

The political and economic complementarity of neutrons and x-rays

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While neutrons and x-rays largely keep to themselves in the subatomic world, the scientific communities that use them to study molecules and materials have always been intimately connected. The synergistic development of experimental techniques, and the complementary nature of the information they provide, are well documented and will automatically emerge as a unifying theme of this meeting. This talk will focus on how the neutron and x-ray user communities have worked together beyond the purely scientific domain, to ensure that they have access to the big, expensive and – to the general public – rather mysterious machines that their research programs require. We are reaping the rewards of that work in Australia right now, making it a good time to recap how we got here, and how we are continuing to build so that the 2010s will ultimately prove to be a milestone but not a high point that takes another 50 years to surpass.

The role of antioxidant-protein interactions in phospholipid membranes

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Oxidative damage of cellular phospholipid membranes has been linked to a variety of disease pathologies, including cardiac disease, Alzheimer's and other ageing-related illnesses. The oxidation of unsaturated and polyunsaturated fatty acid chains found in membranes leads to alteration in their physical properties, which ultimately affect biological function and may lead to these diseases.

Polyphenols are naturally occurring phytochemicals present in a number of fruit and vegetables that are of interest for their anti-oxidative powers, for example in functional foods. These polyphenols inhibit lipid oxidation in cellular membrane surfaces, although the mechanism of this inhibition is not entirely clear. Moreover, the polyphenols have significant binding affinity for proteins, which can lead to the formation of soluble and insoluble protein-polyphenol complexes. Significantly, in the presence of casein proteins the oxidation inhibition the polyphenols in the membrane may be significantly enhanced. Thus the antioxidant pathway appears to involve these protein/polyphenol complexes, as well as direct antioxidant action by the polyphenol .

Here we discuss neutron and x-ray scattering results from phospholipid membranes, looking at the positioning of two examples of polyphenolic antioxidants in phospholipid membranes, quercetin and phloretin, the antioxidants' impact on the membrane organisation, and the interaction between antioxidant and extra-membranous protein. This information sheds light on the mechanism of antioxidant protection in these systems, which may be used to understand biological responses to oxidative stress.

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Neutron scattering gives a new perspective on a protein translocon

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Typically, about 30% of a cell's proteome is translocated across membranes and these proteins must overcome a significant hydrophobic barrier. Most employ large protein complexes called translocons which provide a pore through the barrier. Determining the dynamic structures of these pathways is demanding and here we show that neutron scattering can resolve the individual components of a bacterial translocon which uses the "porin" protein OmpF. Neutron reflectivity was used to follow, in real time, the OmpF-mediated insertion of colicin N into a lipid monolayer. Then, small angle neutron scattering experiments defined the three dimensional structure of the colicin-OmpF complex. This data in conjunction with surface pressure studies of the monolayer and Brewster Angle Microscopy imaging revealed an unconventional translocation route which was dependent on the presence of OmpF into the membrane.

Towards a molecular mechanism for the protective effects of sugars on membrane damage during dehydration

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Some organisms have evolved the ability to increase their tolerance to dehydration and freezing by accumulating small solutes (for example sugars) which stabilise membranes against deleterious phase transitions. The phase behaviour and transition kinetics of membranes in the presence of sugars is therefore of primary importance in understanding freezing and dehydration damage. There are two main explanations for the membrane stabilising effects of small sugar molecules:

1. The hydration forces explanation relies on a short-range repulsive interaction due to the hydration of lipid head groups. The removal of the solvent brings membranes into close contact and the short range hydration interaction induces a lateral compressive stress in the membrane. This compressive stress is responsible for transitions from the lamella liquid phase.
2. An alternative explanation, the water replacement hypothesis involves a very specific interaction between sugars and the lipid head group, and close proximity of the sugar molecule to the lipid head group. This explanation is commonly invoked to explain the “anomalous” cryoprotectant properties of trehalose.

The localisation of sugar molecules with respect to the lipid head groups, and the concentration profile of sugar between lipid bilayers should provide insight into the validity of these two models. We present the x-ray and neutron scattering and neutron scattering over a range of scattering vectors and discuss the power selective deuteration of sample components.

Structural analysis of membrane protein arrays used in biotechnology

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Proteins can be immobilised on surfaces to make arrays with potential uses in tissue engineering, proteomics and point of use diagnostic devices. Membrane proteins can be immobilised onto flat gold surfaces in a specific orientation by using a single cysteine residue that will form a gold-thiolate bond. The membrane layer is completed by the immobilisation of a lipid with a thiol head group to the gold surface. Previous studies have focused on trimeric OmpF for membrane structural biology [1] but here we use the transmembrane section of the monomeric protein OmpA (TmOmpA). The Z domain of Staphylococcus aureus protein A has been engineered into the N-terminus of TmOmpA to create the protein ZZctOmpA. The Z domain can bind immunoglobulin G (IgG) at its constant region leaving the variable regions free to bind antigen. The structure of this model protein array was probed using magnetic contrast neutron reflection (MCNR). MCNR uses polarised neutrons which reflect differently from a magnetic metal layer according to their two spin states (spin up and spin down). The magnetic layer deposited between the silicon substrate and the gold surface provides additional scattering length density contrast to very complex layer systems without needing to make any changes to the biological layer. The collection of two complimentary but independent data sets allows for more accurate modelling of the resulting high resolution data. The data presented will show the assembly steps for creating the array detailing the surfaces used, the ZZctOmpA and lipid components as well information on the orientation of bound antibody and antigen.

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X-ray and neutron diffraction studies of ordering phenomena in multiferroic materials

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Multiferroics are advanced materials which exhibit strong electric and magnetic polarizations simultaneously. They are promising candidates for novel applications with the potential to dramatically increase data storage capacity and processing speeds. However, the underlying physics is not yet understood. Competing theories of inherent electronic structure and ionic displacement have attempted to explain the coupling of the polarizations, but no experimental evidence currently exists to distinguish between the models.

Both x-ray and neutron diffractions are invaluable techniques to investigate the magnetic, orbital and structural properties of these complex oxides, and in particular the combination of both can be particularly insightful.

After a general introduction to multiferroics and the specifics of the used diffraction techniques I will talk about our results on two specific oxides. LuFe_2O_4 exhibits multiferroic behavior arising from frustrated charge order while hexaferrite $\text{Ba}_{0.8}\text{Sr}_{1.2}\text{Zn}_2\text{Fe}_{12}\text{O}_{22}$ exhibits multiferroic behavior arising from frustrated spin order. Comparison between resonant x-ray diffraction and neutron diffraction suggests that, in addition to the magnetic order, there is a second order parameter in the multiferroic phase of hexaferrite.

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Influence of applied magnetic field on magnetovolume effects – re-entrant ferromagnet $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$

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Large magnetocaloric effects (MCE) are generally observed in materials which undergo first order magnetic transitions (FOMT) and simultaneous field-induced magnetic and structural transformations [1, 2]. Magnetovolume effects are found to play a large role in the MCE [2, 3]. This has led to increased attention being paid to understanding the influence of magnetostructural coupling on MCE behaviour [4]. By replacing Pr atoms with relatively small Y atoms in the 2a site of PrMn_2Ge_2 , we have successfully designed the re-entrant ferromagnet $\text{Pr}_{0.5}\text{Y}_{0.5}\text{Mn}_2\text{Ge}_2$ - canted ferromagnetic Fmc to canted antiferromagnetic AFmc at $T_N^{\text{inter}} \sim 170$ K; AFmc to Fmc at $T_C^{\text{Pr}} \sim 62$ K. We have investigated magnetovolume effects at the FOMTs T_C^{Pr} and T_N^{inter} using Wombat@OPAL (20-320 K B=0.0 T, B=4.0 T).

The lattice constant a (B =0 T) has been found to be smaller in the AFmc region than in the Fmc regions resulting in magnetovolume effects of $\Delta a/a \sim 0.17\%$ at T_C^{Pr} and $\Delta a/a \sim 0.15\%$ at T_N^{inter} . By comparison, in a field of B= 4 T the lattice parameter a exhibits a monotonic behaviour with temperature indicating that the magnetovolume effect has been removed by the 4 T field. This behaviour can be understood in terms of a field-induced metamagnetic phase transition from AFmc to Fmc within the AFmc region as confirmed by our magnetic measurements.

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***In situ* investigation of lead –free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ piezoelectric ceramics under an electrical field via high intensity neutron powder diffraction**

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In this work we investigate the average R3c structure and micro-structure of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) ceramic *in situ* under different applied electric fields using a high intensity neutron diffraction technique. A careful refinement and justification are made, in conjunction with electron diffraction data, to provide new insight towards the understanding of the ferroelectric and piezoelectric behaviour of BNT. It is found that the applied electric field introduces texture in the form of increased preferred orientation, increases the polar displacements of the cations relative to the oxygen anions but also, most importantly, induces microstructural changes (for example, twinning defects) at very fine scales within the R3c rhombohedral phase matrix at room temperature. The latter defects contribute to the electromechanical coupling behaviour observed in BNT.

A theoretical framework for soft x-ray resonance enhanced Bragg diffraction

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With resonant x-ray diffraction, the incident x-ray energy is tuned to the vicinity of an absorption edge in the material. The absorption process provides an element-specific enhancement to the diffracted intensity of up to three orders of magnitude, which allows the investigation of structure-forbidden superlattice peaks [1]. The rare-earth borocarbides RB_2C_2 are a family of compounds with a wide variety of ordering schemes. Particularly, Dy, Tb and Ho all exhibit strong ordering of the 4f orbitals. It has previously been reported [1] that the energy dependence of the resonant intensity in DyB_2C_2 is more complex than can be provided for by having a single resonant oscillator at each absorption edge. This is proposed to result from a significant intra-atomic electrostatic multipole moment present in the valence 4f shell which interacts with the core-hole in the d-shell during the resonance process and causes a splitting of the energy levels [1].

Soft resonant x-ray diffraction was performed on HoB_2C_2 at the UE46 beamline at BESSY II in Berlin, Germany, at temperatures down to 1.5K. The energy dependence of the scattered intensity is analysed on the basis of this Core-Hole splitting formalism.

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Resistance of interfacial β -casein to chymosin enzymatic degradation

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Based on our previous research we have revealed the resistance of an isolated ordered protein film subjected to the denaturant solution[1]. Besides using the 'flow trough' technique[2] we also employed the 'dropping method' and premixed solutions to investigate the nanoparticles trapped by protein at the air/liquid interface[3]. The different responses correspond to the different initial conditions even though the components of the reactions are the same. Here we report the interactions between β -casein and chymosin at the air/liquid interface. The proteolysis of β -casein by chymosin in solution has been well documented. At the air/liquid interface the hydrophobicity of the protein molecules cause the deformation in the configuration of the proteins. Simultaneously the molecules also could be aligned orderly at the air/liquid interface. We used the β -casein and chymosin solutions to form an adsorbed layer at the air/liquid interface and then the forming solutions were replaced by phosphate buffer. The chymosin and β -casein solutions were introduced underneath β -casein as well as chymosin films respectively. The structural changes represent the competitions between these two molecules at the air/liquid interface. As well we premixed β -casein with chymosin in phosphate buffer prior to forming an adsorbed layer at the interface. From the premixed solution experiments we could extract the structural information of the film composed of the β -casein proteolytic fragments and chymosin. The difference in the structures of the absorbed layers is attributed to the hydrophobicity competitions of the two molecules and the orientated protein-enzyme interaction.

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Dynamic interplay between spin crossover and host-guest function in porous coordination polymers

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Porous coordination polymers (also commonly known as metal-organic frameworks) have received widespread attention due to their rich host-guest interactions and chemical versatility. This field has undergone extensive advancement in recent years with efforts to design framework materials that have highly specific properties, such as selective guest sorption/desorption, electronic and magnetic function, gas storage and negative thermal expansion. [1]

The family of materials $\text{Fe(L)M(CN)}_4 \cdot x(\text{guest})$ (M = Ni, Pd, Pt) has been investigated for spin crossover (SCO). By utilizing a number of techniques including magnetic susceptibility, x-ray and neutron diffraction, and thermogravimetry we have established that these materials show dynamic interplay between the spin transition and its host-guest function, that is, SCO-induced guest sorption and guest-induced SCO. [2, 3] More recently, we have discovered unprecedented guest-induced physicochemical properties including multistep and unusual hysteresis.

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High-internal phase emulsions under shear. II. Co-surfactancy and shear stability

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Large changes in the rheology of high internal phase aqueous-in-oil emulsions using an oil-soluble polyisobutylene-based primary surfactant (PIBSA) are provoked by very small quantities of water-soluble polyacrylamide based co-polymers (PAM) acting from the aqueous phase. The effect of hydrophobicity change using C₁₂, C₁₄ and C₁₆ tails, under shear was studied using small-angle neutron scattering and simultaneous *in situ* rheology measurements. The scattering parameters indicate that PAM drastically lowers the droplet-oil interfacial tension causing large droplet deformation under shear and much lowered emulsion yield stress. With PAM, the surfactant monolayer at the droplet surface becomes more responsive to droplet shape change, and redistributes in response to shear which the PIBSA only system does not.[1] Although oil insoluble, PAM also reaches the nanoscale PIBSA micelles in the oil phase, changing their size and content in ways predictable from the hydrophilicity of the different PAMs. PAM does not, however, strongly affect the viscosities at high shear rates, shear thinning and thickening are unaffected. Droplet size, droplet-droplet flattening and linkage determine the viscosities observed, not droplet-oil interfacial tension. We infer from this that droplet motion under shear does not involve much transient droplet deformation as the droplets move by each other.

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Structure of HSA at the air-water interface and effect of fatty acid on HSA - silica nanoparticles interaction

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The structure of Human Serum Albumin (HSA) at the air-water interface was studied using x-ray reflectivity. The adsorbed protein structure indicates severe denaturation of the protein with a dense top layer of α -helices and a diffuse bottom layer. The latter was only detectable at high bulk concentrations of HSA (>1 mg/mL). Our results indicate that HSA adopts a "train-and-loop" structure[1] at the air-water interface.

Complimentary neutron and x-ray reflectivity measurements at the air-water interface proved to be a sensitive method to study the structure[2] of protein-nanoparticle complexes[3]. Fatted and defatted variants of HSA behave differently[4] in their interaction with silica nanoparticles. The difference in the neutron surface reflectivity signal for SiO₂ nanoparticles mixed with fatted and defatted HSA was interpreted as a combination of three factors: increase of structural stabilisation induced by the hydrophobic interaction of fatty acids with HSA, weaker electrostatic interactions between F-HSA and the silica nanoparticles, and the propensity of DF-HSA to self aggregate via intermolecular disulfide bonding. Structural analysis of the protein corona adsorbed at the air-water interface was performed using neutron reflectivity. Protein to nanoparticle ratios in the surface layer were also compared.

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Medical applications of synchrotron radiation: growth and outlook for an emerging field of science

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The Australian Synchrotron Imaging and Medical Beamline (IMBL) is in the early phase of operations. In about 2 years it will be ready for the commencement of large animal and human research programs. This talk will present the history of medical research at synchrotrons, much of it from a personal view, starting with the first human angiography program at the Stanford Synchrotron Radiation Lightsource and ending with an overview of the IMBL. The development of imaging technologies such as K-edge subtraction and phase-contrast, along with radiation therapy modalities such as micro-beam radiation therapy and synchrotron stereotactic radiation therapy, will be described. Recent experimental results from research groups in Canada and Australia will be presented in relation to future programs at the Canadian Light Source and the IMBL.

Shedding light on neurodegeneration; SAS and misfolded proteins

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The misfolding pathways that lead to cytotoxic species vary between diseases such as Alzheimer's (AD), Huntington's and Parkinson's but there is a common link in that these pathways all involve some form of oligomeric species, which have been suggested to be the "toxic principle" in these diseases, in contrast to the prominent extra- or intra-cellular fibrillar deposits of aggregated protein that are regarded as end products of the pathological process [1].

To elucidate possible folding pathways for the amyloid β peptide of AD ($A\beta$) we made time-resolved, stopped-flow SAXS measurements at the Australian Synchrotron on $A\beta$ 1-40 and $A\beta$ 1-42 peptides in dilute NaOH (13mM) that were rapidly mixed with pH 6.9 phosphate buffered saline containing Cu^{2+} ions. These showed that protofibril formation occurred in less than one second in either control or Cu^{2+} -containing buffer and that further evolution of the fibrils in subsequent seconds followed a non-linear pattern. Static measurements on the peptides that had been reacted with sub-micellar concentrations of the lipid mimetic, N-lauroylaminopropyl-N',N'- dimethylamine oxide (LDAO) and a dipeptide formed of tyrosine 10 cross-linked $A\beta$ 1-40 [2], however, gave a stable well-defined "Y" shaped structure for both the di-tyrosine linked peptide and LDAO- associated $A\beta$ 1-42. The "Y" shape is reminiscent of the Fc antibody fragment. Since the di-tyrosine linked peptide is neurotoxic, as in the case of cytotoxic antibodies, its two arms may carry ligands able to cross-link cell membrane receptors to initiate a cytotoxic cascade.

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Towards a model for positron transport in soft-matter for PET

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Positron emission tomography (PET) is an established medical imaging technology for pinpointing abnormalities in living tissue [1]. The accuracy is however limited by the fact that high-energy positrons emitted by the source (the region of the abnormality) must slow down from keV to less than 100 eV before positronium (Ps) formation is appreciable, and the subsequent signature back to back gamma radiation can be detected [1]. The image point is therefore displaced from the point in the source at which the positron actually originates and, since there is a distribution of such displacements governed by the physics of the scattering processes, the overall image is blurred. This fundamental limitation on the spatial resolution of PET has long been recognised, but until now has not been possible to quantify with any great rigour, for two distinct reasons:

- (i) the structure of the soft condensed matter and coherent scattering of positrons have not been taken into account in previous modelling; and
- (ii) not all cross sections for the scattering processes have been available.

In this paper, we utilise the recently developed kinetic theory of positrons in soft condensed matter [2], firstly to find a general expression for the rate of Ps formation as a function of distance from a spherical source, and secondly to carry out numerical calculations using scattering and Ps formation cross sections measured recently [3] at the Australian Positron Beam Line Facility at ANU, with an established static structure function [4] for liquid water.

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Light responsive nanostructured matrices for pulsatile drug delivery

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Stimuli-responsive systems may improve drug delivery and therapeutic outcomes by providing pulsatile active release. Lipid-based liquid crystal systems (LLCs) are being investigated for this purpose as they have thermodynamically stable nanostructures which determine drug release rate from the material. Using Small Angle X-ray Scattering (SAXS), we have previously shown reversible control over the nanostructure and consequent drug release rates of LLCs. This was achieved by 'switching' between structures through the use of temperature changes. However, for some applications, direct heat is not practical and a non-invasive stimulus, for example light, would be preferable. In this study, external activation of changes in lipid packing and consequent phase changes are induced spiropyran-based dyes incorporated into LLCs which photoisomerise to manipulate lipid packing.

The effect of irradiation of LLCs containing a photochromic spiropyran dye and its monolaurate derivative were compared. On irradiation with UV light, LLC containing the alkylspiropyran derivative induced changes in the nanostructure, whereas the non-alkylated spiropyran did not. Spiropyrans isomerise via ionisation and so provides a physical 'wedge' in the packing of the lipid amphiphiles in the LLC nanostructure. The non-alkylated derivative had little effect on structure, and is hypothesised to partition out of the nanostructure on ionization, resulting in little disruption to lipid packing.

Photo-activation of the alkylspiropyran derivative resulted in phase changes in LLCs. It is anticipated that this approach can be applied to control changes in drug delivery rate from LLCs, and hence provide novel, reversible, 'on-demand' drug delivery systems.

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Effect of a static magnetic field in radiotherapy: a nanodosimetric study

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Despite significant advances in surgery, radiotherapy, and chemotherapy, cancer is still one of the leading causes of death in Australia and worldwide. In this respect a crucial issue in radiotherapy is to investigate new technologies to achieve higher effectiveness of cancer treatment. The aim of this project is to improve the tumor response by overlapping the radiation dose with a homogeneous magnetic field within the tumor. This study is also significant for MRI guided radiation therapy, as it concerns the effect of a potential interference of ionising radiation and magnetic field.

The hypothesis of the study is that at nanoscale level a moderate magnetic field may modify the spatial distribution of low energy δ -electrons produced by high linear energy transfer particles and the microscopic energy deposition pattern in DNA segments, leading to clustered damage of DNA without affecting the overall macroscopic absorbed dose distribution in the patient.

Preliminary cell survival experiments in low energy x-ray field in the presence of a 1.5T magnetic field, performed at CMRP in collaboration with the Millennium Institute for Cancer Research (Australia), support this hypothesis and warrant further investigation to understand this phenomenon.

Using the Geant4-DNA Monte Carlo code, ionisation cluster size distributions were calculated for electrons, protons and alpha particles moving in transverse magnetic fields up to 10T. For the electrons, energies typical of δ -electron spectra present in radiotherapy treatments were used, while for the two kinds of ions energies up to about 10 times the Bragg peak energy were considered. The ionisation cluster size distribution was studied in a nanometric target representing a short DNA segment. The interactions of particles were modelled down to the eV scale.

The mean number of ionisations caused, the energy deposition spectrum and the probability of producing a double strand break in the DNA were obtained. For all these quantities, the values obtained for different magnetic field strength showed a relative variation on the order of 1%. However, taking the statistical uncertainties of the simulation results into account, the overall variation of track structure parameters and biological effectiveness of the radiation has to be assessed as not significant.

This implies that any experimentally observed changes in the biological effectiveness of radiation are not likely to be related to the spatial redistribution of the δ -electrons deriving from the application of a magnetic field.

Currently radiobiological measurements are taking place at the single cell ion microbeam facility of the Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany to study experimentally the effect of magnetic field on cell survival curves, when exposed to alpha particles beam.

A structural and computational study of the formation of the carbamoylcyanonitrosomethanide anion

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Small polycyano anions, such as dicyanamide and tricyanomethanide, have captured the attention of chemists as their unique properties have resulted in their inclusion in applications as diverse as magnetically ordered coordination polymers and room temperature ionic liquids [1,2]. The dicyanonitrosomethanide (dcnm) anion is of particular interest, as it readily undergoes the addition of a range of nucleophiles, with the addition of water to a nitrile group yielding the carbamoylcyanonitrosomethanide (ccnm) anion [3] (Figure 1). While this provides a convenient route to *in situ* ligand synthesis the mechanism of the reaction is poorly understood. In this study the single crystal neutron structure of $(\text{Et}_4\text{N})_2(\text{ccnm})_2 \cdot \text{H}_2\text{O}$, collected on the Koala – Laue diffractometer, provided accurate information used for a computational study into the electronic structure of the anion and hydrogen bonding within the system. *Ab initio* calculations were also used to determine a possible mechanism for the formation of the ccnm anion.

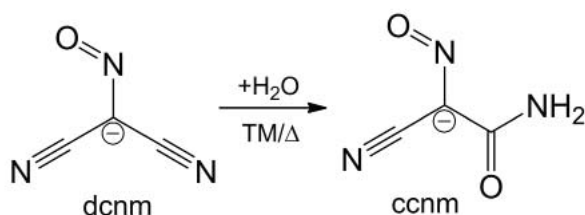


Figure 1. The nucleophilic addition of water to the dcnm anion.

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Strategies for modelling short-range order in molecular crystals

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Modelling short-range order in molecular crystals requires modelling interactions within and between molecules. This means developing models that allow for molecular flexibility, and if needed molecular reorientation and flipping. This presentation will outline some newly developed strategies for modelling the disorder and short-range order in molecular crystals, and then calculating the resulting diffuse scattering, with a focus on organic molecular crystals. The approach uses Monte Carlo simulation, combined with a range of ways of parameterising the intermolecular interactions.

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The use of Chebyshev polynomials in the free form fitting of featureless neutron reflectivity data

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The majority of reflectometry analysis nowadays uses a simple, but coarse, slab construction where a scattering length density profile is approximated using slabs of uniform scattering length density. This approach is extremely successful but runs into problems where the SLD profile varies continuously and an analytic profile is not available or not known 'a priori'. One such example is the segregation of ions in room temperature ionic liquids. In these systems the reflectivity profiles have little apparent information as the ions are extremely small. Here I will outline the application of Chebyshev polynomials to reconstruct the scattering length profile of a room temperature ionic liquid at the air-liquid surface.

Such an approach is free-form and could be employed to model other systems in which there are unknown regions.

Using small-angle x-ray scattering to gain insight in the catalytic regulation of signaling enzymes in health and disease

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Small-Angle X-ray Scattering (SAXS) is a powerful tool for studying the structure of biological macromolecules in solution. The utilization a synchrotron x-ray source provides very rapid data collection and this allows protein samples to be subjected to in-line fractionation during the SAXS experiment. We have applied this methodology to investigate the changes in molecular size and shape that regulate the activity of Src-family kinases, a family of important cellular signaling enzymes.

The Src-family kinases (SFKs) c-Src, Blk, Fgr, Fyn, Hck, Lck, Lyn and Yes are multidomain intracellular protein tyrosine kinases that act as key effectors in numerous signal transduction pathways. While the overall domain organization and core regulatory mechanism are well conserved across the family (1-3), each SFK is characterized by an N-terminal “unique” region (UR), which modulates its cellular role. We are interested in the structural basis of UR function.

The hematopoietic family members Hck and Lyn exist in multiple isoforms, which differ in their UR sequences. We have applied a variety of biophysical methods, including SAXS, to study how the different URs affect the structure, ligand-binding, self-association and catalytic activity. Our results indicate that there are isoform-specific differences that influence receptor-targeting and basal, as well as, inducible catalytic activity, with implications for the roles of these kinases in immune responses in health and disease.

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This work is supported by an AINSE Research Award

Structure, dynamics and function of a replisomal protein complex

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Knowledge of the structure of a protein can be very informative in determining its function, however, a structure alone does not tell the whole story. In the case of large, dynamic multi-protein systems where a coordinated network of interactions and enzymatic functions are involved, structural and biochemical information may be gainfully combined with knowledge of dynamics [1]. One such system is the bacterial replisome, which consists of more than a dozen interacting proteins and is capable of rapid DNA replication. As such, it is a good model system and a ripe target for antibiotic development. We have focussed on an interaction that involves one of the key organisational centres of the Gram-positive bacterial replisome, the DnaB helicase and its loading partner, DnaI, which together form a tight 6:6 complex prior to loading of the hexameric helicase onto DNA, after which DnaI dissociates [2]. We have separately measured the dynamics of DnaI, DnaB and their complex using elastic, quasielastic and inelastic neutron scattering on IN6 at ILL (Grenoble, France).

These measurements have established that the molecular flexibility and diffusive motions are significantly decreased when DnaI and DnaB are complexed, with DnaB having the greatest flexibility when free. Further to this, complexation results in an increase in structural rigidity with the DnaB-DnaI complex having a significantly higher effective force constant both above and below the temperature of dynamical transition. The vibrational density of states was also extracted, revealing that the DnaI-DnaB complex has less inelastic vibrational modes than DnaB and DnaI below the absolute value of 20 meV.

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X-ray and neutron scattering studies of the molecular chaperone α -crystallin enables localization of ligand binding sites

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α -Crystallin, the main constituent protein in the crystalline lens, is an important molecular chaperone both within and outside the lens where it prevents the aggregation and precipitation of a wide variety of target proteins, for example under conditions of stress. Presently, the structural relationship between α -crystallin and its target proteins during chaperone action is poorly understood. This is partly due to the polydisperse and dynamic nature of this chaperone, which has prevented its crystallisation and hence determination of its atomic structure. In an attempt to improve our understanding of this relationship, we have recently conducted Small angle x-ray (SAXS) [1,2] and neutron scattering (SANS) studies [3]. By measured the radius of gyration (R_g) from SAXS experiments, in combination with other biophysical techniques, we have concluded that the target protein α -crystallin is located within the fenestrations on the exterior of the α -crystallin oligomer at temperatures between 20 to 30°C, and that under mild stress, reduced α -lactalbumin (at 37°C) and malate dehydrogenase (at 42°C) are located on the surface of the oligomer. A more direct approach to investigate this binding interaction is to use the combination of SANS, contrast matching and isotopic substitution. We used hydrogenated α -crystallin and the target protein α E-crystallin (hydrogenated and deuterated), on their own and upon formation of a complex under harsh stress conditions at 65°C. By measuring R_g values, we demonstrated that α E-crystallin resides within the central cavity of the α -crystallin oligomer at high temperature.

From our studies, we have shown that SAXS and SANS provide important structural information on these polydisperse systems. Moreover, a combination of SANS, isotopic substitution and contrast matching, without the reliance on other biophysical techniques, enables definitive information to be gained on the location of the target protein when bound to oligomeric α -crystallin.

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Shape reconstruction of biological macromolecules involved in defence against viruses and those that interact with viral proteins

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Small-angle x-ray and neutron scattering, complemented by analytical ultracentrifugation, electron microscopy and x-ray crystallography, was used to investigate the subunit assembly and structural changes that occur within a number of important protein and protein-DNA complexes.

Type I restriction-modification (R-M) systems are comprised of two multi-subunit complexes, the methyltransferase (~160 kDa), responsible for methylation of DNA and the restriction endonuclease (~400 kDa), responsible for DNA cleavage [1-3]. We investigated the “switch” that occurs between the methyltransferase and endonuclease, mediated through the addition of two 120 kDa HsdR subunits [4].

MA(p17) from HIV-1 is a multifunctional protein responsible for regulating various stages of the viral replication cycle. To achieve its diverse function, MA interacts with host cell proteins, including the ubiquitous calcium-sensing calmodulin (CaM) protein, which is up-regulated upon HIV-1 infection [5]. We investigated the conformational changes that occur upon CaM binding to form the CaM-MA complex.

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Up-coming neutron polarisation analysis capabilities for 6 OPAL instruments

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Polarised neutron scattering has long found its applications in the study of magnetic materials. The separation of magnetic scattering and nuclear scattering allows us to pinpoint the detail magnetic structure from atomic scale to nano-magnetic particles and micron-size magnetic domains and to study magnetic excitations. A few examples include canted magnetic moments in NdFeB magnet, the search for short-range and long-range order in spin-glass, multilayer thin-films for spintronics application, magnetic nanoparticles, 'phason' mode in spin-density waves, and low-dimensional magnetism. In addition to magnetism studies, using polarized neutrons to enhance the signal in hydrogen-rich materials in SANS is now becoming wide spread. This latest development comes from the increasing availability of polarization analysis in SANS instruments. At ANSTO, work is underway to provide neutron polarization analysis capability for 6 OPAL neutron scattering instruments. These instruments include the high-intensity diffractometer Wombat, SANS Quokka, reflectometer Platypus, and spectrometers Sika, Taipan, and Pelican. The method of choice is polarized helium-3 neutron spin-filter. This method has the advantage of covering a wide neutron energy bandwidth, large span of scattering angles, large beam cross-section, and is a low background technique. In this presentation, we will provide examples to illustrate what neutron polarization analysis can do on the 6 instruments, explain the characteristics of the polarize ³He method, and report on the latest status of the project.

Sample environment projects and operations at the Bragg Institute

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The Bragg Institute received from the Australian Government at the height of the global financial crisis funding for the construction of a set of new instruments, a new neutron guide and new Sample Environment. The project included a 12 T asymmetric vertical magnet, dilution system, gas handling and vapour mixing systems for loading and sorption measurements. These projects are now in the building phase.

A new methane gas rig for *in situ* study of methane-hydrates formation is in an advanced project phase while new equipment to be commissioned by the end of the year includes a six axis robot for automated sample changing into a cryogenic vessel and for texture measurements and a rapid crystal sample cooler for the quasi laue diffractometer. The status of these projects and implication for the operation team in the near future will be discussed.

Recently commissioned equipment include an 11 Tesla horizontal magnet for SANS with ^3He fridge insert, a 1 Tesla electromagnet for reflectometry with cryocoolers, a 300°C 10 position sample changer for SANS and a furnace and environmental chamber for the strain scanner 100kN load frame, a stopped flow mixing cell for SANS and an impedance spectrometer for reflectometry.

The most successful in house SE equipment so far has been the robotic automated sample changer, responsible for over 50% of the published papers on the High Resolution Powder Diffractometer, Echinda.

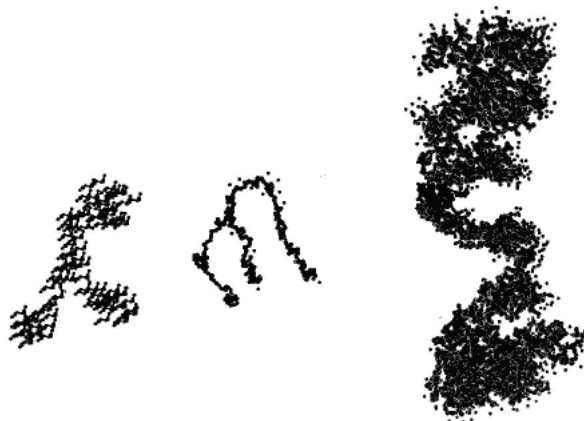
Advancements at the National Deuteration Facility: deuteration of oleic acid, lipids and other molecules for neutron studies

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Deuteration of lipids and other long-chain fatty acids is an essential first step in preparation of samples for many neutron scattering experiments; particularly those associated with Small Angle Scattering or Reflectometry. When studying surfactants or lipids at the air-water interface, a non-deuterated hydrocarbon chain has a Scattering Length Density (SLD) almost identical to that of air and is essentially invisible to neutrons. However, when deuterated, these chains have a large SLD and stand out very clearly from both air and the water subphase. In other studies, where one may wish to observe the interaction between other hydrocarbon-based chemicals or biological molecules with lipids or surfactants, there is often a lack of contrast in the system which can be overcome by deuteration of the tail component of these lipids or fatty acids.

Oleic acid forms an unsaturated tail component in many phospholipid molecules that are fundamental to the structure and functioning of cellular membranes. The recent success of the NDF chemical deuteration team in producing deuterated oleic acid on a gram scale will be discussed. Deuterated precursors, synthesised by NDF, were converted to deuterated oleic acid by a multi-step reaction scheme on a laboratory scale. This will allow the synthesis of many deuterated lipids and surfactants where deuterated oleoyl chains are essential in the backbone of the target molecule, greatly increasing the scope of neutron experiment design given the availability of deuterated oleic acid from NDF/ANSTO on such an unprecedented scale. Biophysical investigations into how cellular membranes function are of vital importance in understanding the mechanisms of neurodegenerative diseases, as well as the action of bacterial toxins on our cells. The synthesis and availability of a variety of functionalised deuterated lipids and other molecules from NDF for surface modification and molecular assembly will also be discussed.



The representative SAXS-derived structures shown are di-tyrosine A β on the left, LDAO A β centre, A β 1-40 fibril right.

The work in this paper is for NDF which is co funded by NCRIS and ANSTO

ANBUG Award for Neutron Science

Powder diffraction data analysis: beyond the Rietveld method

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Dr Maxim Avdeev has been actively working in the field of neutron diffraction for more than 10 years. The versatility of the technique allowed him to contribute in many areas of condensed matter physics and solid state chemistry. The classes of materials he studied using neutron scattering range from superconductors and magnetically ordered systems to piezoelectrics and solid electrolytes.

The experience he gained at major international neutron centres, namely the pulsed research reactor IBR-2 at the Joint Institute for Nuclear Research in Russia and the Intense Pulsed Neutron Source at the Argonne National Laboratory in the USA, allowed him to successfully complete the commissioning of the Echidna high-resolution neutron powder diffractometer at OPAL and then to establish an effective user program for this instrument. The Mail In service he proposed for Echidna has a great success since it drastically increased instrument scientific output and expanded the OPAL user base both in Australia and overseas (USA, Canada, UK, China, Taiwan, Singapore, India).

In addition to his constant effort to improve the instrument reliability and the service provided to the neutron beam user community, Maxim has also been actively engaged in teaching through his participation to AINSE and ANSTO neutron schools and co-supervision of AINSE funded post-graduate students.

Maxim has published over 100 scientific papers with co-authors from more than 60 research organisations in 28 countries. His h-index is 16.

ANBUG Award for Career Achievements in Neutron Science

The Renaissance in Powder Diffraction - An Australian Perspective

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CJH has been strongly involved in the development and application of high resolution neutron powder diffraction over many years. He contributed to the establishment of the first Australian high resolution diffractometer, which recorded its first patterns around 1980, and in the use of this instrument he pursued developments in instrument physics (peak shape analysis), computer programs for data analysis (LHPM/Rietica), methodologies for quantitative phase analysis (QPA), and data analysis using maximum entropy methods.

The applications he undertook include fundamental measurements on rutile and anatase, studies of phase transitions in alkali metal hydroxides, detailed investigations on zirconia engineering ceramics, and extensive studies of phase transitions in perovskites and related materials. His work led in 1995 to the award of the degree of D.Sc. by The University of Melbourne, and has provided material for the book 'Applications of Neutron Powder Diffraction' coauthored with E.H. Kisi and published by Oxford University Press in 2008. CJH was a Leverhulme Visiting Professor, Department of Earth Sciences, University of Cambridge during 2008 and 2009, and is currently Conjoint Professor, School of Engineering, The University of Newcastle.

Short-range order in functional oxides

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The polar nanodomains in lead-based ferroelectrics such as PZN ($\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$), PMN ($\text{PbMn}_{1/3}\text{Nb}_{2/3}\text{O}_3$) and PZT ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) are thought to play a significant role in their physical properties. Using neutron diffraction, the population and nature of these domains has been explored as a function of temperature above and below the ferroelectric phase transition. It is found that the domains in PZN consist of plate-like regions within which the Pb ions are displaced in parallel. This domain structure proves to be largely intact in the paraelectric phase for at least 80K above T_C . The B-site ordering remains unchanged, as might be expected. Further, the displacive behaviour of the O, Nb and Zn atoms can be modelled through an energy term based on bond valence sums and the global instability index.

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Phase transformation of propane-methane clathrate hydrate

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Gas hydrates pose a major risk of disruption to marine pipelines of the oil and gas industry. At the temperatures and pressures in these pipelines gas hydrates can form large solid plugs. The gas mining industry, lacking reliable information on hydrate formation and dissociation processes, currently takes extreme measures to reduce the risk of hydrate formation. A clear understanding of these processes would allow implementation of effective strategies to avoid production losses in gas pipelines [1].

The CSIRO “Wealth from Oceans” flagship, has built a hydrate flow loop chamber (HYTRA) to provide an optical view of hydrate formation in deep sea pipelines. Interpretation of the observations from HYTRA requires complementary methods, such as neutron scattering, to quantify the phases liquid water, ice and gas hydrate components in a multiphase mixture at various pressures and temperatures.

We present achievements to date in our neutron scattering studies of the phase transformations and the phase boundary of methane-propane hydrates. Although we have not yet managed to replicate a flowing gas-liquid mixture, we have performed a range of neutron diffraction and small angle neutron scattering (SANS) experiments close to sub-sea geological conditions.

In situ neutron diffraction experiments of hydrate reaction processes, using the powder diffractometer (Wombat), provide insights into the kinetics of crystallite formation and dissociation from solid and liquid water phases. Furthermore these experiments elucidate the importance of the heat flow of the reaction processes [2]. With *in situ* SANS experiments we aim to probe the hydrate nucleation process. Our first SANS experiments, on Quokka, reveal rapid uptake of methane-propane gas on ices crystallites well below the accepted phase boundary, offering the prospect of valuable insights in planned future experiments using a gas-liquid flow loop.

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Development of defect perovskites for use as cathode materials in lithium ion batteries

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The development of new high capacity cathodes is becoming increasingly important as currently used materials reach their critical energy density limit. Defect perovskite structures such as $\text{Li}_{3x}\text{La}_{0.67-x}\text{TiO}_3$ and $\text{Li}_x\text{La}_{0.33-x}\text{NbO}_3$ are an alternative due to their high ionic conductivity, structural flexibility and high intercalation limits [1-2]. However, in order to further develop the properties of defect perovskites, a thorough understanding of the structural changes, which occur during lithium intercalation and how these affect the electrochemical properties, is essential.

We have previously synthesised the perovskite structures $\text{Sr}_{0.8}\text{Ti}_{0.6}\text{Nb}_{0.4}\text{O}_3$ (STN) and $\text{Li}_{0.18}\text{Sr}_{0.66}\text{Ti}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (LSTN), both composed of lighter components than $\text{Li}_{3x}\text{La}_{0.33-x}\text{NbO}_3$. While STN intercalated only a small amount of lithium via chemical means, LSTN readily intercalated lithium. Neutron studies of LSTN before and after chemical lithium intercalation provided significant insight into the structural behaviour of lithium during the initial intercalation process. Electrochemical studies revealed that STN could intercalate up to 0.2 mol of lithium per formula unit with little structural alteration. Again LSTN was able to intercalate a larger amount of lithium electrochemically via a two phase reaction forming a Li-rich and Li-poor phase.

This contribution will address the structural changes, which occur in LSTN during chemical and electrochemical intercalation and in STN during electrochemical intercalation. The observed structural changes provide significant insight into the origins of many of the observed electrochemical properties such as specific capacity, reversibility and ionic conductivity.

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***In situ* neutron diffraction study of the kinetics of hydrogen absorption and desorption in Mg based materials**

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The potential of metallic magnesium for hydrogen storage is limited by its high absorption/desorption temperature (>300 °C) and sluggish sorption kinetics. These drawbacks can be reduced by using ball milling and doping with suitable catalysts [1,2]. The body centre cubic compound $Ti_{0.4}Mn_{0.22}V_{0.28}Cr_{0.1}$ (called BCC) and carbon nanotubes (CNT) have shown significant catalytic enhancement of the sorption properties of MgH_2 [3]. We have probed the effect of these catalysts on atomic structure and sorption kinetics by *in situ* neutron diffraction using the Wombat diffractometer at the OPAL reactor. Samples of Mg, Mg-10wt%BCC and Mg-10wt%BCC-5wt%CNT were prepared by ball milling. The kinetics of hydrogen absorption and desorption were studied on Wombat, with high pressure cell and high temperature furnace designed specifically for these experiments. Diffraction patterns were collected over one absorption/ desorption cycle of the Mg and Mg-BCC samples (at 250°C) and four absorption/ desorption cycles (at 200, 250, 300 and 350°C) of the Mg-BCC-CNT sample. Although the heavy isotope of hydrogen (deuterium) was used, beam attenuation increased substantially during the absorption part of the cycles (high pressure of 22 bar), so all data had to be corrected for attenuation before the diffraction patterns could be assessed. The reaction kinetics were found to follow the Johnson-Mehl-Avrami (JMA) equations. We compare kinetics of deuterium absorption and desorption in these samples through the JMA order parameter (n) and reaction rate (k) and relate this information to the performance of BCC and CNT as catalysts.

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Using neutrons to study lithium-ion batteries

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Neutron diffraction has distinct advantages in the study of Li-ion batteries, such as high sensitivity towards Li positions and occupancies, and large penetration depth for bulk analysis. This talk will showcase our results from both *in situ* and *ex situ* neutron diffraction studies of crystalline electrode materials in Li-ion batteries. In particular, the developments in the construction of electrochemical cells that resemble their real-life counterparts but are suited to *in situ* neutron diffraction studies. Notable *in situ* neutron diffraction results on commercially available Li-ion batteries, for example, time-dependent structural evolution of electrode materials correlated to the state-of-charge of the battery (Figure 1). Our progress in establishing a facility at the Bragg Institute where electrochemists can bring novel electrodes with good electrochemical properties, and undertake *in situ* or *ex-situ* neutron diffraction experiments to determine structural processes at different stages of the electrochemical cycle.

The culmination of this work is aimed at providing a real-time understanding of critical structural processes occurring at the electrodes, from which further research can be tailored or developed. The results presented are intended to highlight the insight one can achieve by marrying neutron diffraction with electrochemistry.

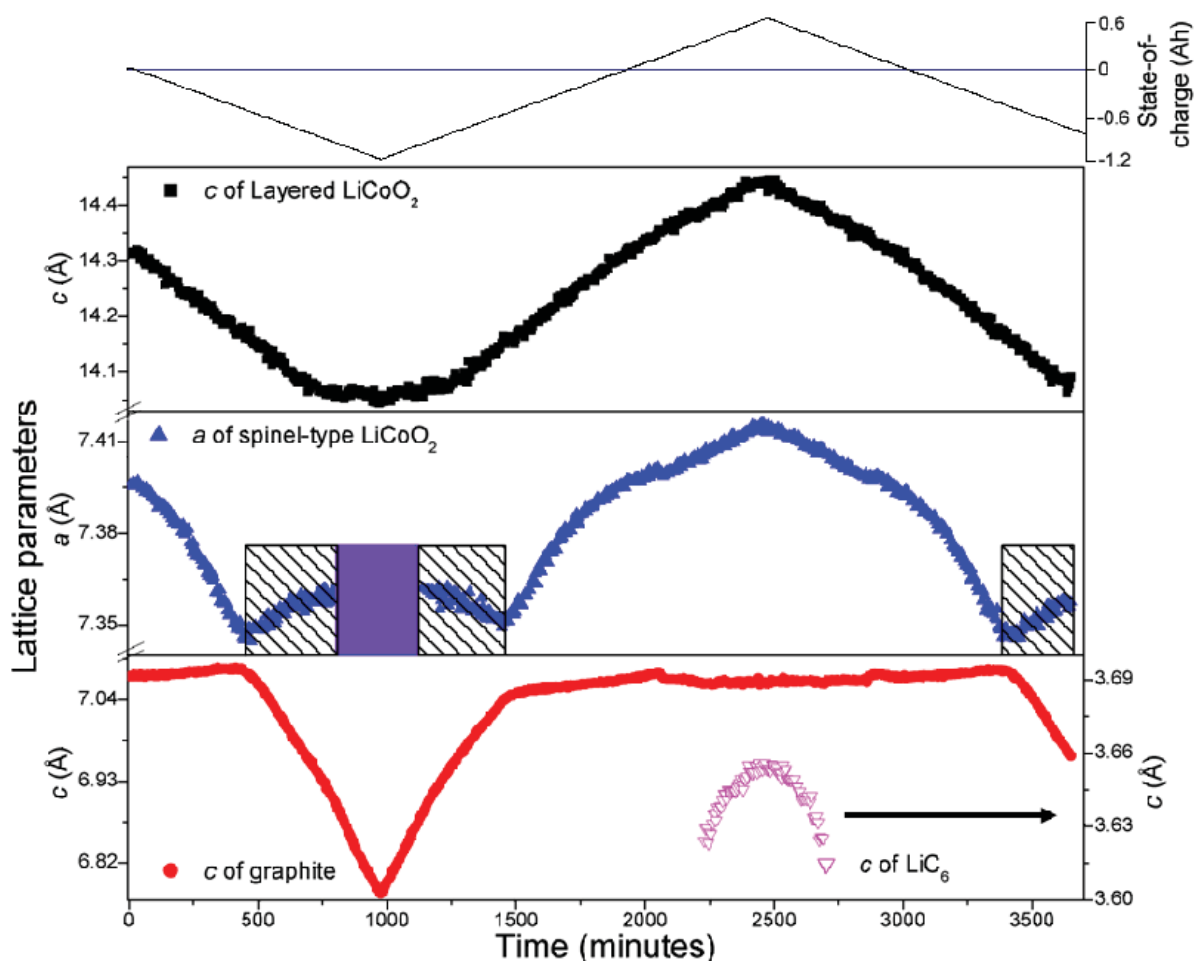


Figure 1. Variation of selected lattice parameters of the crystalline phases in a commercial Li-ion battery directly correlated to the state-of-charge. These parameters are derived from multi-phase sequential Rietveld refinements. The anode is comprised of graphite and LiC_6 , while the cathode is composed of layered and spinel-type phases of LiCoO_2 .

Electric-field-induced strain mechanisms in lead-free 94%(Bi_{1/2}Na_{1/2})TiO₃-6%BaTiO₃

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High resolution neutron diffraction has been used to investigate the structural origin of the large electric-field-induced remanent strain in 94%(Bi_{1/2}Na_{1/2})TiO₃-6%BaTiO₃ ceramics [1]. This material is of particular interest as a potential substitute for environmentally-unfriendly lead zirconate titanate (PZT) in high-strain actuator applications [2]. The virgin material was found to be a mixture of near-cubic phases with slight tetragonal and rhombohedral distortions of a⁰a⁰c⁺ and a⁻a⁻a⁻ Glazer tilt types, respectively [3]. Application of an electric field of 4.57 kV/mm transformed the sample to a predominantly rhombohedral a⁻a⁻a⁻ modification with a significantly higher degree of structural distortion and a pronounced preferred orientation of the c-axis along the field direction. These electric-field-induced structural effects contribute significantly to the macroscopic strain and polarization of this system [4].

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Can neutrons determine elastic constants better than ultrasound?

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For some years now, we and others have been developing methods for extracting the single crystal elastic constants from polycrystalline samples using neutron diffraction and uniaxial stress. The method is simple in principle. Each reflection arises from a subset of crystals having a common vector, the scattering vector. Shifts in the reflection positions give the average strain for this subset of crystals. All that remains is to perform a tensor transformation and average over the available orientations perpendicular to the scattering vector [1]. In reality however, the averaging returns a different result for different assumed micromechanical states in the sample with uniform stress (Reuss) and uniform strain (Voigt) providing two extreme cases. It is also rather sensitive to sample texture in some cases where the applied stress and measured strains are not parallel. We have now overcome the texture issue using either a full texture measurement on the KOWARI diffractometer or by using a one-dimensional pole density (March) function. The problem of the micromechanical state can also be handled by equating the internal elastic strain energy (from our diffraction measured strains) with the external elastic strain energy (from strain gauges) or other computational tricks.

When we apply the method to real materials, we find some remarkable results. First, we can determine details of the elastic moduli that ultrasonic methods struggle with – such as the sign of c_{14} in $\alpha\text{-Al}_2\text{O}_3$ (sapphire) which has been incorrectly reported in the literature for more than 3 decades. Second, we can determine elastic constants for new and emerging materials such as Ti_3SiC_2 and Ti_3AlC_2 [2]. Third, contrary to expectation, we find that a range of ductile AND brittle materials micromechanically lie very close to the uniform stress limit. These themes will be developed further in this presentation.

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Neutron powder diffraction studies of magnetic order in Ru-based high temperature magnetic superconductor

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We present a systematic temperature and magnetic field dependent neutron powder diffraction (NPD) study of Ru-based cuprate superconductor $\text{Ru}_{0.9}\text{YSr}_2\text{Cu}_{2.1}\text{O}_{7.9}$ (Ru1212Y) [1-4]. This compound is known to exhibit coexistence of superconductivity and long-range magnetic order. Our powder sample was prepared by high temperature and high pressure technique [4] at NIMS, Japan. Our NPD measurements were carried out using the high intensity powder diffractometer (Wombat) at the OPAL research reactor. Appearance of magnetic $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, \frac{1}{2}, \frac{3}{2})$, and $(\frac{1}{2}, \frac{1}{2}, \frac{5}{2})$ peaks, below $T_M = 140\text{K}$, confirmed long range antiferromagnetic (AFM) order of the Ru atoms in this system, with propagation vector $\kappa = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, and a magnetic unit cell with doubling of the three crystallographic axes of the atomic unit cell. The ratio of intensities of antiferromagnetic peaks are consistent collinear alignment of Ru moments parallel to the $\langle 1\ 0\ 1 \rangle$ axis. Contrary to the reports of ferromagnetic (FM) order below T_M suggested from magnetization studies, our NPD data showed no change in the intensity of nuclear Bragg peaks below T_M where a FM component would appear. NPD patterns measured in magnetic fields ranging from 0-6 Tesla showed destruction of AFM order with increasing field. When this powder was loosely packed, NPD suggested field-induced FM order, consistent with the response reported by a Ru1212Gd sample [3]. However, when tightly packed our Ru1212Y sample showed no sign of FM order, indicating that grain reorientation dominates the response to magnetic field in loosely packed samples.

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Stresses and more – Materials Science at the neutron diffractometer STRESS-SPEC at FRM II

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Diffraction methods are a powerful tool for analyzing stresses, applied stresses or residual stresses. Both x-ray and neutron diffraction can be used for this purpose. The interest in neutron stress analysis stems from the high penetrating power of neutrons when compared to laboratory x-ray sources, i.e. several cm instead of a few tens of μm . This opens up the possibility to analyze residual stresses in the interior of technical components rather than just at the surface. With the advent of second and third generation synchrotron sources, hard x-rays have become a powerful competitor for stress analysis in bulk solids. One might have thought that due to the high penetrating power of hard x-rays and the very high brilliance of synchrotron sources neutrons would have been driven out of business. However, this has not happened and neutron instruments dedicated to stress analysis have not become short of users. As a consequence, new instruments for neutron stress analysis have been commissioned or are under construction to this very day. The neutron diffractometer STRESS-SPEC located at Germany's new neutron source "Forschungsneutronen-quelle Heinz Maier-Leibnitz" (FRM II) in Garching is such a dedicated instrument for engineering and materials science applications [1, 2]. This contribution will focus on some recent experiments on spatially and time resolved residual strain, texture and phase analysis to highlight the capabilities of a modern neutron diffractometer. In addition an overview on current instrumental and methodical developments (e. g. robot positioning system, through surface strain measurements) will be given.

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An update from the Australian Synchrotron SAXS/WAXS beamline

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The SAXS/WAXS beamline is an advanced and highly flexible facility for small and wide angle scattering x-ray analysis. The beamline has been running since January 2009, conducting a wide variety of measurements across a diverse range of scientific disciplines, particularly in biology and medicine, chemistry and materials science. The beamline has most often been used for in-situ experiments, analysing weakly scattering samples, high throughput analysis and temperature-dependence studies. This talk will outline the beamline's current capabilities illustrated through examples of interesting and advanced experiments that have been carried out, and an update on recent developments in the capabilities and performance of the instrument.

Kookaburra - a state-of-the-art USANS instrument

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An ultra-small-angle neutron scattering (USANS) instrument, named Kookaburra, is to be built at ANSTO's research reactor OPAL. This instrument will extend the range of experimentally measurable length scales currently accessible through the already existing SANS instrument Quokka by two orders of magnitude into the micrometre regime. Therefore, the combined USANS/SANS utilisation at ANSTO will allow the characterisation of microstructure over 4 orders of magnitude in size (1nm to 10 μ m).

Kookaburra is to be installed at the cold-neutron guide CG3, and will use the classical Bonse-Hart method. The instrument will individually operate at two different wavelengths to optimally accommodate weakly and strongly scattering samples at one sample position. This contribution will discuss the layout and conceptual design of Kookaburra, and its expected performance is compared to that of the currently best-in-performance reactor-based USANS instrument BT-5 at NIST.

POSTERS

Opals characterised by neutron scattering

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Australian opal accounts for as much as 90% of total world precious opal production contributing approximately AU\$1 billion per annum to the economy opal is hydrous silica with the general formula $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The ordered arrays of colloidal silica spheres (100 to 350nm in diameter) are responsible for the play of colours through the Bragg diffraction of visible light. Such precious opal is found close to similar opals which have no play of colour. In this preliminary study using USANS it was found that gem quality opal can be distinguished from the adjacent non-gem quality opal.

Australian opal contains between 6 and 10% water which is confined with a high mobility. This water has been linked to the susceptibility of opal to crack. [1] In this study we took three different types of opals and compared the water different water motions. This work extends the study of water confined in; clays, cement pastes, to opals comparing the environments and the water motion by quasi elastic neutron scattering [2-4].

The neutron scattering techniques were well able to characterise the differences between the different types of opals showing the differences both in water movement and the arrangements of the silica spheres.

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Symmetry of ferroelectric phase of SrTi¹⁸O₃ determined by *ab initio* calculations

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Strontium titanate (SrTi¹⁸O₃) is known to display a quantum paraelectric behavior. Its dielectric constant saturates at low temperatures and does not increase with cooling due to quantum fluctuations present in the system. Only in 1999 Itoh *et al* [1] discovered that substituting regular ¹⁶O with the ¹⁸O isotope stabilizes the system and allows a transition into a ferroelectric phase below 23K.

The mechanism of the transition and the structure of the new phase have not been conclusively determined by experiment. The new phase displays ferroelectric properties and there are new peaks present in the Raman spectrum. However, diffraction experiments indicate that the structural distortion accompanying the transition is minimal, while Raman and NMR measurements provide evidence for both the order-disorder mechanism and the displacive mechanism to be an applicable explanation of the transition.

We applied density functional theory calculations and lattice dynamics analysis to show that the paraelectric tetragonal phase of the regular SrTiO₃ is inherently unstable. By distorting the structure along the direction of the soft mode present at the centre of the Brillouin zone we obtained an orthorhombic, ferroelectric structure of SrTiO₃ which is energetically favourable over the paraelectric one. Lattice dynamics calculations show that our new structure is stable and the frequencies of the phonon modes present in it are in good agreement with the experimental values published so far.

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Characterisation of RF plasma polymerised polyterpenol thin films for applications in electronics and as biologically active coatings

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Organic polymers have a variety of current and potential applications in biological interfaces and sensors, in micro-electromechanical systems, and in organic electronics. Non equilibrium plasmas are gaining popularity for the fabrication of polymer thin films as the method allows for deposition of smooth, defect free and uniform films from organic composites that may not necessarily polymerise through conventional thermo chemical pathways. A major constituent of tea tree oil, terpinen-4-ol is known for its biocidal and anti-inflammatory properties. Plasma polymer films of terpinen-4-ol (polyterpenol) possess attractive optical and electrical properties, transparency to the visible range, with prospective applications in organic optoelectronics as gate insulating materials and as encapsulating layers for the organic circuitry. Tunable onset degradation temperature and low post-annealing retention rates indicated polyterpenol is a potential sacrificial material for microelectronics and to produce sealed nano-channels for biomedical testing applications. Moreover, polyterpenol thin film coatings deposited on glass substrates at low power conditions have been shown to retain the antibacterial properties of its precursor against selected human pathogenic bacteria and prevent adhesion and proliferation of the bacterial cells on the film surface.

Since varying the deposition parameters significantly influences the chemical and physical properties of the resultant polymer, understanding the effect the process conditions have on the material properties of polyterpenol is essential for optimisation of the film for a given application. This study investigates the chemical composition and morphology of polyterpenol thin films as a function of deposition conditions, such as time, pressure and input RF power. The polymer thin films are analysed using XPS, FTIR, Raman Spectroscopy, XRR, NR, Spectroscopic Ellipsometry and AFM.

A modern approach to high performance neutron beams at the OPAL Reactor

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We will present an overview of the modern technologies brought to bear on the design of a new cold neutron optical systems at ANSTO (and those rejected). In particular, this presentation will cover the modern materials and geometries available, such as ballistic guides, conic section mirrors, new substrates and coatings, and modern artificial intelligence-based optimization strategies. We will show how these can be applied to maximize the performance – and hence scientific output – of the current and future instrumentation at the Bragg Institute. The total gains in instrument performance are varied, but between 20% and an order of magnitude are achievable compared to traditional methods, depending on the technique.

Single-crystal neutron diffraction and oriented single-crystal raman spectroscopy of zinc and cadmium cyanide

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The high symmetry cubic structures of the simple cyanides of the group 10 elements present archetypal examples of framework coordination polymers, interpenetrating networks [1] and materials with large negative thermal coefficients of expansion (NTE) [2] and for all three reasons have attracted intense interest at different times over the last 30 years. The structural chemistry is readily understood in terms of the cyanide anion acting as a linear linker with strong coordinate bonds between the metal and both the C and N ends of the ligand. Similarly, the NTE is explained in terms of low frequency phonon modes of the cyanide group [3].

The structural chemistry is, however, complicated by potential ordering of the cyanide groups, this leading to two different assignments of the space group based on x-ray crystallography [1] and powder neutron diffraction [2]. Further insights into this question may be gained from MAS NMR spectroscopy [4] and Raman spectroscopy of polycrystalline materials [5]. We report the application of single crystal methods (neutron diffraction and Raman spectroscopy) to the structural characterisation of $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$. For $\text{Zn}(\text{CN})_2$ high quality neutron structures have been obtained using the Quasi-Laue diffractometer, Koala but owing to the high neutron cross-section and gamma emission from Cd it has been possible to monitor several stronger reflections from the surface of the crystal using the high intensity powder diffractometer, Wombat.

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Negative thermal expansion in Prussian blue analogues

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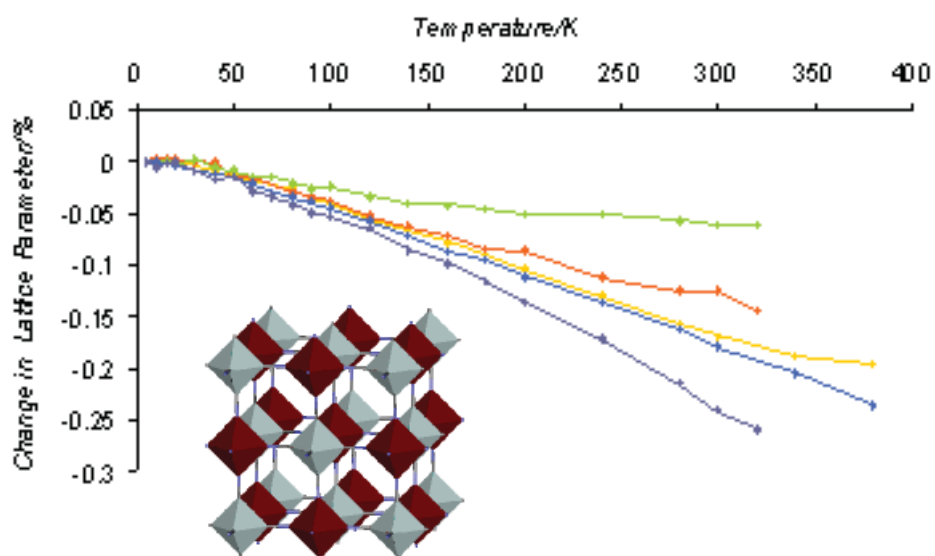
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Materials that show the unusual property of negative thermal expansion (NTE) have potential applications in a variety of areas including the production of high precision instruments. The contrasting thermal expansion properties of NTE materials with “regular”, positive thermal expansion materials allows them to be combined to form composite materials where the thermal expansion is tuned to a specific value or negated entirely. [1]

Here we have been investigating NTE in Prussian blue analogues, a series of cyanide bridged coordination compounds. [2] By systematically altering the composition of these materials we observe changes in the thermal expansion showing the effect of a range of different factors on the NTE. Investigations were carried out using both X-ray and Neutron diffraction techniques, providing complementary information on the properties of these compounds.



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The negative thermal expansion properties of tetracyanidoborate coordination framework materials

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Coordination frameworks are extended crystalline networks composed of repeating units of metal ions coordinated to ligands, and in this work, the ligand is the cyanido ion, CN^- .

This work focuses on the negative thermal expansion behaviour of a family of isostructural tetracyanidoborate compounds of type $\text{M}[\text{B}(\text{CN})_4]$, where $\text{M} = \text{Li}, \text{Na}, \text{Cu(I)} \text{ and } \text{Ag(I)}$. These four compounds are composed of two identical interpenetrated nets of tetrahedral tetracyanidoborate anions bonded in a tetrahedral geometry to metal ions. The Li, Cu(I) and Ag(I) compounds are completely isostructural, while the Na framework has a slightly different orientation of the two interpenetrated nets with respect to each other.

Negative thermal expansion (NTE) describes the tendency of a material to shrink upon heating and has been demonstrated in a number of cyanide-bridged framework materials to date, including the isostructural compounds $\text{Zn}(\text{CN})_2$ and $\text{Cd}(\text{CN})_2$. This work extends the current knowledge of NTE in cyanide-bridged materials by allowing a systematic examination of the effect of changing the metal ion on the resultant NTE. Results to date from synchrotron powder x-ray diffraction, neutron powder diffraction and single crystal x-ray diffraction indicate that two of these compounds undergo amongst the largest isotropic NTE currently published. The magnitude of NTE in these compounds appears strongly correlated with their observed metal-nitrogen bond distances, rather than with the covalent or ionic nature of the interaction between the metal and the cyanido ligand.

This work is supported by an AINSE Postgraduate Research Award

Neutron diffraction study on the modification of multi-walled carbon nanotubes by microwave irradiation for hydrogen storage

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Hydrogen storage behaviour in multi-walled carbon nanotubes (MWNTs) after microwave irradiation has been investigated. Two batches of MWNTs, each with a different range of nanotube diameters (from 20 to 40nm and from 60 to 100nm), were subjected to microwave irradiation for different periods of time. The formation of defects was confirmed by both transmission electron microscopy and Raman analyses, where the defect density increased with increasing irradiation duration. Disordered amorphous carbon layer has been detected on the MWNTs after the microwave irradiation. The hydrogen storage capacity of the MWNTs was examined by thermogravimetric analysis at room temperature. It was found that the hydrogen storage capacity of the irradiated samples was approximately 5 times higher than that of the as-received MWNTs. To study the effect of hydrogenation on the structure of MWNTs, *in situ* neutron diffraction studies of deuterium sorption at room temperature has been carried out. Regardless of the diameters of the MWNT, the lattice expansion associated with the deuterium adsorption in the MWNT samples was larger than that of the un-irradiated MWNTs after deuterium adsorption. This result indicates that microwave irradiation can allow more active sites for hydrogen molecules to be stored in MWNTs. However, there was an optimum duration of microwave irradiation for each batch of MWNTs. Exceeding this duration the amorphous carbon would be too thick, which was detrimental to the hydrogen uptake.

This work is supported by an AINSE Research Award

Probing oxidative stress on cellular membranes

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Oxidative stress on cellular membranes induced by reactive oxygen species is implicated in a number of neurological and cardiovascular diseases. The cell membrane is a complex structure providing a semi-permeable barrier to the external environment allowing communication between the inside and outside. Upon oxidative stress, the membrane is thought to undergo structural modification leading to a change in the physical properties.

Interaction between proteins such as phospholipase A2 (PLA2) and alpha-synuclein (α -syn) with cell membrane is of interest because it is thought they protect the membrane from oxidation in their own way. PLA2 catalyzes the hydrolysis of glycerophospholipids leading to production of free fatty acids. It is believed this enzyme preferentially hydrolyses peroxidized fatty acid esters from the membrane that can then be subsequently detoxified by glutathione peroxidase. Evidence shows oxidative stress in conjugation with methionine sulfoxide reductase can create an α -syn methionine oxidation and reduction cycle which may protect highly unsaturated phospholipids from oxidative damage.

A variety of techniques have been used to probe oxidized model membranes under physiological conditions. Liposomes and tethered membranes made of a combination of synthetic phospholipids and cholesterol have been utilised as models. Techniques such as electrochemical impedance spectroscopy, small angle neutron and x-ray scattering have been used to measure a change in the thickness and density of the bilayer upon oxidation. Other techniques include attenuated total reflection infrared spectroscopy and HPLC.

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X-ray and magnetometry investigation of a potential ferromagnetic semiconductor: HoN

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Very little experimental information is available about the magnetic properties of the rare-earth nitride series, despite theoretical predictions that certain members should behave as ferromagnetic semiconductors with a high remnant magnetization [1, 2]. Such materials are the subject of widespread research as they could function as efficient electron spin polarisers for injection into traditional semiconductors, thereby providing an avenue to hybridise spintronic and semiconductor technology [3]. In this work we investigated the potential ferromagnetic semiconductor, HoN, which recent theory has predicted should be a narrow-gap semiconductor in both its paramagnetic and ferromagnetic state [1]. Past experiment work on bulk rare-earth nitrides has been complicated by the highly reactive rare-earth chemistry [4]. Here we employed a method of depositing thin films capped with a thin yttria-stabilised zirconia (YSZ) cap to protect against oxidation which allowed for prolonged investigation under standard atmospheric conditions. HoN thin films of 35-500nm were deposited on c-plane sapphire substrates using low energy ion-assisted deposition, and capped with a 25nm YSZ cap. X-ray diffraction shows the films have a polycrystalline NaCl structure with a lattice constant that agrees with past work and theoretical predictions for the lanthanide series. X-ray reflectometry was used to determine the nanoscale structure of the film, and suggested the HoN layer grew with relatively low interface roughness on the substrate and a 3nm inter-diffusion layer was formed between the film and cap. Ultra-violet spectroscopy suggests that two distinct band-gap transitions exist in HoN, and we compare these values with values calculated from DFT band structure calculations. Magnetometry measurements showed remnant magnetization and coercivity indicating a ferromagnetic transition with a low Curie temperature of 20K.

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Phonons and spin waves in Ni₂MnGa – inelastic neutron scattering experiments with TAIPAN

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The Heusler alloy Ni₂MnGa is prototype of a novel class of materials, denoted as ferromagnetic shape memory alloys (FSMA), which combine the properties of ferromagnetism with those of a thermoelastic martensitic transformation. In particular, FSMA in their martensitic state allow for mechanical or magnetic-field induced giant strains of 5-10%, ideal for FSMA applications as actuators and sensors.

The **phonon** dispersion in Ni₂MnGa has been extensively studied by inelastic neutron scattering (INS) for the acoustic modes in the austenitic (cubic) phase, where the transverse TA₂ mode in [110] direction shows an inherent lattice stability towards the martensitic transformation. In the martensitic (tetragonal) phase the acoustic modes also show an anomaly in [110] direction [1]. An additional mode, emanating from an incommensurate lattice vector, is interpreted as a phason mode, associated with the charge density wave resulting from Fermi surface nesting [2]. Measurements of **spin waves** by INS were up to now restricted to the initial slope of the dispersion curve in both, the austenitic and martensitic ferromagnetic phase of Ni₂MnGa [3,4].

We have started to extend acoustic **phonon** dispersion measurements to the optical branches, and **spin wave** dispersion measurements to the full Brillouin zone, using the thermal TAS TAIPAN. We report data obtained so far for the austenitic phase of Ni₂MnGa. Measured phonon and spin wave dispersion data are both compared with published *ab initio* calculations of the lattice and spin dynamics for this compound.

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Using SAXS and SANS to characterise the complex formed between the antimicrobial protein hydramacin-1 and fast-tumbling bicelles

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Hydra secretes highly potent, yet selective antimicrobial proteins (AMPs), that allows this organism to shape its microbiota [1]. Amongst the AMPs released is hydramacin-1 (HM-1), a 60 residue protein which shows bactericidal properties against multi-resistant bacteria strains through disruption of target cell membrane functions [2-3]. The structure of HM-1 [3] shows a unique fold within the scorpion toxin-like superfamily. The structure reveals particular partitioning of hydrophobic tryptophan rich surfaces by a belt of positively charged amino acids. This structural arrangement is likely to be responsible for the observed aggregation of bacteria cells and represents HM-1 antibacterial properties.

This presentation describes the use of SAXS and SANS to model the interaction of recombinant HM-1 with fast-tumbling bicelles (with a q range of 0.25 to 0.55; where q = the long-chain/short-chain (detergent DHPC) lipid ratio) composed of different ratios of the long-chain lipids DMPC and DMPG, and to clarify the hypothesised membrane fusogenic mechanism of HM-1 activity.

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***In situ* characterisation of lattice structure evolution during phase transformation of Zr-2.5Nb**

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The α - β phase transformation behaviour of Zr-2.5Nb (wt.%) has been characterized in real time during an *in situ* neutron diffraction experiment. The Zr-2.5Nb material in the current study consists, at room temperature, of α -Zr phase (hcp) and two β phases (bcc), a Nb rich β -Nb phase and retained, Zr rich, β -Zr(Nb) phase. It is suggested that this is related to a dynamic equilibrium of the solubility of Nb atoms in the Zr bcc unit cells. In addition, Vegard's law is applied in calculating the composition of the β -phase and is compared with the phase diagram calculated by thermal expansion experiments.

Keywords

Zr-2.5Nb; phase transformation; neutron scattering; Vegard's law; phase diagram

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Neutron scattering of ATP dependent Chl1 and Chl2 magnesium chelatase subunit complexes

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Magnesium chelatase catalyses the insertion of Mg(II) into protoporphyrin IX to make magnesium protoporphyrin and the enzyme consists of three separate protein subunits called ChlI, ChlD and ChlH. This seemingly simple reaction is potentially one of the most interesting and crucial steps in the chlorophyll biosynthetic pathway, owing to its position at the branch-point between heme and chlorophyll biosynthesis. The ChlI and ChlD proteins form a double hexameric ring complex based on the recently determined structure of the homologous bacterial magnesium chelatase complex determined by cryo-electron microscopy. The ChlI subunit is also able to form a single ATP dependent hexameric ring complex in the absence of ChlD. The plant and algal system is complicated by having two homologous ChlI subunits which are differentially expressed in a 1:2 ratio. In this study we used neutron scattering with contrast matching to determine the assembly order and stoichiometry of the mixed Chl1-Chl2 complex from *Chlamydomonas reinhardtii*. The key questions we wanted answered were: Is the order of subunits around the hexameric ring random or ordered. If it appeared ordered what was the stoichiometry and order of the subunits around the ring.

Neutron scattering data and x-ray scattering data sets have been acquired and we are currently fitting the data to various models.

Neutron reflectometry and dual polarisation interferometry studies of the antimicrobial peptide maculatin 1.1 in supported lipid bilayers

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Maculatin 1.1 is a member of a small group of α -helical antimicrobial peptides isolated from the skin secretions of Australian amphibians. Previous studies using solid-state NMR, surface plasmon resonance, quartz crystal microbalance, calorimetry and fluorescence measurements have revealed that this peptide acts via different mechanisms dependent on concentration and membrane charge, which lead to the disruption of bacterial membranes.

Neutron reflectometry and Dual Polarisation Interferometry (DPI) have been used to study the interaction of maculatin 1.1 in supported lipid bilayers that mimic the essential charge characteristics of eukaryotic and prokaryotic membranes. DPI studies have revealed differences in the interaction with supported lipid bilayers. Maculatin was observed to bind irreversibly to neutral (eukaryotic) bilayers, with moderate disruption of bilayer order. In an anionic (prokaryotic) system, maculatin appeared to bind reversibly and induced a significant initial bilayer disruption that recovered with time. In neutron reflectometry studies using acyl chain deuterated bilayers, maculatin reduced the neutron scattering contrast between the bilayer surface and interior for the neutral (eukaryotic) membrane, with little effect on anionic (prokaryotic) bilayers.

Together these two complementary techniques, in conjunction with previous studies, offer new insights into the mode of action of this antimicrobial peptide. Analysis of DPI and neutron reflectometry data is ongoing, with additional results to be presented.

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Using bond valence sums to model short-range order

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Modeling short-range order in oxides is a valuable way of learning more about how they function. However, it relies on modeling the interactions between atoms and molecules. It has been shown that the global instability index, derived from the bond valence sum approach to evaluating the stability of crystal structures, can act as a useful approximation to the detailed density functional theory-derived energy calculations. The advantage is that the bond valence sum is quick to calculate compared to the DFT energy, essential when the model crystal used is of the order of 32 unit cells on a side. This presentation will discuss the use of bond valence sums and the global instability index in the Monte Carlo modelling of short-range order in oxides, and compare the resulting calculated neutron diffuse scattering with data collected using the Wombat instrument at ANSTO.

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Controlling interfacial properties of thin films using rationally designed biosurfactants

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Bio-produced peptides show great potential for replacing petroleum-based compounds in foaming applications. We recently reported such a class of rationally designed peptides (~2 kDa), which have the ability to reversibly and precisely control the stability of foams [1-2], and used neutron reflectometry to investigate the correlation between interfacial structure, mechanical properties and foamability [2, 3].

The current challenge hindering application of these biosurfactant peptides is that the cost of production is much higher compared to traditional surfactants. A different, but related approach, is the use of biosurfactant proteins. Due to their size however, proteins have a much higher degree of complexity compared to peptides, and therefore will have different interfacial characteristics. In this work, we studied a designed biosurfactant protein in order to begin to understand this. Neutron data was gathered using the Platypus reflectometer and coupled with interfacial mechanical measurements, and demonstrated that strong interfacial elasticity can be either due to accumulation of large protein aggregates at the interface under some conditions, or simply due to large molecular size under others. These results gave insights into interfacial structure which will be invaluable in designing a biosurfactant which overcomes current technological barriers.

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Polymer modified human galectin-2 for enhanced therapeutic application

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PEGylation, chemical modification using poly(ethylene glycol) (PEG), is one of the most used methods to improve the function of pharmaceutical proteins by enhancing their stability and extending circulation life time [1]. Human galectin-2 (hGal-2), a protein showing great potential for therapeutic application, has recently been engineered to enable site-specific PEGylation [2]. The engineered hGal-2 C57M mutant shows enhanced aggregation stability while PEGylation offers further improvement including prolonged in vivo circulation half-life time.

Bioactivities of hGal-2 and its PEGylated form have been studied by isothermal titration calorimetry (ITC) and surface plasmon resonance (SPR), showing that the protein retains its binding ability after PEGylation. Using non-deuterated protein sample, we have studied the conformation of PEGylated hGal-2 by small angle neutron scattering (SANS) [3]. The SANS results reveal that the conformation of PEG within the conjugate sample strongly depends on conjugate concentration, and suggests repulsion forces between PEG molecules plays an important role in improving hGal-2 stability. A deuteration method for hGal-2 has recently been established at the National Deuteration Facility within ANSTO. It is expected that significant insights into the structure of PEG will be obtained by using these deuterated hGal-2 to selectively highlight PEG molecules, thus providing a solid basis to elucidate structural information of PEG-hGal-2 conjugates.

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The magnetic defect in antiferromagnetic gamma manganese copper

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Single crystals of face centred tetragonal manganese-copper alloy containing 10 at. % copper were examined on SPAN at HMI. Of interest was the large diffuse scattering intensity near the 001 position. This is due to the magnetic defect induced by the copper impurity in the antiferromagnetic manganese and the components transverse to the antiferromagnetic direction of this defect are those seen at the 001 position. Uniaxial polarisation analysis along the three Cartesian directions was used to attempt to isolate the magnetic scattering. The polarisation dependence was modelled using chiral components to make up the defect. These in one limit result in a collinear picture and in the other limit are helical. The results of the analysis will be discussed in terms of the likely chirality of the defect.

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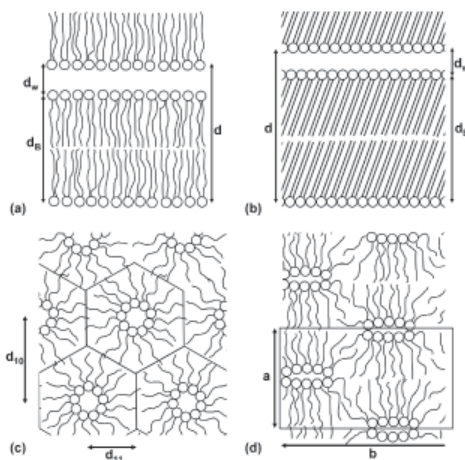
Development of cryo-preservation for high value provenance collections of recalcitrant plant species used in post-mining restoration

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A collaborative project between: RMIT University, Curtin University, University of Queensland, University of WA, the Botanical Gardens and Parks Authority (WA), Alcoa Australia, and Worsely Alumina.

The major goal of this collaboration is to understand the major factors that determine the ability of various recalcitrant plant species to survive cryogenic storage, with particular relevance to post mining restoration of bauxite mining activities in South Western Australia. The area of research RMIT will focus on is on improving our understanding of the biophysics of freezing damage in cell membranes.



When biological tissue is frozen, the formation of ice within the tissue leads to freeze-induced dehydration of unfrozen cells. This freezing damage is a combination of: temperature effects, the direct effects of ice, and the effects of dehydration. Membrane dehydration is severe; membrane bilayers can undergo lethal phase transitions, such as the transition from the stable bilayer phase to a non-bilayer phase, such as the inverse hexagonal phase. The figure shows various membrane bilayer phases (a) fluid phase (b) gel phase (c) inverse hexagonal (d) inverse ribbon.

These phase changes are believed to be one of the main contributors to cell damage in seeds and cryopreserved tissues. As well as structural phase changes, recent research indicates there may also be dehydration induced lateral phase separation of the phospholipids components of the membrane.

In this project, synthetic 'complex model' membranes will be created using phospholipids and used to replicate the behaviour of plant cell membranes. Initially these 'complex models' will consist of dioleoylphosphatidylethanolamine (DOPE) and dioleoylphosphatidylcholine (DOPC) phospholipids, at different ratios, with different hydrations and with varying solute (sucrose) concentrations. Later, more complex systems will be developed, based on information received from collaborators in WA, who are currently analysing the membrane composition of several recalcitrant species.

Using a combination of analytical techniques such as: Differential Scanning Calorimetry (DSC), Small Angle X-ray Scattering (SAXS), and Small Angle Neutron Scattering (SANS), the biophysical properties (ΔH - Enthalpy, T_m - Transition Temperature) and structural information (bilayer 'd' spacing and lipid locality) of cell membranes can be measured.

Using these state of the art analytical techniques we will develop an understanding of behaviour of a complex model system as the bilayers transit through their various phases. By using this information in computer simulations, we can then develop a rational approach to the optimisation of cryogenic protocols.

Low temperature nuclear orientation studies of the magnetic structures of $RNiAl_4$ in applied magnetic fields

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The family of metamagnetic compounds $RNiAl_4$ (R = rare earth) exhibits a range of interesting magnetic behaviours. There are multiple magnetic phases, and crystal field driven differences in anisotropy and behaviour for different rare earth ions (R). $TbNiAl_4$ is an illustrative example. It has two phase transitions (three phases) as a function of temperature in low applied magnetic field, and at least three phases as a function of applied magnetic field at low temperature [1]. Coupled with the first of these field driven transitions is a large inverse magneto-caloric effect (MCE) [2]. Recent neutron diffraction studies on single crystal $TbNiAl_4$, in applied magnetic fields, show the onset of an incommensurate antiferromagnetic ordered phase above the first field induced phase transition [3]. This observation vindicates the existence of the higher entropy state at higher applied field that is required for an inverse MCE but contradicts the predictions of other authors who suggest a spin flop transition [4].

Low Temperature Nuclear Orientation (LTNO) can also be usefully applied to $TbNiAl_4$ and other $RNiAl_4$ compounds to investigate magnetic structure. In the case of the Tb compound, neutron activation is used to create *in situ* ^{160}Tb LTNO probes. Noting that $TbNiAl_4$ crystals must be annealed after thermal neutron irradiation in order to remove damage and restore full gamma-ray anisotropy [5], we have new LTNO results for annealed $TbNiAl_4$. Here we have used applied fields extending to 9 tesla, a magnetic field sufficient to traverse the first metamagnetic transition even at very low temperature. These results support the model of magnetic structure revealed by the earlier neutron diffraction studies.

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Characterisation of engineered surfaces and molecular sensing by neutron and x-ray reflectometry

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Examination of nanoscale thin-films and surfaces in Australia using reflectometry has entered a “golden age” using the Platypus time-of-flight neutron reflectometer and associated x-ray facilities at OPAL. This presentation will concentrate on studies of engineered thin-film nanostructures, as well as processes that take place at surfaces such as molecular sensing and biological interactions. These studies represent a cross-section of results from the first 18 months of operation of the Platypus neutron reflectometer. Systems that will be reported include magnetic thin-films, biomimetic cellular membranes, diblock copolymer thin-films, solar cells, and light emitting surfaces created by organic molecules and fluorescent dendrimers.

Structure of casein micelles under high-pressure

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The casein micelle is a complex consisting of low-structure casein proteins (α -, β - and κ -caseins), existing in a loose and highly hydrated framework which stabilises nanocrystals of insoluble colloidal calcium phosphate (CCP) in solution, and are a major protein constituent of milk. The detailed structure of the ~300 nm and roughly spherical micelles, including the existence of any sub-structure, and the disposition of the CCP within the micelle, are questions that have been incompletely addressed by numerous groups, particularly using small angle neutron and x-ray scattering.

Of further recent interest has been understanding of how the casein micelle structure responds to high pressures, and the reversibility of these changes. Knowledge of how the micelle breaks down under applied pressure may give more information on the internal organisation of the micelle, while there is significant interest the role of the CCP in stabilising the protein structure. This may also serve as an insight to the thermodynamics of protein denaturation and folding extendable to other proteins.

We report on detailed structural work performed using (ultra-)small angle neutron scattering (USANS) in multiple isotopic contrasts, which has allowed us insight into the casein micelle structure over three orders of magnitude in length scales. The casein micelles were then subjected to up to 350 MPa of applied hydrostatic pressure while being continually measured *in situ*, allowing us to gain the first detailed structural information on the nature of the casein micelle break-down, and the extent of reversibility of the observed changes. This information gives insight into the as-yet unresolved issue of whether the casein micelle is made up of smaller “sub-micelle” fragments and provides a basis from which to further investigate the effects of environmental conditions (for example, pH and temperature) on the protein complex’s structural stability.

Diffuse scattering in brownmillerites

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Brownmillerite ($\text{Ca}_2\text{FeAlO}_5$), also known as the ferrite phase (C4AF), plays an important role in the hydration process of cements. The crystal structure of brownmillerite contains perovskite-like layers of corner-sharing octahedra alternately stacked with layers of tetrahedral chains. Iron and aluminium are distributed on the octahedral and the tetrahedral site, although aluminium preferentially occupies the tetrahedral site. The solid solution series $\text{Ca}_2(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_5$ (brownmillerite: $x=0.5$) shows a phase transition from space group Pnma to I2mb at $x=0.28$. The two space groups describe a different ordering pattern of two configurations of the tetrahedral chains: in Pnma the chain configuration changes from one layer to the next, whereas in I2mb only one type of tetrahedral chain is present in the structure. Planes of diffuse scattering have been observed in electron diffraction patterns of sulfate-resisting Portland cement clinkers [1]. In high-temperature single-crystal x-ray diffraction experiments we observed planar diffuse intensities in brownmillerites of the $\text{Ca}_2(\text{Fe}_{1-x}\text{Al}_x)_2\text{O}_5$ series as well as in compounds substituted with manganese. The diffuse scattering and its relation to observed antiphase boundaries [2] and the high-temperature phase transition to an incommensurate structure [2] is investigated by Monte Carlo simulations, x-ray and electron diffraction.

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An extraordinary magnetovolume effect revealed by high-resolution NPD

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Ba₃BiIr₂O₉ is a 6H-type hexagonal perovskite built of BiO₆ octahedra sharing corners with Ir₂O₉ face-sharing octahedral dimers. Ba cations occupy the 12-coordinate perovskite B sites. The compound behaves quite conventionally at high temperatures, with a second-order phase transition at ~750K from the P6₃/mmc parent symmetry to C2/c. [1] Comparison of lattice parameters with the series Ba₃LnIr₂O₉ (Ln = lanthanides) shows that they are closer to the 4+ valent than the 3+ valent lanthanides, suggesting oxidation states of Bi⁴⁺ and Ir⁴⁺.

However, NPD data collected below room temperature reveal highly unusual behaviour. Ba₃BiIr₂O₉ shows a very large (1%) asymmetric volume increase on cooling through at a very sharply defined transition temperature T* = 72K. Rietveld-refinement indicates that the sole statistically significant structural change accompanying this volume increase is a sudden 4% increase in the length of the Ir–Ir bond, which lies along the c axis, at T*. There is no change in space-group symmetry, no evidence of lattice strain due to short-range order and no change in the volume of IrO₆ or BiO₆ octahedra. There is no evidence for long-range magnetic order, although a sharp drop in magnetic susceptibility at T* suggests short-range AFM interactions within Ir₂O₉ dimers. The effect can therefore only be explained by a fundamental change in the nature of the Ir–Ir bond. Here, we will present experimental evidence alongside detailed *ab initio* calculations aimed at determining the origin of this effect.

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High-temperature thermal stability of Ti_2AlN and Ti_4AlN_3 : a comparative diffraction study

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The susceptibility of Ti_2AlN and Ti_4AlN_3 to high-temperature thermal dissociation in a dynamic environment of high-vacuum has been investigated using *in situ* neutron diffraction. Under high vacuum, these ternary nitrides decomposed above 1400°C through the sublimation of Al, and possibly Ti, to form a surface coating of TiN_x ($0.5 \leq x \leq 0.75$). The kinetics of isothermal phase decomposition were modelled using the Avrami equation and the Avrami exponents (n) of isothermal decomposition of Ti_2AlN and Ti_4AlN_3 were determined to be 0.62 and 0.18 respectively. The apparent activation energies for decomposition in these MAX phases were also determined. The characteristics of thermal stability and phase transitions in Ti_2AlN and Ti_4AlN_3 are compared in terms of the rate of decomposition, phase relations and microstructures.

***In situ* observation of pearl chain formations of dielectric particles under an electric field by small-angle neutron scattering**

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The objective of this study is to develop an *in situ* method, using small angle neutron scattering, for observing pearl chain formations of dielectric titanium dioxide fine particles under an electric field. The anisotropy in the distribution of dielectric particles suspended in a liquid medium of low dielectric constant (e.g. silicone oil) is assumed to be significantly different under the different electric field strengths (up to 5×10^6 V/m). The energy balance between the dielectric polarization energy and the thermal fluctuation energy, following the Boltzmann distribution, is important for determining the anisotropy in the distribution of titanium dioxide particles in suspension. It can change at different electric field strengths and solid concentrations. The intended experiments in this study focused on the effect of electric field strength/ solid concentrations on anisotropy in distribution of dielectric particles at different electric field strengths (0, 0.5×10^6 and 1×10^6 V/m) and different solid concentrations (0.2 and 2 vol.%). There was a weak scattering anisotropy around the beam stop in the horizontal direction, which refers to the parallel direction to the electric field. It was electric field and concentration dependent. Anisotropy was found at high electric field and high solid concentration (at 1×10^6 V/m at 2 vol.%) while almost no anisotropy was observed at low electric field and low solid concentration.

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Elucidating alumina micro- and nanostructure by neutron and x-ray techniques

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Gibbsite calcination, the last step in the Bayer process used to produce Metallurgical Grade Alumina (MGA), is a thermally driven dehydroxylation reaction which is accompanied by a structural rearrangement of the crystal lattice. More radical design, and scaling of calciner technology, is dramatically improving energy efficiency, but also significantly increases the structural complexity of the product alumina. Due to the wide range of particle sizes, rapid heating rates, short residence times and other inhomogenities in the modern calcination process a diversity and mixture of aluminium oxide products are formed, and deviations from the average transition alumina structures are also observed. This is caused by local disorder which, using traditional diffraction methods, results in significant peak broadening which combined with the overlapping peaks for the transition aluminas complicates structural analysis. Techniques which can overcome these problems, such as solid-state NMR, x-ray absorption spectroscopy or Atomic Pair Distribution Function (PDF) on synchrotron or neutron diffraction data, can provide much needed new information on the structural relationships within these materials.

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Using neutrons to improve energy materials for transportation applications

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Creating an energy-system for transportation applications that is both environmentally and economically sustainable is one of the greatest challenges facing the scientific and engineering communities. One candidate for the energy carrier is hydrogen, which has a high energy to mass ratio, and is well suited to fuel-cell applications. The commercial viability of such systems is demonstrated by the increasing examples of prototype commercial vehicles, including the fuel cell bus trial in Perth, and companies such as General Motors, Honda, and BMW announcing they will supply hydrogen vehicles from 2010 for government authorities, specifically for regions with hydrogen refuelling facilities. [1] A second method of storing energy in on-board systems is through the use of batteries, such as in plug-in hybrid electric vehicles. The US Obama administration announced in August 2009 a budget of \$2.4 billion dollars specifically for electric vehicles, to help the U.S. reach the goal of 1 million plug-in electrics on the road by 2015 [2]. Batteries are already in use in many hybrid-electric vehicles, although future transportation may combine different energy storage methods such as hydrogen-powered fuel cell electric vehicles, which were strongly supported by the previous US Bush administration. Neutron scattering is essential for the study of sustainable energy materials, including the areas of energy carriers, such as lithium in battery materials and is almost ideally suited to studying hydrogen in materials. Recent research discoveries in the areas of hydrogen and battery research for transportation applications made through neutron scattering will be presented.

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Studying heavy and transition metal ion binding behaviour of silk using radioisotopes

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This study examined the binding behaviour of selected heavy and transition metal ions (Co^{2+} , Cu^{2+} and Cd^{2+}) by silk fibres and powders using a highly sensitive radiotracer technique. Different silk degumming regimes were used, by changing the temperature, time and alkali concentration and studied their influence in binding. Ultrafine silk particles ($d(.5)=700\text{nm}$) were fabricated from degummed silk fibres using a combination of wet attritor milling, spray drying and air jet milling systems [1]. The results showed that binding was pH dependent and reversible. Rate of binding as well as the amount of metal bound was substantially higher for non-mulberry silk Eri and Muga compared to mulberry silk. Binding increased substantially with the increase in alkali hydrolysis during degumming. Silk particles absorbed metal ions faster than fibres. Copper (II) binding was the fastest; nearly 100% of the Cu^{2+} was bound at pH 8 within 5 minutes in some silk materials. Re-exposure studies showed that 45-100% of absorbed ions were released rapidly at pH 3 in 30 minutes. Comparison of the loading capacity of the sorbents with commercial resins under the same condition showed that the former absorbed metal ions more efficiently. Earlier study showed potential use of mulberry silk fibres for separating actinide ions such as U^{4+} and Th^{4+} . Results from the present study suggest that more efficient silk sorbents, Eri and Muga powders can be further investigated to study binding efficiency of actinide ions and other economically and environmentally relevant materials.

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Chaperone interaction of α B-crystallin with target proteins

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The molecular chaperone, α B-crystallin, has the ability to prevent amorphous and fibrillar aggregation of proteins implicated in human diseases, for example β - and γ -crystallins in cataract, amyloid A β peptide of Alzheimer's disease and α -synuclein of Parkinson's disease. Co-localization of α B-crystallin with the fibril-forming protein, α -synuclein, in Lewy bodies and evidence for their interaction *in vitro* suggest an involvement of α B-crystallin in the response to cellular stress and in amyloidogenesis.

The National Deuteration Facility offers biological and chemical deuteration of molecules for the neutron beam and NMR user communities. Deuterated α B-crystallin was produced with 73% deuterium incorporation level. Its structural and functional characteristics were consistent with those of hydrogenated α B-crystallin.

We studied interactions of α B-crystallin with α -synuclein by SANS on NG7 beamline at NCNR. Each component was measured at three contrast points (40%, 70% and 99% D₂O). The data showed a good approximation of matching points, i.e. hydrogenated α -synuclein at 40% and deuterated α B-crystallin at 99% D₂O. No structural changes were seen in either protein over 4 hr at 37°C. Consistent with previous models (SAXS, cryo-EM), α B-crystallin molecule formed a globular oligomer. *Ab initio* shape models of α -synuclein were consistent with previous data (Rekas *et al.* Eur Biophys J, 2010, 39:1407), showing elongated shapes.

Data of the complex in 40% D₂O allows to see only α B-crystallin structure. It indicated a progressive increase in dimensions with time. Data collected at 70% D₂O (both components visible) showed the same trend. However, no changes were observed in data collected at 99% D₂O (only α -synuclein) over time, though the species were larger than those in the absence of α B-crystallin. This might indicate formation of a complex in which α -synuclein molecules intercalate and displace α B-crystallin subunits.

Chemical order in FePt₃ thin films: a new approach to create ferro/antiferromagnetic interfaces

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In this paper we report on a new approach of creating a magnetically modulated structure, without changing materials composition, stoichiometry or lattice structure, namely by artificially controlling the degree of chemical order in the thin film material. This new approach offers the intriguing possibility to study exchange coupled systems of virtual single crystalline quality, avoiding structural changes and interface roughness.

The material, FePt₃, has the extraordinary property of ferromagnetic (FM) and antiferromagnetic phases coexisting at the same temperature, only determined by the degree of chemical order [1]. By alternating the substrate temperature during growth, epitaxial FePt₃ superlattices are formed, comprising an artificially modulated FM/AFM layering sequence. A direct effect of such an exotic FM/AFM interface is the observation of a high exchange bias upon field cooling through the Néel temperature. In order to follow the evolution of exchange bias within these self-biased structures, epitaxial thin films without superlattice modulations have been grown at different degrees of chemical order. A comprehensive analysis reveals the interconnection of frustration and exchange bias between AFM and FM domains of the same material. Due to the mono-stoichiometric homogeneous nature of the film, a unique combination of neutron and x-ray techniques has to be used in order to analyse the magnetic structure. High angle neutron scattering using the triple axis spectrometer TAIPAN at the Bragg institute reveals the antiferromagnetic order on an atomic scale, while depth-resolved magnetic characterization is carried out using the polarized neutron reflectometry technique.

Our findings on the multilayer structures have recently been accepted for publication in Physical Review B.

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Multilayer Films for OLEDs Studied by Neutron Reflectometry

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The performance of organic semiconductor devices such as organic light emitting diodes (OLED) and photovoltaic cells depends not only on the materials used but also critically on the morphology of the active layers and the interfaces between them. Deposition by thermal evaporation is thought to give well-defined multilayer films with sharp interfaces between the layers. However, it is difficult to probe the physical structure of the film in a non-destructive way. Neutron reflectometry (NR) is an excellent method for investigating the internal structure of thin (typically <100nm) films perpendicular to the substrate.

NR was used to study the out-of-plane structure of thin films formed from evaporated small molecules that are used in OLEDs [1]. A multilayer film of components representative of those found in functional devices (hole transport layer/light emitting layer/electron transport layer) showed that after annealing at a modest temperature the electron transport layer migrated through the light emitting layer, whereas the hole transport/light emitting interface remained unchanged. This significant change in structure did not cause an appreciable difference in the photoluminescence of the stack. These results demonstrate that neutron reflectometry is an effective method to study the delicate interplay between the chemical composition and morphology of OLED films and the effect of thermal annealing on their performance.

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Crystal structural investigation of jarosite solid solutions

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Jarosites belong to the alunite supergroup of minerals. The recent discovery of this mineral group on Mars implies that liquid water exists, or has existed on the Martian surface.[1] The alunite supergroup has the general formula $AB_3(XO_4)_2(OH)_6$ (B = Fe for jarosites) with extensive solid solutions possible in all crystallographic sites. The members of the supergroup are largely isostructural with space group $R\bar{3}m$, $Z = 3$ and similar a and c axis lengths. Plumbojarosite is a notable exception as its c axis is approximately double that of other jarosites and alunites.[2] Conversely, a handful of studies have found that plumbojarosite can be prepared without the doubled c axis.[3] The c axis doubling or lack thereof for plumbojarosite requires further investigation. In addition, the solid solutions of plumbojarosite remain largely unexplored and therefore interesting to see whether there is an amount of lead required to give the doubled c axis. Thus, the crystal structures of plumbojarosites, other jarosites and their solid solutions will be studied by x-ray diffraction, vibrational spectroscopy and neutron diffraction. Neutron diffraction studies of jarosite solid solutions will be used to determine crystal structure and the positions of all atoms. Single crystal vibrational spectroscopy has been shown to be very useful for the study of minerals and the site occupancy of crystallographic sites can be ascertained.[4] However, to date no single crystal vibrational spectroscopic study has been conducted for any member of the alunite supergroup of minerals.

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(b) Martens, W.; Kloprogge, J. T.; Frost, R. L. *The Canadian Mineralogist*, **43**, 1065 (2005)

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An environmental cell for studying molten salt processes *in situ* using energy dispersive x-ray diffraction

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In the titanium industry, a low-cost energy-efficient process is sought to replace the conventional Kroll process. Electrolytic routes have been proposed [1, 2] in which solid titania is reduced to titanium metal at the cathode of a molten salt electrowinning cell operating at ~1000°C. However, an inert alternative to reactive carbon anodes must be found before these processes can be optimised.

The inert anode problem has been in existence since the invention of the Hall-Héroult cell in 1886. To date, it has proven difficult to identify or predict a material which exhibits both adequate corrosion resistance and sustainably high electrical conductivity, based on *ex situ* observations made prior to and following electrolysis. Information obtained in this manner is subject to experimental artefacts brought about by changes that can take place during cell shut-down and the preparation of samples for analysis.

Preliminary investigations by Scarlett *et al.* [3] demonstrated the ability of energy dispersive x-ray diffraction to examine anode materials within laboratory scale cells. In order to extend this *in situ* study to operational molten salt cells, a new furnace and cell arrangement has been developed that is compatible with synchrotron-based energy-dispersive x-ray diffraction. This paper describes the design of both furnace and cell, which are comparable in size with laboratory-scale equipment, along with some of the challenges associated with scaling industrial processes. An overview of the results obtained at a recent experiment on beamline I12-JEEP at the Diamond Light Source is also provided.

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Quasielastic and elastic scattering studies of aligned DMPC multilayers at different hydrations

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Quasielastic neutron scattering (QENS), inelastic neutron scattering (INS) and neutron spin echo spectroscopy (NSE) have been employed to study local as well as collective dynamics of model membranes on a ps-ns time scale. Most of these studies lack a systematic investigation of the behaviour of the model membranes in dependence on their hydration. We started a detailed investigation of hydration effect on model membrane systems. In the presented work, we have used chain deuterated DMPC-d₅₄ to study the dynamics of the lipid head group. The hydration for the samples was adjusted by hydrating them using pure D₂O or a saturated salt solution, resulting then in two different states of hydration. The alignment and mosaicity were checked prior to the measurements for all samples. QENS experiments were performed at the time-of-flight spectrometer TOFTOF at the Munich Research Reactor FRMII. Elastic incoherent neutron scattering (EINS) measurements were performed at the backscattering spectrometers IN13 and IN16 at the ILL. To cover the main phase transition from the gel phase to the liquid phase of DMPC, experiments were performed in a temperature range 5°C to 30°C. For the QENS experiments, elastic incoherent structure factors (EISF) and diffusion constants were extracted, indicating that hydration has a clear influence on the mobility of this system. The integrated intensities from the EINS experiments showed a shift of the main phase transition as a function of hydration coinciding with a mean square displacement ‘temperature transition’.

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Oxygen level dependent lattice dynamics of $\text{Na}_{0.73}\text{CoO}_{2-\delta}$

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The optical and acoustic phonon branches of $\text{Na}_{0.73}\text{CoO}_{2-\delta}$ have been determined using Raman scattering and inelastic neutron scattering, and their correlation with phononic thermal conductivity k_{ph} in terms of oxygen-vacancy concentration δ was investigated. The experimentally observed phonon stiffening of the Raman-active E_{1g} mode suggests that oxygen vacancies may help stabilise texturing of Na ions that gives rise to higher k_{ph} with increasing δ . The generalised phonon density of states characterised using inelastic neutron scattering exhibits subtle stiffening of acoustic and optical phonons with δ , which appears to be responsible for the variations in $k_{\text{ph}}(T)$ profile in the temperature range 323 ~ 923K.

Structural investigation of an expanded urea clathrate material by Laue neutron diffraction

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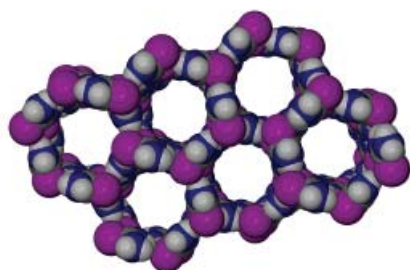
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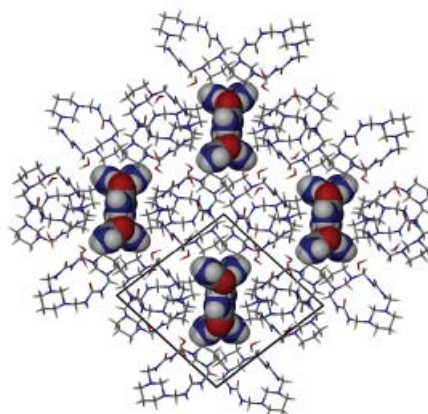
A novel urea-based material has been synthesised and structurally characterized using x-ray diffraction and Laue neutron diffraction.

The compound features bis-urea macrocycles that form a hydrogen-bonded dimer within the expanded urea-clathrate channels. Hydrogen-bonded urea chains propagate perpendicular to the *a*-axis of the triclinic cell. These chains are connected by water molecules to form the expanded clathrate structure (see diagram). The urea molecules are also involved in interactions with the macrocyclic guest species that lie inside the channels.

The structure has been analysed through the use of Hirschfeld surfaces to examine the interplay between the myriad interactions that are present between the nine crystallographically unique molecules. Key to this understanding has been the use of Laue neutron diffraction using KOALA to reveal accurate positions of the hydrogen atoms



Urea Clathrate



Expanded Clathrate

This work is supported by an AINSE Research Fellowship

Magnetic structure and phase transition of TbNi₂Mn

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The structural and magnetic properties of TbNi₂Mn_x with the cubic MgCu₂-type structure have been investigated in detail using field-dependent AC magnetic susceptibility (5-340 K), DC magnetisation (5-340 K; 0-10 T), ⁵⁷Fe Mössbauer spectroscopy (5-300 K) and neutron diffraction methods. Investigation of TbNi₂Mn_x compounds with 0.9 ≤ x ≤ 1.10 indicates that they form with the MgCu₂-type structure within this composition range and that both the lattice constant *a* and the Curie temperature *T_C* exhibit maximal values at Mn composition x=1 corresponding to TbNi₂Mn. The neutron diffraction investigation confirms that space group *Fd-3m* [1] rather than subgroup *F4-3m* [2] describes the crystal structure of TbNi₂Mn.

Detailed analyses of the AC magnetic susceptibility and DC magnetization data confirm that the magnetic phase transition at Curie temperature *T_C*=147K is second order of critical behaviour described by exponents β=0.77±0.12, γ=1.09±0.07 and δ=2.51±0.06. The Mössbauer spectra in the paramagnetic region are fitted using two sub-spectra; this agrees with refinements of x-ray and neutron diffraction patterns which indicate transition metal atoms on both the 8a and 16 sites. By comparison three sub-spectra are required to fit the spectra below *T_C*.

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Advanced modelling and characterisation of ultra-high temperature materials

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In many of today's cutting edge engineering applications, the demand placed on the critical components of a system cannot be met by any single material or alloy. Over the years materials engineers have met these unique challenges with equally unique and complex materials systems, combining the most favourable properties from both metals and/or ceramics.

With Ultra High Temperature (UHT) processes such as nuclear fusion and hypersonic applications, these next generation materials will be subjected to unprecedented heat fluxes and high thermo-mechanical stresses. Therefore these materials will require increased structural strength, thermal creep resistance and high thermal conductivity, as well as low thermal expansion and superior corrosion resistance.

Materials systems currently under research for these UHT applications include metal-metal and metal-ceramic composites, which exhibit highly complex interconnected morphologies. Up until now the prediction of thermal and mechanical properties within these composite systems has been performed via empirical methods.

Recent advances in X-ray and neutron Micro-Computed Tomography (Micro-CT) allows the analysis of these materials at their micro- and meso-structural levels. These reconstructed models, coupled with advanced parallel processing techniques, enables researchers and engineers to conduct thermal modelling as well as Finite-Element Analysis (FEA) to better predict material behaviour at the macro-structural level.

Controlling the structure of polymer brushes using applied voltages

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Polymer brushes are densely grafted layers of polymer molecules tethered at one end to a surface. Repulsive interactions between the chains force them to stretch away from the surface, and these interactions may be carefully tuned to control the degree of stretching. Such a responsive polymer brush layer is an example of a smart surface, where external control of surface properties may be realised.

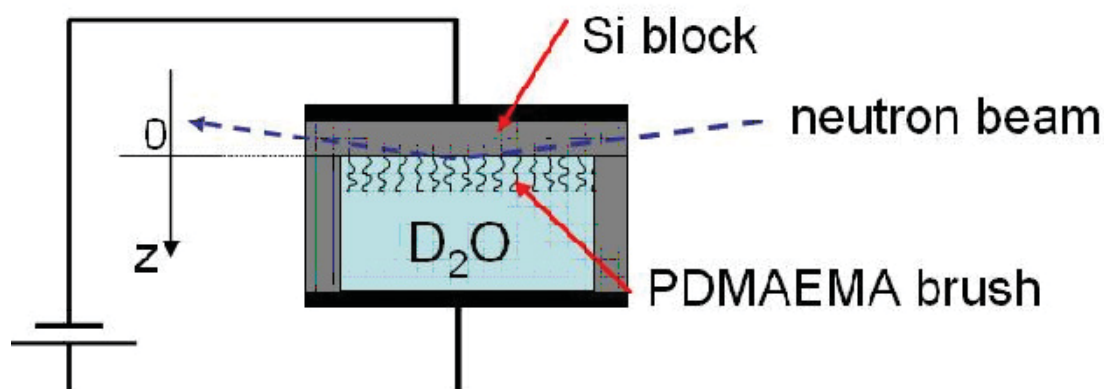


Figure 1. Schematic diagram of a neutron reflectivity experiment to measure the structure of a polymer brush in response to an applied voltage

Ellipsometry and neutron reflectivity (Figure 1) were used to study the effect of electrical stimuli upon charged polymer brushes. The structures of poly(2-(dimethylamino)ethyl methacrylate) (PDMAEMA) weak polybase brushes were measured in response to DC applied voltages in DI water or D₂O, with one electrode connected to the brush-bearing substrate and another parallel electrode a distance away in the surrounding liquid. The brushes were shown to swell or de-swell due to positive or negative voltages respectively, realising remote control of the conformation of the macromolecular layer. This work opens up a number of possibilities for electronically addressed smart surfaces.

Neutron diffuse scattering of $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$ on Wombat

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The aim of this work is to better understand the local (nanoscale) structure of lead-based piezoelectric ceramics with a focus on PZN ($\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$) and identify how this leads to their physical properties, particularly the piezoelectric effect. Diffuse scattering is sensitive to local order in crystals, and so can give information about the polar nano-regions (PNRs) that seem to be crucial in determining the behaviour of PZN ($\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$). Neutron diffuse scattering will be crucial because it is sensitive to the behaviour of the oxygen atoms as the neutron cross-section is relative to the lead unlike with x-rays.

Single crystal diffuse scattering was collected on the Wombat high-intensity powder diffractometer at the OPAL reactor at the Bragg Institute. The difficulty in measuring diffuse scattering come from its relative low intensity compared to the Bragg peaks, some 10³-10⁴ factor smaller. Wombat allows collection of diffuse scattering due to its high intensity and large two-dimensional detector.

Diffuse scattering data from yttria-stabilised cubic zirconia and PZN ($\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$) have been successfully collected, the latter at a range of temperatures. This presentation will outline the data collection and reduction process, and show that diffuse scattering data collected on Wombat is comparable with the best in the world.

This work is supported by an AINSE Research Fellowship (Goossens) and Postgraduate Research Award (Whitfield)

The connection between molecular structure and granular structure of starch

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Starch is the single most important food molecule and is responsible for providing between 50% and 90% of the daily food energy intake globally. Despite being a homopolymer of glucose there is a large amount of complexity that can be found in its different structural regimes. The first level of which is the branch distributions of the starch macromolecules; the second level is the whole starch macromolecules, amylose and amylopectin; the third level is the crystalline-amorphous lamella within the semi-crystalline growth rings; the fourth level is the concentric amorphous and semi-crystalline growth rings. There is limited information available on the connectedness of these different structural levels of starch. This poster will focus upon the influence of the molecular structures of starch and their effect on the granular structures of starch. Specifically an examination of the debranched number distributions of different waxy starches (starches which contain no amylose) will be related to their crystalline-amorphous lamella structure in an attempt to show whether amylopectin's molecular structure does or does not have a marked influence on granular structure.

This work is supported by an AINSE Postgraduate Research Award

Tailored thermal expansion in metal-organic frameworks investigated through neutron and x-ray diffraction

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Metal-organic frameworks (MOFs) are an emerging class of material comprised of metal vertices linked by polyfunctional organic ligands to form extended, crystalline frameworks. MOF chemistry allows a high level of control over a material's physical properties through chemical alteration. Here we present a range of frameworks of similar connectivity [1,2] in which, by systematically altering the linking ligands, we gain a degree of control over the thermal expansion of the material.

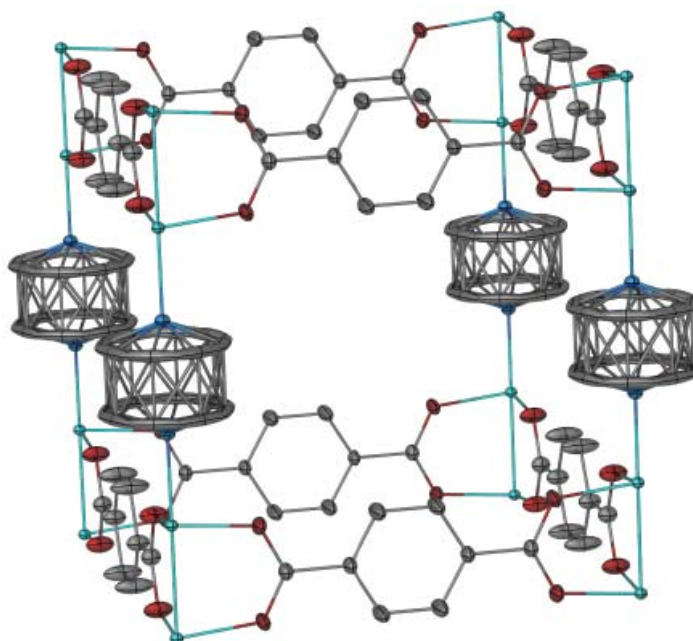


Figure 1. A fragment of the cobalt-paddlewheel framework with 1,4-benzenedicarboxylate (bdc) linkers and (disordered) diazo[2.2.2]bicyclooctane (dabco) pillars.

Figure 1 shows a representative member of the framework series. By altering either the bdc or dabco ligand, we can selectively control thermal expansion. We observe these structural changes through variable temperature neutron and x-ray diffraction.

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Synchrotron micro-diffraction and neutron diffraction analysis of high performance tool steel AISI H13

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The phase transformation, strain changes and carbide precipitation within cryogenically (-196 °C) treated high performance tool steels (AISI H13) before and after tempering have been examined using both laboratory XRD and synchrotron monochromatic micro-diffraction. Tempering resulted in the diffusion of excess carbon out of the martensite phase and consequent unit cell shrinkage. The vanadium-rich cubic M₈C₇ carbide phase was identified in all tempered samples with the concentration being the greatest for the rapidly cooled cryogenically treated sample. On tempering the martensite became more homogeneous as compared to the same samples prior to tempering. For cryogenically treated samples, the effect was most pronounced for the rapidly cooled sample which was the least homogenous sample prior to tempering but was the most homogenous sample after tempering as was also the case for the carbide phase. This suggests that the considerable degree of disorder resulting from rapid cryogenic cooling results in the beneficial release of micro-stresses on tempering thus possibly resulting in the improved wear resistance and durability observed for cryogenically treated tool steels.

Synchrotron micro-diffraction was also used to examine phase, grain and strain evolution within AISI H13 hot work tool steel during quenching. The phases identified, using monochromatic micro-diffraction were used to index Laue diffraction patterns recorded under the same conditions. On quenching from the austenite temperature region, austenite is transformed to martensite. Measurements below the M_s temperature were made at 325, 275, and 25 °C. It has been found that martensite is more strained than its parent austenite due to its carbon supersaturated structure. The martensitic grains (defined by regions of crystallite misorientation < 10°) became smaller and more strained as the temperature that the sample was cooled to from the austenitising temperature of 1000 °C was reduced.

Neutron diffraction analysis, as a potentially complementary method to XRD, was carried out to investigate the microstructural changes of the martensitic phase in AISI H13 tool steel during cryogenic treatment. The martensitic unit cell lattice parameter decreased with decreasing temperature, however this effect is probably due to the thermal shrinkage with the thermal shrinkage coefficient calculated to be 1.65×10^{-6} on the basis of the diffraction data. There was no significant trend observed in the {211} diffraction peak full width half maximum during cryogenic treatment indicating that the tetragonality/strain of the martensite did not change dramatically as the temperature was decreased from room temperature to -190 °C .

Characterising the interaction between a pore-forming antimicrobial protein and membranes

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Antimicrobial proteins (AMPs) are host defence molecules that protect organisms from microbial infection by disrupting membrane integrity [1]. Amoebapore-A is an AMP and its activity is hypothesised to be regulated by a pH-dependent dimerisation event [2]. Based on the solution structure of monomeric amoebapore-A, it is proposed that this dimerisation is a prerequisite for the formation of a hexameric oligomer that forms a pore within the cell membrane [2]. The aim of this project is to characterise the dimerisation and the interactions of amoebapore-A with membrane models.

SAXS measurements were carried out at ANSTO to characterise the relative monomer/dimer populations as a function of pH and protein concentration. Size and shape of the dimer were investigated to gain detailed structural information about the dimer structure. Neutron reflectometry was performed using Platypus at ANSTO to structurally characterise membrane-protein interactions. Changes in membrane properties driven by APA-1 association, structure and dimensions of the protein-membrane complex, and the amount of protein absorbed onto the membrane under different conditions were investigated. This information will be used to assess current proposed mechanisms of amoebapore-A activity.

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Texture measurements on the WOMBAT diffractometer

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Some recent texture measurements on the WOMBAT diffractometer are reported here. The high neutron flux and the position sensitive area detector (with high angular coverage) are ideal for fast texture measurements. We have shown that for typical metals and alloys high quality textures can be obtained within a fraction of an hour. An Eulerian cradle is used to automatically rotate the sample to ~1000 unique orientations and collect diffraction patterns. The data analysis has been streamlined and users have an option of extracting measured pole figures or recalculated pole figures from full Rietveld refinement, using the MAUD [1] software. Examples of these measured textures have been shown. Future plans include adding different sample environments to measure *in situ* texture and automating sample changes to increase the throughput.

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Low temperature neutron diffraction on LiNbO₃

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Ferroelectric material LiNbO₃ has been widely used in many optical devices, such as modulators for fibre-optics communication systems [1] or holographic applications [2-3], due to its good electro-optic, photorefractive and nonlinear optical properties. The LiNbO₃ is a uniaxial crystal belonging to the trigonal system. At ambient temperature it is ferroelectric, and belongs to the rhombohedral space group *R3c* with 10 atoms in the unit cell. Above 1480K LiNbO₃ undergoes a structural phase transition to paraelectric rhombohedral phase (*R3̄c*). Extensive studies have been carried out for temperatures at and above room temperatures. Very few studies were reported at low temperatures. Fernandez-Ruiz *et al* have reported anomalous structure feature of LiNbO₃ at 55K and 100K using neutron diffraction [4]. However, the findings are not very convincing as the experimental error bar is quite big. We recently performed neutron diffraction on both congruent and near stoichiometric LiNbO₃ samples from 4K to 100K. We did not observe clear anomalous structure features within experimental uncertainties.

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The tropoelastin R515 residue in tropoelastin assembly and structure

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Elastic fibres impart elasticity and resilience to tissues such as skin, lungs and blood vessels [1]. The major component of elastic fibres is elastin, which, in turn, is formed from its soluble precursor, tropoelastin. The process of tropoelastin assembly into elastic fibres consists of distinct stages of coacervation, microfibrillar deposition and cross-linking into mature elastin. It has been proposed that tropoelastin may be cleaved at its arginine 515 (R515) residue at some stage during elastin assembly [2]. This R515 site resides within a section of domains crucial for coacervation and cross-linking [3,4]. It is also proximal to a hinge region thought to contribute significantly to the tropoelastin structure [5].

To explore the likelihood of tropoelastin cleavage during elastogenesis and the significance of the R515 site, the functional and structural properties of an R515A tropoelastin mutant were compared with the wild-type and cleaved species. Both the R515A and the cleaved tropoelastin isoforms exhibited decreased propensity for coacervation, abnormal cross-linking, and reduced cell attachment relative to the wild-type species. Initial probing of the R515A tropoelastin structure with antibodies revealed decreased accessibility of the cell-interactive C-termini. Small angle x-ray scattering subsequently indicated a conformational twist in the bridge region leading to possible shifting of central functional domains and obvious spatial displacement of the C-terminal region. This would account for the impaired cell interaction and self-assembly of the R515A mutant reminiscent of the cleaved species. Our findings suggest that R515 contributes significantly to the structure of the tropoelastin bridge region, which, in turn, allows normal self-assembly and cell interaction. Tropoelastin cleavage at this site is unlikely to occur at least until after the cross-linking stage, and some species most likely remain uncleaved for essential elastin-cell interactions.

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A time of flight polarization analysis spectrometer – Pelican

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A new inelastic neutron scattering instrument called Pelican is currently under construction for the OPAL research reactor at ANSTO. The instrument will be situated in the neutron guide hall, on a supermirror guide looking at the OPAL cold neutron source. It combines a variable focus HOPG monochromator and a Fermi chopper system to deliver neutrons with wavelengths in the range of 2.4 Å to 6.3 Å. A linear PSD detector bank will allow simultaneous collection of scattered neutrons over a large solid angle. Both sample and detectors will be accommodated inside a high vacuum chamber. The extra polarization analysis option will add more power to the instrument in separating magnetic scattering from nuclear scattering. The progress update for the construction of the instrument will be presented.

Quantitative texture measurement with fixed wavelength neutron diffractometer

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This research presents a practical and flexible method to quantify the preferred orientation or texture of poly-crystalline material. A fixed wavelength neutron diffractometer (KOWARI) has been used in measuring the Orientation Distribution Function (ODF) of three different materials, VIZ. an industrial extruded α -phase alumina rod, hot-pressed Ti_3SiC_2 and Ti_3AlC_2 blocks. A MATLAB® program has been written and some new techniques have been introduced for extracting the pole-figure (PF) density from the experimental raw data, and for constructing the PF on 5 x 5 hemi-spherical grids. The MATLAB® based texture calculation toolbox - MTEX® [1] was used for the ODF calculation. Texture results for all three materials are presented in a couple of different ways and the directly measured result will be compared with a commonly used one-dimensional pole density distribution – the March function [2]. The March estimation was found to be insufficiently precise to predict the distribution of crystallites needed for the computation of precise elastic properties. This quantitative texture analysis provides a powerful tool to investigate the micromechanical behaviour of poly-crystalline materials.

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Small angle x-ray scattering study of TiO₂ mesoporous structures in highly concentrated surfactant/non-aqueous solvent systems

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TiO₂ mesoporous structures have attracted much attention because of their excellent functional properties for enhancing the efficiency of various technologically important applications, such as solar energy conversion[1], batteries[2] and catalysis[3]. Here, we report the evolution of mesoporous TiO₂ structures by choice of surfactant and non-aqueous solvent, such as ethylene glycol, glycerol, or formamide, in which the titania is synthesised. For the highly concentrated surfactant solutions[4], the final TiO₂ porous structure and surface area were affected by the solvent. SAXS reveals that ordered TiO₂ mesoporous structures have been obtained when using formamide as the solvent. Gas sorption data shows that the surface area of the mesoporous TiO₂ was as high as 198m²/g after calcination at 400°C. The temperature dependant phase changes of the surfactant/TiO₂ systems will be also discussed in this presentation.

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