Turning OSIRIS into a World-leading Terahertz Neutron Spectrometer – Outline Proposal

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This proposal seeks to enhance the scientific remit and excellence of the STFC and the ISIS User Community in energy, nanomaterials, and catalysis research via a one-stage, low-risk upgrade of the OSIRIS instrument to equip it with a Beryllium filter. At present, OSIRIS is a high-resolution inelastic neutron spectrometer operating at low energies. These technical capabilities have addressed a diverse range of science including the emergence of below-gap spin excitations in quantum magnets [1], molecular diffusion in nano-confined media [2], and the collective response of metallic melts at high temperatures [3]. Extending OSIRIS' energy range well into the Terahertz domain (1 THz $\sim$ 4 meV), whilst providing an outstanding energy resolution, a high incident neutron flux, and high-resolution diffraction capabilities, will represent a quantum leap in the breadth of scientific and technological challenges amenable to detailed exploration and study at ISIS and the STFC.

Facing the Hydrogen-storage Challenge with a New OSIRIS

The quest for efficient hydrogen-storage materials remains a key scientific challenge with profound implications for long-term global sustainability, as recognised by the UK Research Councils' Science Strategy over the next decade [4]. Neutron spectroscopy at frequencies up to 10 THz is an exquisite probe of the interaction of the hydrogen molecule (H_2) with novel materials. To date, work on the IRIS spectrometer at ISIS has unveiled the consequences of extreme geometric confinement in carbon-based nanostructures [5] as well as identified subtle yet significant quantum-mechanical effects limiting the uptake capacity of metal-doped nanographites [6]. Prerequisites for the success of this work have been: (1) an exceptional spectral resolution in the THz range (e.g., $\sim$0.02 THz at 4 THz), imperative to pin down the underlying symmetry of the H_2-substrate complex, or to discriminate between multiple adsorption sites; (2) synchronous access *in a single measurement* to the quasielastic region (<0.25 THz) over an appropriate momentum-transfer range, in order to follow H_2 mobility as a function of temperature, pressure, or surface coverage; and (3) simultaneous high-resolution neutron diffraction measurements, to track changes in molecular and substrate structure upon H_2 uptake. However, the low incident flux afforded by IRIS' natural-nickel neutron guide makes these spectroscopic measurements not only very challenging, but also restricts quite severely the subset of materials amenable to study. Such is the case of heavily doped metal intercalates like CaC_6 [7]. These compounds can adsorb H_2 dissociatively and reversibly, making them outstanding candidates to explore, within the same material, the transition between reversible molecular physisorption and dissociative chemisorption. Owing to synthetic limitations, a study of the phase diagram of the H_2-CaC_6 composite system would require an order-of-magnitude increase in neutron flux at THz frequencies relative to present capabilities on IRIS. This task is achievable by placing a Be-filter on the higher-flux OSIRIS instrument. Further, OSIRIS would also offer much-improved diffraction capabilities, as well as an extension of the currently accessible spectral frequency range from 5 to 10 THz. All these combined instrumental improvements will also prove critical in the study of more complex hosts, including metal-organic frameworks [8], nanoporous polymers [9], negative-thermal-expansion supramolecular solids [10], and nanostructured metal oxides [11]. In a similar vein, the study of THz motions and stochastic diffusion in chemical hydrides has proven quite elusive to date. The recently discovered $LiNH_2BH_3$ and $NaNH_2BH_3$ are the first two examples of a large family of metal amidoborane compounds able to release H_2 at room temperature with no toxic borazine emission [12]. The role of soft rotational and translational modes involving $-NH_2$ and $-BH_3$ functional groups in the stable crystal, and how these morph into diffusive motions leading to H_2 formation remains unexplored. To this end, it would be necessary not only to zoom into the quasielastic region with a high neutron flux, but also to follow THz spectral features as a function of temperature and H_2 release, both tasks ideally suited for the new OSIRIS spectrometer. In addition to the applicants, a number of leading 5* UK university departments including *Oxford Chemistry* and *Birmingham Materials* are actively engaged in the study of these materials.

Nanomaterials, Chemical Catalysis, and THz Neutron Spectroscopy

Traditionally, neutron spectroscopy has been regarded as a bulk condensed matter probe, with a sensitivity reaching millimolar levels only under very favourable circumstances (e.g., hydrogenous materials). But recent advances in materials science can be exploited to advance beyond this paradigm, as it is now possible to secure sufficient quantities of high-quality (monodisperse) nanomaterials exhibiting exceptionally large surface-to-volume ratios (100's m^2/cm^3). Equally important is that current and future nanomaterials research transcends a purely academic interest. Commercial applications of this booming area of materials science have already become a reality and include, to name a few, wound dressings that exploit the antimicrobial properties of metal nanocrystals, body implants based on nanocrystalline zirconia and silicon carbide, or titanium- and zinc-oxide sunscreens. Neutron spectroscopy is thus confronted with the opportunity (and challenge) of becoming a powerful surface-sensitive technique to investigate dynamical phenomena at the nanoscale. Unlike traditional surface-science approaches neutron scattering also offers the exciting prospects of operating under experimental conditions matching closely those required for practical applications (e.g., constant pressure or chemical potential, solid-liquid and buried interfaces, fluid flow in nanopores, etc).

For example, carbon-supported platinum and platinum nanoalloys are one of the most promising catalysts for low-temperature H_2/O_2 fuel cells. The advantages of platinum over other metals relate to its innate ability to dissociate H_2 as well as its superb resilience to oxidation and poisoning. The interaction of hydrogen with platinum nanoparticles of sizes below 10 nm is crucial to catalytic performance, the dissociation into chemically bound hydrogen atoms being a crucial, yet poorly understood, step in the overall electrochemical cycle. Recent work on OSIRIS has probed the kinetics of H_2 dissociation at quasielastic frequencies [13]. Full access to the THz window will allow a direct measurement of key H_2 bond-breaking mechanisms. Similarly, chemical transformations in host-guest catalytic media such as zeolites are both technologically relevant and a significant challenge to experimental and theoretical techniques owing to the fine balance between weak binding forces and steric constraints hindering localized molecular motions and translational diffusion inside nanopores [14]. Diffusion rates within the zeolite are critical to performance, and a sound understanding of the underlying physical chemistry is crucial to optimize a plethora of industrial processes including fluid catalytic cracking, hydrocarbon separation, or catalytic dewaxing. In spectroscopic terms, this task requires access to the THz range, in order to follow subtle changes in the low-energy vibrational density of states of both host and guest species, and to relate these changes to transport properties and structure, all of them amenable to detailed investigation on an upgraded OSIRIS instrument.
Other science areas which will greatly benefit from an OSIRIS upgrade include:

• ***In Biology,*** lattice modes modulate the geometry of hydrogen bonds to drive proton transfer in enzymatic catalysis and the base-pair opening of DNA strands [15]. Also, the bio-protective effectiveness of sugars hinges on the presence of low-energy vibrational modes at $\sim$1 THz, yet their structural and dynamical origin has remained elusive to date [16].

• ***In Soft-condensed matter,*** the semi-crystalline nature of polymers such as P3HT, PEEK, or PET offers an additional means of tuning interfacial properties such as biocompatibility, wettability, and chemical activity [17]. A high neutron flux will enable the routine investigation of these complex materials, hard to secure in large quantities. Simultaneous access to spectroscopic and diffraction data is also a prerequisite to unravel the microscopic behaviour of polymer chains coexisting in amorphous and crystalline phases.

• ***In Solid-state Ionics,*** the relation between structure and transport properties lies at the heart of the utilization of ionic and protonic conductors in practical applications [18]. The ability to study both of these simultaneously will be a great asset, and high neutron fluxes will be necessary to investigate non-hydrogenous and dilute systems.

• ***In Geophysical and Technological Materials,*** unveiling the origin of thermodynamic anomalies such as negative thermal expansion requires access to the low-energy vibrational density of states over wide regions of the T-P and compositional phase diagrams [19].

• ***In Strongly-correlated Electron Systems*** such as heavy-fermion compounds [20] or the pnictides [21], the position, width, and splitting of low-energy resonances provide much-needed insight into the role of spin fluctuations in high-temperature superconductivity. In addition to an extended frequency range, the upgraded OSIRIS will provide a substantial reduction of instrument background levels, of crucial importance in the study of these materials.

• ***In Nanomagnetism,*** high-resolution neutron spectroscopy provides direct access to the electronic Hamiltonian responsible for unusual properties such as quantum tunnelling of the magnetization. Exchange and anisotropic interactions lead to small energy splittings of order 0.1 THz. High-pressure studies up to 17 kbar have already been performed on IRIS under very favourable circumstances [22]. Extension of this work to lower-spin ground states and more extreme conditions would require a significant increase in flux and lower background levels.

References

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