John Neil Sherwood

World renowned crystal scientist and imperfectionist

Organic crystalline materials are ubiquitous in our everyday life as highlighted by many examples: pharmaceuticals; personal products such as soap and candles; confectioneries such as chocolate and ice cream; agrochemicals such as crop protection products; electronic materials such as piezoelectric and non-linear optic (NLO) devices. Understanding, characterising and defining the crystal growth of these materials and, in particular, the pivotal inter-relationship between their growth conditions and the physical chemical properties of the resultant crystals owes so very much to the seminal work, spanning more than 6 decades, of Professor John N Sherwood of the University of Strathclyde who died at the age of 87 on the 4th December, 2020. Despite their obvious utility, the crystal and crystallisation science of organic materials, and indeed for that matter organic solid-state chemistry itself, is surprisingly, even to the present day, under-researched when compared to inorganic materials.

John was born in Redruth, Cornwall, the son of William Henry Cyril Sherwood, a French and Games teacher, and Lily Rose who worked as part of the housekeeping team, for the LamFranchie family. When John was 12, the family moved back to Bradford to be nearer their wider family and also to enable his attendance at Aireborough Grammar School. Here, he performed very well gaining a place to study chemistry at Bede College, University of Durham. It was at the university that he met his fellow student and future life partner, Margaret Enid Shaw from Huddersfield who was studying Geography, Biology and Education at Neville's Cross College.

It was also at Durham, following graduation, that he developed his interest in the crystal growth of organic materials. In his PhD work, under the supervision of Dr Sam Thomson, he prepared large, pure, single crystals of anthracene and used ^{14}C-labelled tracers to measure, for the first time, its self-diffusion thus quantifying the key roles played by both vacancy point defects and line defects in the self-diffusion process.

John and Margaret married in 1958 and, following post-doctoral work at the University of Hull, he was appointed as a lecturer in chemistry at the Royal College of Science and Technology in Glasgow, later the University of Strathclyde. There, he established the first research centre dedicated to studies of the crystal growth and perfection of organic single crystals. Importantly, his previous work on self-diffusion had demonstrated that, even with careful preparation, the limited range of organic crystals available at that time were highly imperfect with high dislocation densities and concomitantly significant grain boundary substructure. They had also shown how the presence of impurities could lead to misleading results. Hence, the research sought to examine in detail the influence of imperfections on the physical and chemical properties of the crystals with the overall aim to produce ultrapure (<1 ppm total impurity), highly perfect (zero dislocation content) and large (>10 cm^3) single crystals of organic materials. The new centre also provided crystals and deuterated crystals, as well as advice on technical aspects of crystal growth, for other researchers. In many ways, the research mimicked industrial work on microelectronic materials, with more than 200 different compounds being purified by multi-pass zone refining, crystallised from the solution, vapour and melt phases and characterised by solvent etching and X-ray topography. However, he was the first to apply this holistic approach to organic materials and, indeed, the purity and perfection achieved by his centre has yet to be matched, even today.

Since the early days of the Organic Crystal Growth Centre, John had a steady stream of PhD students, research assistants and academic visitors from India and his group built up a very strong alumni there. He made many return visits to India where he gave lecture tours, attended conferences and provided advice to the community there on crystal growth. John and Margaret often went to India together and they greatly enjoyed travelling around the country and absorbing the country's stunning architectural history and vibrant culture.

The group's interest in generation of lattice defects through crystal growth led to its obvious progression into the mechanical properties of organic materials. In particular, if the defect content in 'as-grown' crystals were to be minimised then the fundamental properties associated with the deformation of these materials would need to be assessed as to whether they behaved in a similar manner to more conventional materials such as metals and semiconductors.

Organic crystals can exhibit an enormous range of mechanical behaviour from what might be regarded as "normal" characteristics of brittleness and friability, through "waxiness," with increased plasticity, to the extreme case of "plastic crystals". This last class of materials and their behaviour intrigued many physical chemists and John's group addressed the key question as to whether plastic crystals were true solid phases or simply meso-phases similar to liquid crystals?" Such plastic crystals are high temperature and symmetry materials formed from "spherical" molecules whose entropy of transition from their "brittle" phases, is quite high. In contrast, their entropy of melting is low and close to the communal entropy. This implies that the molecules in the plastic phase have gained a high degree of vibrational and rotational freedom at their transition and only have to gain translational freedom upon melting. Their most obvious property is that they are highly plastic and can flow under only slight uniaxial pressures and, in extreme cases, under gravity.

Comparative studies on these three groups of organic solids were made using a multi-technique analytical approach encompassing collaborative work with Riso National Laboratory in Denmark. In this, studies of the influence of temperature, pressure and the mass of the diffusing species on the self-diffusion process were coupled with measurements of NMR relaxation times with positron annihilation spectroscopy being used to define the exact nature of the lattice defects involved. The studies revealed that normal organic and

waxy organic solids, comprising anisotropic molecules, diffuse by vacancy motion at low rates. In contrast, in the plastic crystals diffusion occurs much more rapidly and the point defects vary from simple vacancies in materials at the least plastic end of the range to more complex behaviour in those at the most plastic extreme. The latter encompasses the formation of di-vacancies and volumes with a higher degree of molecular relaxation involving multiple vacancies. Through this work, the organic solid state arguably became the most comprehensively characterized state of matter, at least as far as point defect properties were concerned.

Snapshot of the Sherwood group in the late 1980s. Back row (left to right): Hugh Gallagher, Bob Docherty, Gerry Lamble, Alison Littlejohn Kristof Woijciechowski, T Shripathi, Rile Ristic, unidentified, Graham Simpson, Amer El Korashy, Kevin Roberts, Stephen Doyle, Bernard McCardle, Bob Fabian and Choon Sup Yoon. Front row (left to right): Helen Morrison, John Sherwood, Evelyn Shepard and Jenny Wilson.

The X-ray topography characterisation of the absolute perfection of the crystals greatly contributed to the success of the Organic Crystal Laboratory and this work received a significant boost through the construction of the UK's Synchrotron Radiation Source (SRS) at Daresbury in the late 1970s. Through collaborative work with groups from the University of Warwick and Durham, a new X-ray topography facility was built up at the SRS. This led not only to improved methods of topography analysis, but also to their wider exploitation for in-situ studies of crystallization, solid-state reactivity and mechanically-induced deformation. In the latter case, the intensity, spatial resolution and strain sensitivity afforded by the SRS enabled unique studies of defect motion in explosive materials such as PETN, RDX, TNT and HMX. In-situ observation of dislocation motion in these materials under tensile strain was carried out with the associated defect structure (deformation slip patterns, lattice twinning and dislocations) characterised for the first time. These vital experiments provided base-line information for the analysis of the defect behaviour under the higher stresses associated with the shock initiation and hence operational stability of these materials.

Throughout this time, John, through his membership and later chairmanship of the SERC's Synchrotron Radiation Facility Committee, was a great champion for the UK's SR science community. As a member of the SERC's Science Board he played a major role in making a case for the establishment of the European Synchrotron Research Facility at Grenoble and ultimately the SRS's successor, the Diamond light source at Harwell.

Industry uses crystallisation to both isolate and purify materials and indeed some 70% of chemical manufacturing processes involve dealing with materials in their solid-state at some stage in their production. Careful control of the crystal growth process is vital to ensure the quality and efficacy of crystalline ingredients and hence the core expertise of John's group was much in demand by the chemical and pharmaceutical industries. His group worked extensively with industrial partners through a range of projects including improving the purity of products such as terephthalic acid (ICI), adipic acid and hexamethylenediamine (DuPont) for improved polymer fibre production, understanding the deleterious wax crystallisation in middle distillate fuels in relation to flow improvement (Exxon Chemical) and solving crystallization problems associated with particle production (Astra-Zeneca, GSK, Pfizer and Roche). The industrial impact of the group's work inspired more fundamental crystallisation research notably the challenging problem of secondary nucleation, addressing the issue as to why in industrial processes some crystals grew whilst others did not with such behaviour resulting in a wide dispersion of particle sizes. Combining in-situ microscopy with defect characterisation his group quantified the role of defects, notably lattice strain and edge dislocations in reducing and promoting crystal growth respectively.

In the 1980s, John's group joined the UK's Joint Optoelectronic Research Scheme (JOERS) into organic NLO crystals for application in fibre-optic communications systems. Through collaboration with colleagues in the department's theory and laser chemistry groups, the growth of these challenging materials together with the characterisation of their second order non-linear optical tensors as a function of crystal perfection was examined. The challenge of the project was to crystallise NLO source molecules, which had high dipole moments and easy electron transfer, into acentric polymorphic structures which could, in turn, be grown as large single crystals with high perfection and optical transparency. As with other crystal properties, it was shown that optical performance was strongly correlated with both polymorphic form and crystal perfection. Crystal engineering procedures, such as side group addition either to alter the intermolecular packing or to induce chiral functionality were used to ensure the structural acentricity needed. Due to their polar nature, the growth of these materials required painstaking approaches in the design crystal seeding techniques in order to prepare the large single crystals needed. The research delivered crystals of nearly a dozen different NLO compounds confirming not just their excellent NLO properties but also equally their high potential with respect to their ferroelectric, piezoelectric, pyroelectric and acousto-optic characteristics.

John published more than 250 high quality journal papers whose examination reveals his strong collaborative ethos and inclusive style which enabled the assembly of large, interdisciplinary teams to tackle significant scientific and industrial research challenges. During his career, his research progressed from the examination of an imperfect and poorly understood, but at least, single, anthracene crystal to the development of a range of the considerably more perfect NLO materials. His research work has made a massive contribution to the better understanding of the nature and properties of the imperfections in organic crystals and in doing so has provided a route map as to how their final perfection can be achieved.

John was awarded his DSc and promoted to a Professorship in 1977 and, around that time, he was elected as a Fellow of the Royal Society of Edinburgh and a Fellow of the Royal Society of Chemistry. He also contributed widely to the scientific community through his work for the research councils, his industrial consultancy and his leadership activity within the crystal growth community. In the latter case he was a founder member of the British Association for Crystal Growth (BACG) and, as its Chair, led it's re-vitalisation in the mid-1990s, notably by enhancing its inclusivity and scientific diversity, and promoting emerging talent through his instigation of the BACG's Young Scientist Award. Later, he served as the association's President and received an honorary membership at its 40th anniversary meeting.

John Sherwood held a succession of senior academic offices at Strathclyde over the twenty year period up to 1998. He was elected to many of them, including the most senior post open to staff, Vice-Principal. He won the confidence of his fellow academics and the respect of all those he worked with by his courtesy and personal warmth to all, regardless of their position, and by the sure and certain knowledge that he stood for the core values of the academic community, even in challenging times. Whilst he retired into emeritus status in 2002, he continued to write and publish his work for many more years, only stopping quite recently when, sadly, ill health took its toll.

As a research assistant in the 1970s and later as an academic colleague, John proved to be an excellent mentor and friend, readily and unconditionally providing critical appraisal of my scholarly work, encouraging me to collaborate and gain wider international experience. Such support, helped me to develop my own research work providing a pathway to an eventual academic career, I will always be most grateful to his memory for this. I know also that I am not alone in having been collegially supported and mentored in this way.

John Sherwood was, without doubt, a giant within the crystal growth and organic solid-state chemistry fields and his presence will be greatly missed by the community to which he made such a vibrant contribution.

John's wife Margaret predeceased him earlier in 2020 and he grieved deeply for her loss. He is survived by his daughters Rosemary and Jennifer, his four grandchildren, one great grandchild and his younger brother David.

Kevin Roberts is Brotherton Professor of Chemical Engineering at the University of Leeds in the UK.

Bibliographic note on sources: Fifty Years as a Crystal Gazer: Life as an Imperfectionist, J N Sherwood, Crystal Growth and Design 4 (2004) 863-877

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