First and Last Papers from the SRS: From Metal Clusters to White Hot Oxide Liquid Drops

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Being the first storage ring in the world to be exclusively dedicated to X-ray experiments, publishing the first paper from the outset in 1981 was a watershed moment for those involved: "Near-edge X-ray Absorption Spectra for Metallic Cu and Mn"[1]. Conditions were not ideal, with stored beams only intermittent and stations and software scarcely commissioned. Nevertheless, even with the simplest of X-ray Absorption Spectroscopy measurements, international impact of this work came from state-of-the-art analysis, recently developed, of X-ray Absorption Near-edge Spectroscopy or XANES[2].

The new Physics of XANES incorporated the strong multiple scattering of photoelectrons with energies of 60 eV or less. Unlike band structure calculations, these were real space calculations of clusters, without the prerequisite of periodicity and a well-defined reciprocal lattice. It was also the case that the XANES experiments themselves were of the highest resolution to that date, and therefore a good test of the XANES calculations. For the first time we were able to demonstrate the sensitivity of XANES to clusters increasing in size from one to the many shells of atoms represented in the experiments. In particular with different fine structure patterns for different clusters of metals meant that XANES could probe size-dependent effects: for example, nanosize metals in heterogeneous catalysts. Over the ensuing years, the Daresbury Laboratory XAS analysis code EXCURV incorporated multiple with single scattering into the same analysis package[3], with successful applications particularly in the field of the characterisation of catalysts and also geological systems.

Over the next 27 years, with new dedicated storage rings being built world-wide, culminating in the ESRF, SPring-8 and the APS, the SRS gradually became less competitive as a light source, and was eventually, of course, superseded by the Diamond Light Source[4]. However, the evolving disadvantages of increasingly uncompetitive emission and the need to shoehorn insertion devices into what was essentially a dipole machine was, in many ways, overturned by innovations in environment stages, detector systems and computer modelling. These succeeded in keeping the SRS internationally competitive[4]. All of this came about because it was recognised by instrumentalists at Daresbury that SR experiments were seldom photon-limited. Accordingly efforts made to increase the count rate and energy resolution of solid state and also gas proportional detectors paid immediate dividends, leading, for instance, to using X-rays to follow *in situ* polymer synthesis[5] and catalysts in action[6] for the first time. In a parallel development, X-ray detectors were assembled in combination, notably EXAFS with XRD[7] and SAXS with WAXS[5] configurations.

Another important development was the incorporation into SR experiments of atomistic simulation, which was coming of age in the 80's. In the context of X-ray SR experiments computer modelling confirmed experimental findings or *vice versa*. Prime examples included predicting the local structures of different cations in glass first established by EXAFS[8], and using EXAFS to ratify the geometry of rare earth dopant structures previously calculated for crystalline fluorites[9]. With the advent of image plate technology, high pressure powder diffraction studies became viable, with surprising results for the simplest of semiconductors and elemental metals held under modest pressures[4]. Alongside these developments were those of X-ray Magnetic Circular Dichroism, invented in perpendicular geometry at the SRS. Measuring element specific magnetocrystalline anisotropy with applications in materials for spintronics, was a major breakthrough and it was made at the SRS[10].

Achievements in Materials Science, Physics and Chemistry made at the SRS between 1981 and 2008 and their legacy, were compiled into a Commentary which appeared in *Nature Materials*, "Two Million Hours of Science"[4], coinciding with the closure of the SRS.

Also published in 2008 came the last major paper from the SRS[11], " Detection of First Order Liquid-Liquid Phase Transitions in Yttrium Oxide – Aluminium Oxide Melts". The research exploited SAXS/WAXS RAPID detectors, which were combined with high speed video imaging and pyrometry to make the first direct observations of liquid-liquid phase transitions in any supercooled system. Transitions in molten phosphorous had been reported from Spring-8 and ESRF, but these were eventually established to be liquid-fluid transitions occurring above the melting point[12]. In our case the laser-heated liquids were supercooled, comprising levitated liquid drops of Y_2O_3-Al_2O_3. Melting at 2100 K these were incandescent brilliant white, shining through the hutch lead glass safety windows. Liquid-liquid transitions were observed with SAXS/WAXS at supercooled temperatures 300 degrees lower than the melting point. To reach temperatures without crystallisation the supercooled liquids were levitated on a column of argon. Measuring only 2 mm across these ultra high-temperature liquid drops could be measured in transmission, because of the optimum focussing achieved on the Dutch Beamline at the SRS.

Liquid-liquid transitions are predicted to be polyamorphic, involving changes in density and entropy, rather than in chemical composition[12]. This distinction was established from *in situ* SAXS/WAXS measurements, the SAXS intensity reversibly traversing a peak at temperatures where the diffuse scattering in WAXS altered, indicating a switch back and forth in polyhedral ordering. These events coincided with an unexpected periodic rotation in the supercooled droplet observed with the high speed video. The rolling action was accompanied by temperature spikes, from which changes in density and entropy across the transition were obtained, quantifying the thermodynamic parameters of the transition and the gradient of the boundary between the two polyamorphic phases. These experiments, in the final allocation periods of the

SRS, finally solved the mystery of low density droplets surrounded by a high density matrix observed from *ex situ* experiments in the mid 90s when Y_2O_3-Al_2O_3 liquids were rapidly cooled[13]. The aerodynamic laser furnace, originally developed at Aberystwyth for use in SR experiments, has subsequently been further developed, in conjunction with German Aerospace in Cologne, so that thermophysical properties – density, viscosity and surface tension – can be accurately measured in liquid oxides at elevated temperatures[14].

References

1 Greaves, G. N., Durham P. J., Diakun G. and Quinn P. *Nature*, **294**, p139-142 (1981) also News and Views, *Nature* **294**, p111 (1981)
2 Durham, P. J., Pendry, J. B. and Hodges, C. H. *Solid State Commun.* **38** 159-162 (1981).
3 EXCURV98: CCLRC Daresbury Laboratory computer program Binsted N. (1998).
4 Greaves, G. N., Catlow, C .R. A., Derbyshire, G. E., McMahon, M. I., Nelmes, R. J. and van der Laan, G., *Nature Materials* **7**, 827-830 (2008).
5 Bras, W., Derbyshire, G. E., Bogg, D., Cooke, J., Elwell, M. J., Komanschek, B. U., Naylor, S. and Ryan, A. J. *Science* **267**, 996-999 (1995).
6 Thomas, J. M. T. and Greaves, G. N. *Science* **265**, 1675-1676 (1994).
7 Couves, J. W., Thomas, J. M., Waller, D., Jones, R. H., Dent, A. J., Derbyshire, G. E. and Greaves, G. N. *Nature* **354**, 465-468 (1991).
8 Vessal, B., Greaves, G. N., Marten, P. T., Chadwick, A. V., Mole, R. and Houde-Walter, S. *Nature* **356**

, 504-507 (1992).
9 Catlow, C. R. A, Chadwick, A. V., Greaves, G. N. and Moroney, L. M. *Nature* **312**, 601-604 (1984).
10 Dürr, H.A., Guo, G. Y., van der Laan, G., Lee, J., Lauhoff, G. and Bland, G. A. C. *Science* **277**, 213-215 (1997).
11 Greaves G. N., Wilding M. C., Fearn S., Langstaff D., Kargl F, Cox S, Majérus O., Vu Van Q., Benmore C.J., Weber R., Martin C.M. and Hennet, L. *Science* **322**, 566-570 (2008).
12 Greaves, G. N. and Sen, S. *Advances in Physics* **56**,1-166 (2007)
13 Aasland, S. and McMillan, P. F. Nature **369**, 633-637 (1994).
14 Langstaff, D., Gunn, Greaves, G. N., Marsing, A. and Kargl, F. *Rev. Sci. Instrum.* **84**, 124901 (2013).