

Self-Assembly of Mesostructured Materials Using Surfactant Templating

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Surfactant templating is now a commonly used technique which uses the highly uniform structures formed by micelles in solution to impose nanoscale ordering on other materials, usually inorganic oxides. The micelles become encapsulated in the inorganic matrix and form ordered arrays. Removal of the surfactant leaves uniform pores with the same size, shape and connectivity as the original surfactant phase. We have investigated extensively the formation mechanism of surfactant-templated silica and titania thin films using time-resolved small angle neutron scattering (SANS) to probe the solution phase self-assembly and neutron and X-ray reflectivity and grazing incidence diffraction to investigate the surface structures. These studies show a complex relationship between mesostructured particle formation in the subphase solution, and formation of the nanostructured film at the interface. The solution interactions between the polymerising inorganic species and the surfactant micelles are similar to those commonly observed for polyelectrolyte-surfactant solutions.

Our insights into the growth of these inorganic films have allowed us to extend film formation beyond the inorganic systems to polyelectrolyte-surfactant films. These polymer-surfactant films are solid and several hundred nanometers thick and contain highly ordered mesostructures. They form spontaneously at the surface of dilute solutions, covering the entire open interface of the container in which they are grown. It is possible to cross-link the films, which makes them sufficiently robust to remove from the liquid surface where they form and can be dried to produce free-standing membranes. These membranes can be used to encapsulate hydrophobic species within the micellar arrays, raising the possibility of application of these membranes in slow-release applications.

We will describe our work on the formation mechanisms of these films using SANS and neutron reflectivity as well as the use of neutron reflectivity to study encapsulation of molecules within the films.

Equilibrium and Non-equilibrium Behaviour of Mixed Wormlike Micelles

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Most early studies on surfactant systems addressed their equilibrium structure, phase behaviour and dynamics at equilibrium. These remain a prerequisite for further progress, but attention started turning to non-equilibrium phenomena.

Here we plan to present results on wormlike micelles formed by aqueous mixtures of lecithin and bile salt. We will start with SANS data that were obtained under equilibrium conditions. Based on these data we propose a model for the composition and structure, in particular the length, of these mixed wormlike micelles as a function of sample composition. Then the intermediate structures during the growth of the mixed micelles are investigated by time-resolved SANS. The growth of the micelles is induced by a reduction in total surfactant concentration, which is realized by rapid mixing with buffer using a custom-built stopped-flow apparatus. The observed structural changes and kinetics are interpreted in the light of existing models describing the growth of wormlike micelles.

Nanoscale Hybrid Objects: a Useful Combination of Chemistry and SANS

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Nanohybrid objects based on polymer and inorganic nanoparticles are of great interest for different reasons. Indeed, the polymer part can help: first to stabilize and organize the particles, second, to increase the amount of chemical functions available in the organic corona and finally, to improve or to mask the properties of the particles. SANS is a well-suited technique for the study of these objects particularly due to the possibility to use contrast matching to see either the particle or the polymer corona.^{1,2} Here we are interested in the synthesis of both silica and platinum nanoparticles grafted with polymers or biological molecules which may be used as probes for biological detection. The method to introduce the polymer consists in using both the “grafting from” technique and controlled radical polymerisation.³ These systems (mainly in aqueous media) are exempt of free polymers so the characterization via SANS can lead to quantitative data such as the amount of chains in the polymer corona and the chains molecular weight. Contrast matching has been used to see only the polymer chains. Platinum particles have been characterized previously using X-ray diffraction and silica particles are studied in H₂O or in the polymer matching index ($\phi_{D_2O} = 0.18$). In both cases, polymerization kinetics was followed by SANS and the polymer corona spectra show a plateau at small q which attests that the objects are individual and well-dispersed.⁴ We used different models to fit the form factor: corona or star polymer (chains connected together to a very small core) depending on the system. From these models, we can determine both the number of chains, the radius of gyration of the polymer corona and the chains molecular weight. Results obtained from SANS have been compared to other techniques such as NMR or TEM measurements. A good correlation has also been observed with the compression isotherms of Langmuir films obtained directly from the polymer-grafted nanoparticles.⁵ The distance between particles may be adjusted depending on the degree of compression. At high compression values, the surface occupied by the objects remains the same without any collapse of the film, due to the presence of the polymer. Neutron reflectivity will be used to study the structure of the monolayer at the different stages of the compression.

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Quenched Disorder and Low Dimensional Nanoconfinement Effects on the Structure and Molecular Dynamics of an Anisotropic Fluid

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Recent neutron scattering experiments have considerably improved the understanding of fluids confined in mesoporous solids. Much efforts have focused on the structure and phase transitions of molecular nanomaterials and the unusual dynamical properties of nanoconfined simple liquids and glassforming systems.¹ Beyond the case of simple isotropic fluids, liquid-crystals present some additional effects related to the existence of partially ordered phases. In nanoporous media, these effects play a crucial role, due to their extreme sensitiveness to the topological details of the confining matrix. Liquid-crystals in random porous materials have been recognized as a unique class of model systems for studying the effects of quenched disorder on phase transitions.²

We have recently demonstrated the predominance of quenched disorder effects in very low-dimensional conditions of confinement.³ They add to usual surface and finite size effects, together with original couplings between the anisotropy of the confined phases and that of the nanoporous container, up to the macroscopic scale. We have focused on octyl-cyanobiphenyl (8CB) as an archetype mesogenic fluid and have chosen the columnar form of porous silicon as a confining matrix. It presents a parallel arrangement of disconnected channels (diameter 30 nm, length 30 μm). The macroscopic alignment of the pores allows to investigate the coupling between the anisotropic characters of both the porous geometry and the confined phase. In addition, quenched disorder effects are induced by the particularly disordered inner surface of the channels acting as a random anchoring field. A combination of wide and small angles neutron scattering experiments performed in normal and grazing incidences have demonstrated drastic effects on the phase sequence, leading to the growth of a short range ordered smectic phase. Consequences on the molecular dynamics have been investigated over an extended time window by incoherent quasielastic neutron scattering, combining time-of-flight and backscattering experiments. A close correlation between the local dynamics and the unusual phase sequence of the confined liquid crystal has been demonstrated from elastic window measurements.⁴ An analysis of the quasielastic region in terms of rotational and translational diffusion mechanisms shows an extreme slowing down of the latter for 8CB confined in porous silicon.⁵

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Crystallisation of Micelles: A Grazing Incident Neutron Scattering Study

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Block copolymers can self assemble into ordered mesoscopic superstructures, (length scale: 1-1000 nm). Such structured materials are not only fascinating but also of great importance in e. g. high-performance materials while miniaturising technology. Small angle neutron scattering is known since long to provide information on the structural arrangements of polymer systems. For crystalline systems often shear was used to bring the samples into a single domain state and allow long range correlations. Another possibility of introducing anisotropy is to confine the polymer close to a solid substrate. The adequate scattering technique to extract the structural information is then grazing incident or near surface small angle neutron scattering (GISANS or NS-SANS).

In this presentation we will highlight the similarities and differences of normal and NS-SANS, exemplifying the scattering techniques for one particular block polymer. The three block copolymer labeled Pluronic F127 tends to agglomerate into micelles when dissolved in water. For higher concentrations or temperatures the micelles will crystallise into a cubic structure. Solid surfaces with different degrees of hydrophobicity were employed as solid substrates. We find a preferred crystallisation of the micelles close to an attractive interface with respect to the micelle shell, whereas crystallization is suppressed close to a repulsive one. In addition the epitaxial growth of crystallites starts at well separated nuclei at the solid interface resulting in crystallite sizes of several μm . Deeper into the crystalline phase different crystallites start to interpenetrate resulting in a reorientation (texture) of the crystallites. This goes along with a reduction of the correlation length parallel to the interface. Entering the crystalline phase from different liquid phases (high and low temperatures) results in distinct crystalline structures or intermediate phases.

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Validation of Neutron Texture Data on GEM at ISIS using Electron Backscattered Diffraction

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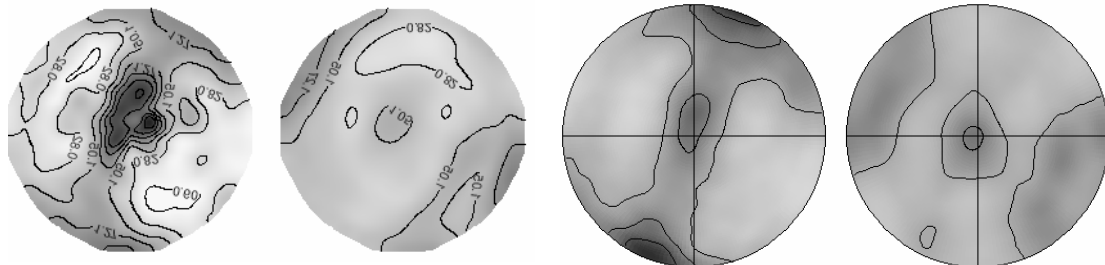
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The high solid angular coverage of the GEM diffractometer at the ISIS pulsed neutron source offers the capability of obtaining quantitative bulk crystallographic texture data in a “single-shot” within a matter of minutes [1]. This enables in-situ texture measurements to be made as a function of temperature to monitor and quantify texture changes during phase transformation or microstructure restoration processes like recrystallisation. For materials scientists data of this type is of up most importance for developing and/or validating models for variant selection during phase transformation and other texture transformation phenomena. The purpose of this paper is to determine the quality of the texture data produced from GEM in order to define a level of confidence for subsequent texture model validation. This has been achieved by comparing textures of sections of a 200mm diameter titanium alloy billet using data obtained from GEM with data obtained using electron backscattered diffraction (EBSD) in a field emission gun scanning electron microscope. In both cases the data were obtained at room temperature. EBSD, unlike time-of-flight neutron diffraction analysis, obtains texture data directly, which for EBSD is via backscattered Kikuchi patterns, so the data obtained perfectly reflects the texture of the material. A typical example of the textures obtained using both methods is shown in the figure below. This comparison, like all made, shows near identical textures both in the general orientation distribution and the level of intensity of the distribution. This clearly proves that the GEM diffractometer is capable of accurately determining bulk textures in a single shot thus confirming its suitability for in-situ high temperature experiments.



Neutron diffraction

EBSD

Water Transport in Concrete using Inelastic Neutron Scattering

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5 billion tons of concrete were made in 2005. While well-made concrete has a long service life giving almost maintenance free structures, many structures are made with inferior concrete and deteriorate. For instance over a billion dollars are spent each year to repair concrete bridge decks in the USA due to damage caused by salt used for de-icing or marine exposure.

Durable concrete limits the ability of fluid to be transported within the structure but poor concrete reacts with the environment as water easily penetrates. There is a considerable debate about how to limit the water penetration. Two types of pores are defined in concrete – capillary pores (diameter $>100 \text{ \AA}$) and gel pores which are smaller. Good quality concrete has discontinuous capillary pores suggesting that in this concrete water transport is controlled by the diffusion of water through the gel pores.

There is an urgent need to understand these processes to better assess the durability. We performed quasi-elastic neutron scattering (QENS) experiments using the spectrometer NEAT at HMI and the backscattering instrument HFBS at NIST on 28 days cured pastes with water/cement ratio between 0.32 and 0.6. The QENS spectra differentiated between: chemically bound, and “glassy” and unbound water molecules [1,2].

When the pastes were dried and water readmitted, the reabsorbed water behaved as the unbound water. This leads to the interesting speculation that it is the transport of water into the gels pores and not through the gel pores that governs the rate of water transport through concrete. If this speculation can be substantiated, we may be able to develop practical tests to forecast the service life of concrete from water transport measurements.

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Neutron Diffraction Study of Strain and Stress induced by Thermo-mechanical Fatigue in Single Crystal Superalloy

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For the Nickel-base single crystal superalloys in turbine blades working under high temperatures, the thermo-mechanical fatigue has been an important factor affecting the performance. Due to the variation in temperature and loading, the plastic deformation and residual stress will be induced into different sections of the blades under working conditions, which will contribute the most to the fatigue. The information on the strain and stress states as well as the structural changes associated with the thermo-mechanical fatigue will help us to better understand the fatigue process.

In present work, we report our recent neutron diffraction study of the three-dimensional strain/stress states of single crystal Nickel-base superalloys after thermo-mechanical fatigue test using the SALSA instrument at the ILL, France. The selected planes of several samples under in-phase cycles of thermal and mechanical fatigue up to failure were measured and compared with a standard sample. The results show that the internal tensile stress and plastic deformation are modified during the cycles and the induced strain and stress generally increase with the number of the cycles. The tetragonal distortion and associated lattice mismatch of the two phases in the alloys are also observed along with the development of the thermo-mechanical fatigue.

Neutron scattering Analysis of Bronze Age Metal Artefacts

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Non-destructive characterisation of archaeological bronze finds of the “Terramare” dwellings, Northern Italy, was carried out by ToF neutron scattering at the spallation neutron source ISIS of the Rutherford Appleton Laboratory, UK. The work provides information on the ancient metal technology during the Bronze Age in that region, with general implications on similar materials throughout Europe.

Six pieces pertaining to three different classes of materials as to use and manufacture, namely; a spear head and a sword blade fragment (weapons), a sickle blade and a knife handle (tools) and two garment pins (ornaments), dating from the Middle to Late Bronze Age, were investigated on the ROTAX and GEM beam lines therefore also providing a comparison between results obtained from the two instruments. Different workmanships were involved in the production of such diverse pieces hence providing evidence for manufacturing signatures. Activation of bronze did not pose serious problems with typical decay times of 2 days for data collection times of 2-3 hrs.

Data collected on ROTAX and GEM provide stable refinements of the phase fractions and lattice parameters by the Rietveld method allowing for the determination of Sn contents in the pieces from the unit cell expansion due to the incorporation of Sn into the Cu-type α -phase. Noticeably, two of the objects exhibit a range of Sn contents as it is evident from broad diffraction peaks (4-8 wt% Sn, 10-14wt% Sn), while the other four artefacts have more defined Sn contents of 8, 9, 10, 14 wt%, respectively. The higher Sn weight fractions are associated with the presence of two bronze phases (α and the eutectoid δ), interestingly coexisting with some pure unalloyed Cu. One sample shows the presence of about 2-3wt% Pb. Varying amounts of oxidation products such as cuprite were identified. A peak broadening parameter derived from the Rietveld analysis provides both a measure of the tin variations and/or of micro-strains indicating cold-working of the ancient metal objects. Correlations between manufacturing procedures and final use of the objects may be envisaged.

Composition and Corrosion Phases of Etruscan Bronzes of Villanovian Age

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This work presents a neutron diffraction study of laminated bronze manufactures performed at the ISIS neutron source. They are part of Etruscan bronze vases discovered in the necropolis of *Osteria-Poggio Mengarelli* and *Cavalupo* in the Vulci area (Viterbo, Italy) of the VIII century B.C. They are considered a distinctive characteristic of aristocracy, which detained military and ritual power. They were found not only in male tombs, thus suggesting that also women played a primary role in such ritual activities. The purpose of these vases was to hold, pour or drink liquids; their presence in the tombs evokes the ritual consumption of fermented and inebriant beverages and the convivial ceremony held by the dominant elites to show and reaffirm their own power through the control and resolution of tensions and internal conflicts. The neutron diffraction study allows to derive information relative to the main composition of the manufactures, the possible presence of alterations and their nature, as well as crusts, and inclusions, structure of the bulk, in a totally non-destructive way. Generally speaking, the determinations of the exact bronze relative Copper/Tin/Lead composition content of the bronzes provide important information on the working process and technologies adopted. The presence of other components is linked to a variety of questions, such as the correct determination of the historical and cultural timeframe as well as, place and method of production of the working processes and technologies adopted., treatment and conditions for restoration and preservation. On the other hand the analysis of corrosion products provides information about the past environments and the physical and chemical events that transformed the object, such as into a partially corroded matrix (burial environment or, exposure to the atmosphere, marine conditions, laboratory environment).

Charge Order and Frustrated Magnetism in an Orbitally-Degenerate Triangular Antiferromagnet

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We explore the effects of frustration on the spin and orbital order in the recently-synthesized layered hexagonal magnet AgNiO_2 where Ni^{3+} ions with spin 1/2 and unquenched orbital moment form an ideal antiferromagnetic triangular lattice. In high-resolution neutron diffraction we observe a structural transition upon cooling to a supercell crystal structure with a periodic arrangement of expanded and contracted NiO_6 octahedra, which we attribute to a triple cell charge order pattern on the Ni sites. This realizes a recently proposed theoretical scenario that in systems with strong charge fluctuations the orbital degeneracy can be lifted by charge order as an alternative to conventional Jahn-Teller distortions. A novel magnetic ground state is observed at base temperatures with the electron-rich Ni sites arranged in alternating ferromagnetic rows on a triangular lattice, surrounded by a honeycombe network of magnetically unordered electron-depleted Ni sites. The role of frustration and easy-axis anisotropy in stabilizing this magnetic order pattern will be discussed.

Single Crystal Neutron Diffraction Study of a Spin 1/2 Square Lattice Antiferromagnet

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The spin 1/2 square lattice antiferromagnet is a system which can be highly frustrated and thus be used to study the effect of quantum fluctuations. α -CuSb₂O₆ is proposed to be a realization of such a system with a square planar Cu²⁺-lattice (S=1/2) in the basal plane. In such a model if the exchange across the diagonal of the square is antiferromagnetic the exchange interactions are frustrated [1]. If there are antiferromagnetic couplings along the edge of the square the frustration is increased and quantum fluctuations are enhanced. In the case of large diagonal exchange the model system is an example of a quantum order by disorder system. In the intermediate regime of more equivalent couplings, a spin-gap phase is predicted which may be a realization of the resonating valence bond state.

In α -CuSb₂O₆ the 180° Cu-O-O-Cu bond across the diagonal of the square implies that the dominant super-exchange is strong, antiferromagnetic and within the ab-plane. The Cu-O-Cu bond angles for nearest-neighbour exchange are close to 90° implying a weaker exchange. In α -CuSb₂O₆ quasi-1D Heisenberg behaviour is reported from susceptibility measurements[2], with a Bonner-Fisher exchange of 49K, which can be associated with the strong exchange across the diagonal of the square Cu²⁺ lattice. An abrupt drop of the magnetic susceptibility at 8.6K has been associated with the development of antiferromagnetic long-range order [2,3]. We present neutron single crystal diffraction measurements on α -CuSb₂O₆. We have reinvestigated the zero field long range order [2,3] with both unpolarized and polarized neutrons. Our measurements have followed the change in magnetic order when applying a magnetic field up to 11.5T giving an insight into the relevant exchange interactions and evidence for a spin gap.

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Pressure Tuning of Magnetic States in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Manganites ($x = 0.25 - 0.85$)

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Perovskite manganites $R_{1-x}A_x\text{MnO}_3$ (R – rare earth, A - alkali earth elements) exhibit rich variety of interesting physical phenomena extensively studied during last years – colossal magnetoresistance, charge and orbital ordering, various types of long range magnetic order, mesoscopic phase separation [1]. The complex interplay of competing interactions forming the rich magnetic and electronic phase diagrams of manganites can be clarified by investigations at high pressure, which provide opportunity to study the modification of the magnetic state and physical properties as a function of controlled variation of structural parameters.

The high pressure effects on the magnetic state and crystal structure of CMR manganites $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.25 - 0.85$) have been studied by means of neutron diffraction over 0-5 GPa pressure and 10 – 300 K temperature ranges. In $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ a suppression of the initial ferromagnetic (FM) state and the onset of the A-type antiferromagnetic (AFM) state was observed at high pressures [2]. In $\text{La}_{0.55}\text{Ca}_{0.45}\text{MnO}_3$ the initial FM state is suppressed by application of high pressure as well and the complex magnetic state involving a coexistence of the A-type and CE-type AFM states develops. In $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ the CE-type charge ordered AFM state is stable in the investigated pressure range [3]. In $\text{La}_{0.33}\text{Ca}_{0.67}\text{MnO}_3$ the complex “Wigner-crystal”-type AFM charge ordered state is suppressed and the appearance of the C-type AFM state is observed at high pressure. In $\text{La}_{0.15}\text{Ca}_{0.85}\text{MnO}_3$ the coexistence of the C-type and G-type AFM states was observed in the whole investigated pressure range. The observed pressure-induced modifications of magnetic states of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ are discussed in terms of the available theoretical phase diagrams.

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A-type Antiferromagnetic Phase and Ferromagnetic Polarons in $^{154}\text{Sm}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ Manganite

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This work is the continuation of our systematic investigation of the $\text{Sm}_{1-x}\text{Sr}_x\text{MnO}_3$ series. Structural investigations (neutron diffraction and electron microscopy), as well as data on resistance, magnetization and second harmonic of magnetization, were performed for $^{154}\text{Sm}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ manganite.

The neutron diffraction studies reveal a structural phase transition at $T_{\text{st}} \approx 135$ K from a high temperature $Pbnm$ space group to a mixture of two $Pbnm$ phases, which are coherently coupled by atomic positions but differ in cell parameters. Above T_{st} , this compound is a paramagnetic insulator. At room temperature, a strained and complex nanostructure state is observed in the high-resolution electron microscopy images. In the $Pbnm$ structure it is generated by the coexistence of twinning domains and weak monoclinic distortions. Below T_{st} , both structural phases begin to exhibit coherent Jahn-Teller distortions, which are different in the two phases. The structural transition is accompanied by the development of a magnetic ordering, so that the ground state is a mixture of ferromagnetism (F) and A-type antiferromagnetism (AF-A). The AF-A order develops in the new low-temperature structural phase II, whereas the F moment is related to high-temperature structure I. The several variants of the magnetic ordering are considered for phase I. A more physically justified scenario is that this phase does not possess an AF-A component and exhibits F ordering with an F moment of $1.9(1) \mu_B/\text{Mn}$ at 1.5 K. In this case, the AF moment of the phase II is found to be $4.1(1) \mu_B/\text{Mn}$ at 1.5 K. As far as we know, it is the first observation of so large Mn magnetic moment, which contradicts the conventional picture where maximal $m_{\text{AF}}=3.5 \mu_B/\text{Mn}$ for the formal Mn^{3+} and Mn^{4+} states. This new unexpected result corresponds to a theoretical prediction based on unrestricted Hartree-Fock calculations. The main peculiarity of this picture is that Mn ions of AF phase are in d^4 state due to electron transfer from an oxygen O^{2-} ion to a neighboring Mn^{4+} ion and the formation of F polarons consisting of two Mn ions separated by an O^- ion. This approach predicts the AF-A ground state, so that our result is obvious evidence in support of such electronic structure.

The transport measurements revealed the polaronic character of the conductivity above 150 K, metallic behavior below 50 K, and colossal magnetoresistance near $T_C \sim T_N \approx T_{\text{st}}$. Metalliclike behavior observed only below 50 K is related to the F phase. The AF-A phase is expected to be insulating. It can exhibit a short range charge ordering that is observed by the electron diffraction at 92 K.

A field hysteresis of the second harmonic of magnetization is found above T_C . These data on the nonlinear response suggest the existence of regions possessing a weak ferromagnetism (WF) in the paramagnetic region which are associated with the AF-A domains exhibiting WF due to Dzyaloshynsky-Moriya coupling. This ordered phase originates below $T_N^* \approx 256$ K as a result of the first-order transition in the structural uniform O' phase (the lattice constants $a > b > c/\sqrt{2}$ in the $Pbnm$ group).

Magnetic Neutron Scattering at Epithermal Energies

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Neutron inelastic scattering with epithermal neutrons of energies $\sim 1 - 2$ eV, has proved extremely useful in the study of anomalous rare earth systems α -Ce and inter-metallic compounds exhibiting α -Ce-like properties such as the ferromagnet CeFe₂ and the superconductor CeRu₂. While it was, or still is, widely believed that the 4f electron in these systems forms an itinerant band, our neutron data reveal that the 4f state remains essentially localized, although it is strongly energy-broadened due, evidently, to the strong hybridization with the other electrons. The magnetic state in these materials is characterized by an energy T_K that varies from ~ 170 meV in α -Ce to $> \sim 500$ meV in CeFe₂ and CeRu₂. Furthermore, in α -Ce we have clearly observed a strong broadening and shift (of ~ 250 meV) in the energy of the spin-orbit excitation, which correlates well with the earlier observations of the progressive increase in the spin-orbit excitation energy and width with increasing characteristic energy T_K in the system CeIn_(3-x)Sn_x, as the Sn content x increases.

Resolving structural issues in Li-ion battery electrode materials with neutron diffraction

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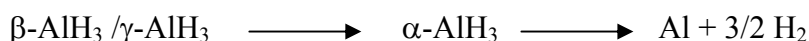
Sustainable energy storage in the form of Li-ion batteries requires new and advanced materials. Li-storage in crystalline electrode materials often invokes significantly structural changes. Knowing these changes is vital for our current understanding, and the design of future materials. Here we show the use of neutron diffraction during our recent material research. Topics include: (1) Li-ion positions in anatase TiO_2 , providing a detailed view of Li-ions in this electrode material. (2) Long range Ni and Mn migration in high voltage spinel $\text{LiNi}_{1/2}\text{Mn}_{3/2}\text{O}_4$. Not observed by X-rays, the extensive migration of Ni and Mn upon lithiation was a remarkable effect that explains the surprising (dis)charge behaviour of these materials at the low-voltage plateau. (3) The effect of nano-sizing on lithiated anatase TiO_2 . Very recently we observed that nano-sizing such an electrode material has large impact on the structure. For instance the solid-solution (single phase) domain appears to be promoted at the cost of the two-phase coexistence, which has important consequences for the performance of these materials as Li-ion battery electrodes.

Hydrogen Storage in Metal Hydrides

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Safe storage and transportation is one of the limiting factors for a wide use of hydrogen as an energy carrier. Storage in solid state is one of the most promising methods for overcoming this obstacle. Hydrogen can be released by applying an external perturbation, e.g. by applying heat. Metal hydrides can exhibit these required properties.

Alane (AlH₃) contains 10 wt% hydrogen and can be synthesized using chemical methods. It releases hydrogen at temperatures close to 100°C and is a promising hydride for hydrogen storage. AlH₃ can exist as several polymorphs; six different forms have been proposed: α , γ , β , α' , δ and ϵ . The crystal structure of α -, β - and γ - and α' - AlH₃ have been determined using powder neutron diffraction data collected at the JEEP II reactor, Kjeller, Norway, and synchrotron X-ray powder diffraction data collected at ESRF, Grenoble, France. Both β - and γ -AlH₃ transform into α -AlH₃, before decomposing into Al and H₂.



Other Al containing hydrides that have potential as hydrogen storage materials are metal alanates. The mixed alanate LiMg(AlH₄)₃ contains 9.7 wt% hydrogen. LiMg(AlH₄)₃ decomposes in a two-step reaction; at 130°C 4.9 wt% hydrogen is released when LiMgAlH₆ and Al is formed, and at 190°C 2.4 wt% hydrogen is released when LiMgAlH₆ decomposes into LiH, MgH₂ and Al. The first step is exothermic, while the second step is endothermic. The structure of LiMg(AlH₄)₃ and LiMgAlH₆ have been determined using powder neutron diffraction data collected at the JEEP II reactor, Kjeller, Norway, and synchrotron X-ray powder diffraction data collected at ESRF, Grenoble, France.



Neutron Radiography and Tomography on Fuel Cells

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Water management is a key issue in the development of low temperature polymer electrolyte membrane fuel cells (PEMFCs). Water is produced by conversion of hydrogen and oxygen to electrical energy and exists mostly in liquid form. On the one hand a certain humidity inside the reaction layers has to be maintained, because only the wet membrane is proton conductive. On the other hand the formation of too much liquid water strongly hinders the gas flow and has to be prevented. Thus investigation of the water distribution is of major interest for development of PEMFCs.

We present novel techniques for contrast enhancement and for visualisation of the water flow dynamics inside PEMFCs. The radiographic images demonstrate that the initial water production starts under the ribs of the flow field. With increasing water accumulation water drops accrue and creep into the channels of the flow field where they agglomerate and move driven by the gas flow to the exit. The PEMFCs were investigated under different operating conditions applying realistic profiles of power consumption.

In order to overcome the limits of 2D-radiography a new method was developed that allows for a tomographic investigation of multiple stack fuel cells, i.e. the water distribution is visualised three dimensionally. This method was applied to large fuel cell stacks (about $14 \times 14 \times 10 \text{ cm}^3$) with up to 5 cells. The water distribution was "frozen" by switching off the gas flows. Water accumulations in the different cells were separately analysed under different operating conditions. Furthermore anode and cathode water distributions were separated and effects like back diffusion or osmotic drag were addressed. The prospects and the limits of this new technique will be discussed.

In situ Study of Compound LaY₂Ni₉ used as Ni-MH Negative Electrode Material

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Intermetallic compounds RM_n (R=rare earths, Y; M=transition metals; n=2 or 5) have attracted increasing interest due to their ability to store reversibly large amount of hydrogen near ambient pressure and room temperature. These remarkable properties allow using them for energy storage applications as negative-electrode in alkaline Ni-MH-type batteries. Despite the good performances already obtained on existing RM₅-type compounds, new materials with improved performances in terms of capacity, cycle life and kinetics are still needed in order to reach the increasing demand of portable energy. The large structural versatility of intermetallic compounds allows to prepare materials resulting of the intergrowth between different RM_n-type families. Thus it is possible to synthesize new compounds obtained from the stacking of RM₅ and R'M₂ layers following the scheme: $RM_5 + 2 R'M_2 \rightarrow RR'_2M_9$.

Recently, we have investigated the structural, thermodynamic and electrochemical properties of the ternary phase LaY₂Ni₉. It adopts a rhombohedral structure derived from the PuNi₃ type ($R\bar{3}m$ space group) that can be described as an intergrowth between LaNi₅ (Häücke phase) and YNi₂ (C15 Laves phase). The electrochemical properties of the alloy have been measured in KOH at ambient temperature and atmospheric pressure. LaY₂Ni₉ exhibits a discharge capacity of 265 mAhg⁻¹ (i.e. 8.3 H/f.u.), corresponding to 66% of the expected one deduced from solid gas capacity (400 mAhg⁻¹).

In the present paper, we will describe the structural and electrochemical properties followed by *in situ* powder neutron diffraction on a LaY₂Ni₉ working electrode. Evolution of the phase abundance and structural parameters will be discussed as a function of the state of (dis-)charge and by comparison with other material electrodes.

IGAn: In-situ Studies of Hydrogen Storage Materials using Neutron Powder Diffraction with Gravimetric Analysis

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Hydrogen storage is one of the key technological barriers in the transition to a hydrogen-based economy. Solid state storage, for instance by metal hydrides, offers the potential for safe and efficient storage. However, no material currently exists that fulfils all the stringent requirements of an ideal solid hydrogen store. Simultaneously combining high storage capacity (>6 wt% hydrogen) with a relatively low release-temperature (<150°C), complete reversibility of the thermal absorption/desorption cycle and finally low toxicity / low cost is a difficult conundrum. All these scientific factors are intimately linked to the crystal structure of the hydrogen store and thus understanding hydrogenation requires a full structural description coupled with a detailed study of the physical-chemical properties of the absorption/desorption process of the system. To achieve this, we have recently developed a system that allows us to perform structural and gravimetric measurements simultaneously on the GEM and HRPD diffractometers at ISIS. The system, named IGAⁿ (Intelligent Gravimetric Analyzer for Neutrons) was constructed by Hiden Isochema Ltd. We report here our initial commissioning measurements on the benchmark system Mg/MgD₂ along with detailed absorption and desorption studies of Li₃N - Li₂ND - LiND₂.