong signal in the middle and then it gradually tails off. Whereas in neutrons, because it's scattering off the nucleus, the diffraction happens at high angles as well so you get

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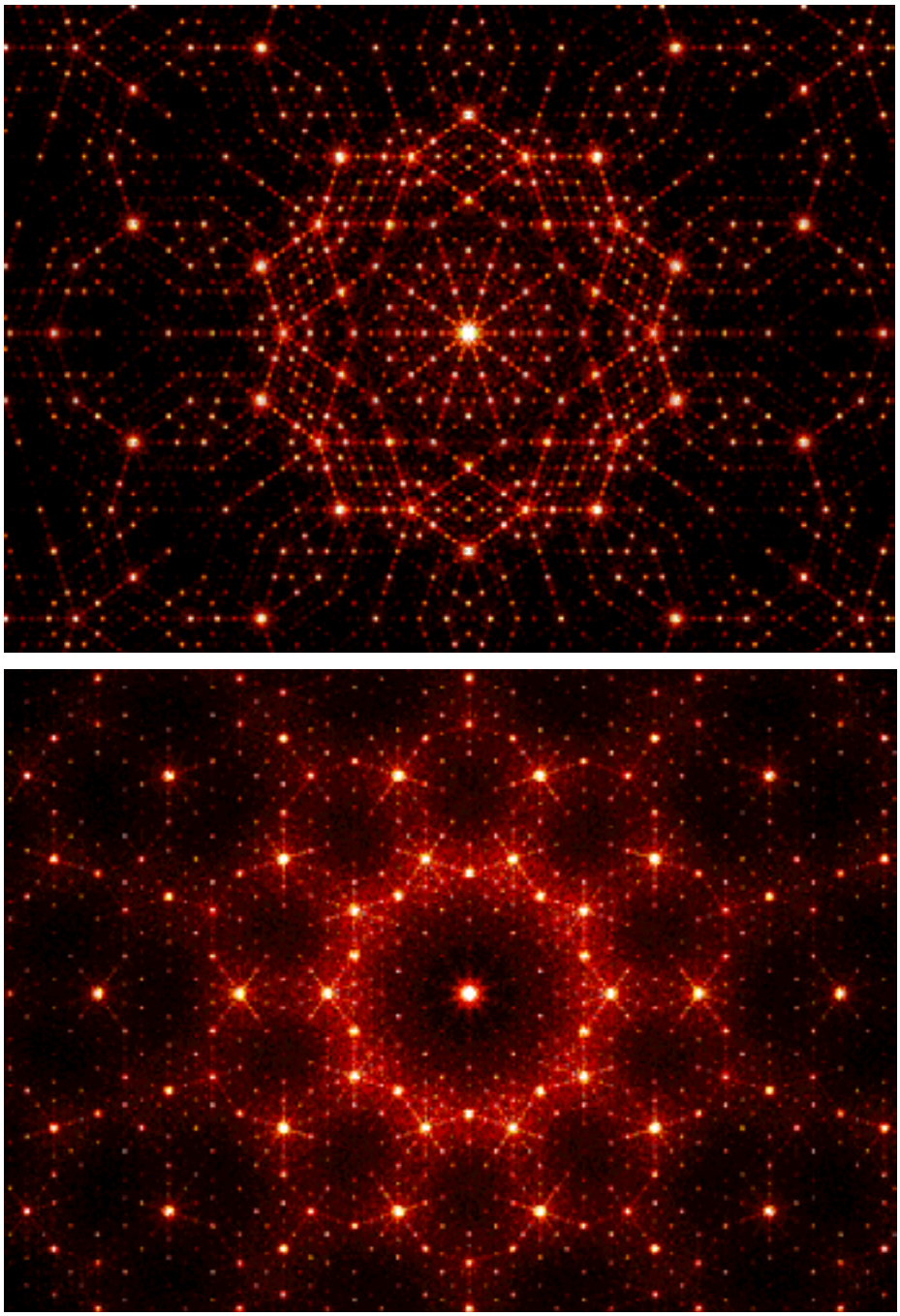


Calculated models of quasicrysals - the lower image includes diffuse scattering and the upper one doesn't.

"The discovery of quasicrystals - materials that showed diffraction patterns with 10-fold symmetry - is something that has happened since I've been doing this work on disordered crystals," says Professor Welberry. "It's one of the most exciting things to have happened in the field because for a century or so people thought that crystallography could only have crystals which were at certain symmetries like a six fold hexagonal or a four fold rotation, but not five fold because you can't make an object that's got five fold symmetry and make a continuous infinitely repeating pattern. And then in 1984 people found real materials, and these are mainly alloys, which do display such symmetries.

"The outstanding problem in this field is that these quasicrystals form alongside crystalline material so the question is how to do you get from this thing with five fold symmetry to an ordinary crystal. That sort of transformation between a crystalline world and the quasicrystalline world is still a very poorly understood topic."

Dewetting and making micro patterns

Micro-patterned substrates play a big role in biotechnology but creating them can be a complex and expensive job. Now a physical chemist at the Australian National University believes she has an innovative approach to making micro-patterned substrates that could revolutionise the whole process. Indeed, building your own micro-patterned surfaces may become as easy as watching rain dry on a window pane.

Many people have described the time in which we live as a golden age of biotechnology. Never before have we had such power to manipulate and work with cells, bacteria, proteins and molecules. The key to much of our success has been our capacity to control and harness specific interactions between biological molecules and cells, and their surrounding environment. And to do that you need methods to separate control cells and molecules.

One way this is achieved is by building surfaces with localised features of controlled surface chemistry and topography such that these patches will specifically bind to the biological substance of interest while the surrounding surface repels that substance.

"When you build a surface with localised features of chemistry and topography you are in effect creating a pattern," says Dr Chiara Neto, a Research Fellow in the Department of Applied Mathematics (Research School of Physical Sciences and Engineering). "And building micro-patterned substrates that selectively bind to specific proteins and cells is of enormous interest in biotechnology and bioengineering.

Making patterns

"Many areas of biotechnology depend critically on the ability to control the positioning of proteins and cells on the micro scale. Biosensors for drug screening, engineering artificial tissues and many cell biology studies are heavily dependent on being able to selectively control the position of a molecule or cell.

"And there are many solutions available for how this might be achieved," she comments. "There are micro-fabrication technologies such as photolithography, micro-fluidic techniques and micro-contact printing. These methods have addressed the problem of creating selective micro patterns and provided elegant solutions. However, these techniques often come with a high price, they can be quite complicated requiring custom chemicals and elaborate equipment, and they often produce micro patterns with very specific applications. They work well but only for a small set of applications."

All of which had Dr Neto wondering if her work on dewetting might not offer a valuable new way of creating selective biological micro patterns.

Dr Neto is a physical chemist who has carried out a range of fundamental investigations on liquid-solid interfaces."

Dr Chiara Neto with an Atomic Force Microscope (AFM), the instrument she uses to study the DIBIP patterns she creates.

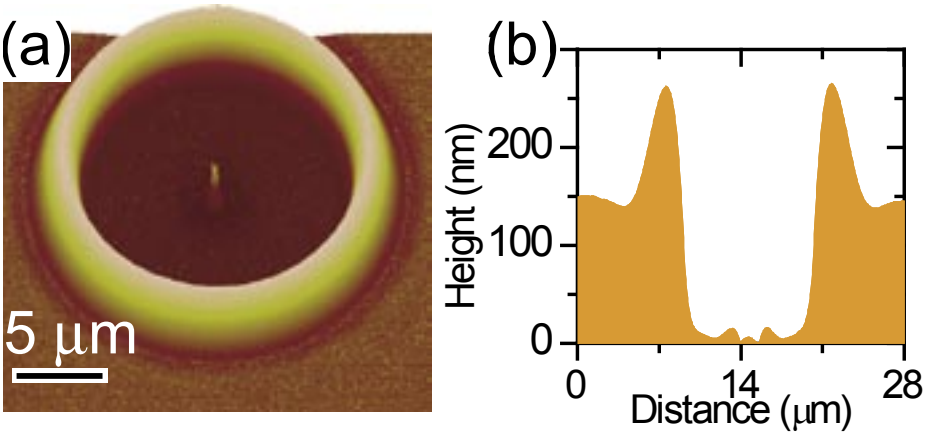
Watching a film decay

"My earlier research was on the stability of thin films and the way they decay," explains Dr Neto. "This is a process known as dewetting.

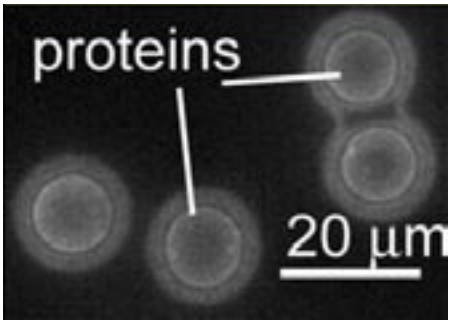
"It's the same process as on a window pane with water on it. Initially you get a film of water but that film decays and holes form in it. These holes grow until eventually the film becomes a series of droplets.

"There's a lot of work published on this field on which films are stable, which aren't stable, and if they are unstable how they decay. However, it's all knowledge from a scientific point of view with little discussion on possible applications.

"Many times I would give talks on dewetting at different labs around the world and a typical question was how might we use this information. You can create these very interesting patterns in a controlled



An AFM image of a hole created during dewetting.



A fluorescence micrograph of micropatterned substrate. Fluorescently labeled proteins can be observed only inside the designated areas.

manner with different areas possessing different properties. Could this knowledge be applied to solve some problem?"

So Dr Neto began investigating how a knowledge of the dewetting process might produce patterns with applications in other areas and quickly became aware of its potential for micro-patterning of biological substrates.

"It became apparent to me that it was possible to create micro patterns using dewetting that would serve a wide range of roles in biotechnology. However, unlike many of the existing techniques, Dewetting-Induced Biological Patterning – or DIBIP for short – is simple, versatile and cheap.

"A good way of understanding what it involves is by considering an example. Proteins readily adsorb to a film of the polymer polystyrene but not to poly methyl-methacrylate (PMMA). Supposing I want to create a pattern in which there are islands of protein-loving surface surrounded by a sea of protein-repelling surface. How might this be achieved? With a little knowledge of dewetting it's easy," says Dr Neto.

"First you coat a silicon wafer with polystyrene. This is done on a spin coater, a basic piece of lab equipment that costs a bit over a thousand dollars. It spins the wafer while you drop a solution of polystyrene dissolved in solvent on top of the wafer. As the solvent dries out this forms a nice even layer of solid polystyrene. Next, you build a layer of PMMA on top of the polystyrene.

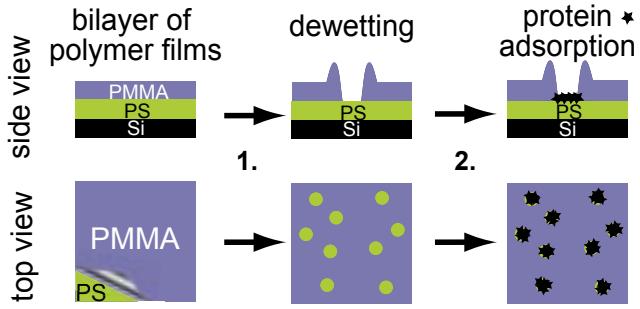
"Then you heat the wafer with its bilayer of polymers till the polymers become liquid. The PMMA is more unstable and begins to dewet or decay. Tiny holes begin opening up in the top layer revealing the underlying polystyrene layer. Because we understand the dewetting process we know how long it takes to form a certain number of holes of a certain size. We cool the bilayer when we we've created the pattern we desire.

"We then expose the pattern to a protein solution and we end up with polystyrene islands covered in protein surrounded by PMMA which is protein free.

"With a few very easy steps this process has produced a patterned substrate that possesses micro-islands of adsorbed proteins separated by a protein-resistant matrix. The size and the distribution of these islands can be controlled simply by varying a few physical parameters, such as film thickness and dewetting time."

Dr Neto with a spin coater, a basic piece of lab hardware and almost all that's needed for the DIBIP process.

FORMATION OF A DIRECT PATTERN WITH DIBIP



A schematic of the DIBIP micro-patterning method.

Make your own patterns

"A unique feature of DIBIP is that it is equally easy to prepare 'direct' and 'inverse' patterns. That is either the round patches can be made of protein-attractive in a protein-resistant background, or vice versa, the patches can consist of the protein-resistant polymer in an attractive background by laying down a layer of PMMA first and polystyrene on top.

"It's a versatile process that can be altered as needed depending on the application for which the patterns are required."

In principal, using different materials you can pattern any biological sample says Dr Neto. She's demonstrated that DIBIP works for protein and she's now working on devising a system for bacteria, in collaboration with Dr Rohan Baker from the John Curtin School of Medial Research. She believes she can also make it work for DNA, peptides, and other biological molecules.

"With DIBIP all you need is a spin coater, a heater and a few commonly available chemicals," explains Dr Neto. "In contrast, lithography needs a clean room, dedicated instruments, expert skills, and requires multiple steps involving photoresists, masks and etchants."

Beyond biotechnology

While Dr Neto is confident DIBIP has enormous potential for biotechnology she also believes there's scope to push the technique into nano-patterning with applications for nanosensors and application specific nanomaterials.

"Once again, it's just a matter of understanding the dewetting process and knowing when to freeze it to leave you with the appropriate sized holes," says Dr Neto.

The study of DIBIP also moves us towards a more complete understanding of protein-polymer interactions and raises the possibility of designing new surfaces for the prevention of bio-fouling.

A provisional patent for the DIBIP method has been granted and Dr Neto is currently seeking suitable commercial partners for collaborative research and licensing in aid of market development.

More info: Dr Chiara Neto <Chiara.Neto@anu.edu.au>

Devil in the detail

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patterns that go much further out into reciprocal space which means in real space you can be much more precise.

"The big disadvantage, however, is that compared to X-ray sources neutron sources are very weak. The best neutron sources in the world are only about as powerful as an ordinary little X-ray generator in an average diffraction lab. But even so, with all the sophisticated detectors it's still amazing what you can do with neutrons."

A new generation of diffuse scattering science

Professor Welberry believes that working with diffuse diffraction is now coming of age as new ways of capturing and analysing diffraction data become available.

"When you consider we're generating higher-quality diffuse diffraction data from laboratory X-ray sources, synchrotron X-ray sources (and Australia will soon have its own synchrotron facility) and neutron sources, and combine this with an every increasing capacity to analyse and build models based on this information, then I think it's fair to say we're entering a new generation of of nano-scale structure determination.

"Nanoscale structure is the 'final frontier' of materials characterisation," says Professor Welberry. "The long-range average structures of most known materials have been characterised by conventional crystallography, and published in standardised formats in extensive databases. The short-range local structures of materials are increasingly well characterised by spectroscopy, and the reporting of results increasingly standardised. The characterisation of intermediate-range nanoscale structure, by contrast, is in a relatively embryonic stage. By applying this new generation of diffuse scattering science to a range of materials I believe we'll be making important advances along this final frontier."

More info: Richard Welberry <welberry@rsc.anu.edu.au>

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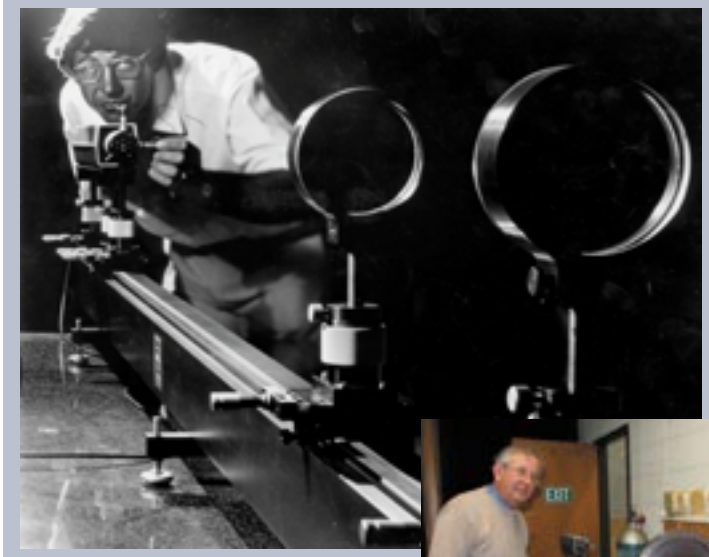
Let there be light

The task of calculating a diffraction pattern from a model is not to be underestimated. Indeed, it's so big that it was beyond the power of the available computers back in the '80s.

"Before the early '90s, computers simply weren't powerful enough to create the diffraction patterns of the things I was interested in so I had to create them in another way," explains Professor Welberry. "I used to make models of atomic arrays in the computer and then create transparencies showing these models as a series of dots. I would then shine a laser light through these transparencies to project a diffraction pattern onto a screen or film in a camera.

"Fortunately, computers became more powerful and since about 1990 I can actually compute the diffraction pattern on the computer. However, the technique of creating diffraction patterns by optical projection has proved an excellent technique for teaching."

So much so that Professor Welberry's set of model slides are still used today to explain to students the power and beauty of X-ray crystallography.



(Left) A younger Richard Welberry (back in 1978) adjusts a laser to obtain scattering patterns from visual models of disordered crystals. (Photo courtesy of the ANU Archives and originally appeared in 1978 in the ANU Reporter.)

(Right) Professor Welberry still has the equipment but now uses computers to generate diffraction patterns from his model arrangements.

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