
Preface—Inorganic solids — properties and possibilities

The papers in this issue were presented at the third Materials Discussion of the Royal Society of Chemistry (MD3), which took place at Churchill College, Cambridge during 26–29 September 2000. The above title attracted around 100 delegates from many countries and a broad range of contributions, reflecting the current state of inorganic materials chemistry. Authors of the Feature Articles were given 25 minutes to present a review of their field, followed by 5 minute presentations of several related Articles. Discussion leaders added their perspectives and chaired the sessions with great authority. It was pleasing to see that all participants including younger scientists contributed to the discussions. The sessions were not recorded, however, I have attempted to summarise their content below. I hope that this will be a useful companion to new readers of these papers, and will bring back pleasant memories to those who were present.

MD3 started with a Plenary Lecture by Sir John Meurig Thomas entitled 'Designing catalytically active sites in micro- and meso-porous hosts'. The needs of the chemical industry to minimise consumption of raw materials and energy, and output of waste products and pollution continue to keep the design of better catalysts at the top of many inorganic chemists' wishlists. Microporous catalysts with pores in the 3.5–15 Å range have developed gradually over the last half-century from naturally occurring zeolites, and since 1992 these have been joined by mesoporous hosts offering 15–250 Å channels. Thomas's thesis was that these two groups of materials could satisfy all the desirable features expected of heterogeneous catalysts. Recent case studies of anchored metallic nanoparticles and epoxidation sites within mesoporous silicas, and cobalt-doped microporous aluminophosphates illustrated his point.

The above themes were revisited in the *Microporous and Mesoporous Materials* discussion chaired by Prof. M. Rosseinsky. The papers (with presenting author and page no. in this issue) concerned molecular insertion into the mineral sepiolite (Ruiz-Hitzky, p. 86), the synthesis and electrochromic properties of mesoporous WO_3 (Baudrin, p. 92), the templation of microporous metal phosphates by macrocycles (Wright, p. 98), and the delamination and restacking of zinc–aluminium double hydroxides (Leroux, p. 105). The possibility of making porous membranes of sepiolite was suggested although Ruiz-Hitzky felt that this would be difficult to achieve. He clarified that the conformation of polyethylene oxide in sepiolite is zigzagged and not helical as normally occurs. The possibility of constructing new mesoporous materials by curving delaminated double hydroxide layers was raised, and Leroux responded that the layers were too rigid for this to be feasible at present. In the general discussion, issues of crystallite size were raised, as mesoporosity can result from the agglomeration of small crystallites. The difficulty of organising acentric molecules within porous materials for non-linear optical uses was discussed. Acentric ordering can be achieved even in centric zeolites, but homogeneity over the length scale of visible light can be problematic.



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The session on *Theory, Calculation and Prediction*, chaired by Prof. J. Etourneau, started with a keynote talk by Canadell (p. 1) on the increasing power of density functional methods applied to electronic structure problems. The subsequent talks described atomistic calculations of thermodynamics and phase diagrams (Allan, p. 63), the prediction of high pressure phases of binary nitrides and sulfides (Schön, p. 69), and experimental and theoretical evidence for Co^{3+} spin state disproportionation and

ordering in the layered oxide $\text{TiSr}_2\text{CoO}_5$ (Doumerc, p. 78). A lively discussion was prompted by the question of whether electronic band structures could yet be calculated reliably for a wide range of materials. Extended Hückel calculations such as those described by Canadell are still dependent on the parameterisation chosen, and thus numerical results such as bandwidths are subject to some variation. Improvements to the local density approximation would be one way of improving accuracy. The difficulties of including electron correlation effects were raised by several people, Hartree–Fock methods were proposed as the best current approach. The general conclusion was that trends in the electronic properties of complex materials such as conducting organics and transition metal oxides could be explained and even predicted by calculation. However, the prediction of absolute properties is not yet reliable.

The *Optical Materials* session (co-chaired by Profs. E. Ruiz-Hitzky and A. Harrison) highlighted both the atomic scale and optical wavelength scale manipulation of inorganic materials to optimise their optical properties. Atomic scale development of phosphors and lasers, and micron scale construction of electro-optic devices and photonic crystals were reviewed in the keynote talk by Denning (p. 19). Other syntheses of photonic crystals were featured in the presentation by McComb (p. 142), and Gurin (p. 149) described how submicron semiconductor particles can be grown within silica glass. He displayed some monoliths to demonstrate their intense colouration to the audience. In response to a question, Gurin reported that the semiconductor particles were reversibly bleached with bleaching times of ~ 10 ps. It was suggested that further particle size control could be achieved by varying the xerogel porosity. Much of the discussion was devoted to the growth and properties of photonic crystals. Control of the regularity and size of the silica spheres used by McComb is crucial, and the problems of point defects, grain boundaries and dislocations in the sphere packings revisited familiar problems in solid state chemistry.

Two sessions were devoted to transport properties. *Ionic Conductors and Battery Materials* (chair: Prof. J. Irvine) started with a keynote paper by Norby (p. 11) showing how simple models for defect formation can aid the design of new anionic conductors. One of his principal conclusions, that good anion conductors should be cation ordered but anion disordered, was borne out by the subsequent report of fast oxide-ion conductivity in $\text{La}_2\text{Mo}_2\text{O}_9$ type materials (Goutenoire, p. 119). The other talks concerned aspects of lithium battery electrodes and conductors; intercalation or deintercalation into layered Mn/Co (Bruce, p. 113) and Ni (Croguennec, p. 131) oxides, and microstructural development of the $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ perovskite (Várez, p. 125). The possibility of correlated cation and anion motion and the desirability of electronic conduction accompanying ionic transport were discussed. It was felt that electronic conductivity often assists ionic conduction; in the case of oxide ion conductors this may be through the separate transport of oxygen atoms and two electrons, which recombine after motion. Many materials aspects of ionic conductors were raised; thermal expansion, shearing of layers (e.g. in Li_xNiO_2), phase transitions and grain boundary resistances are all problematic. Nanostructured intercalation hosts lessen some of these problems; these can be prepared by the irreversible transformation of unstable layered hosts such as $\text{Li}_x(\text{Mn},\text{Co})\text{O}_2$ into a nanostructured spinel phase.

The *Electronic Materials* discussion featured conducting manganese and copper oxides. Raveau's (p. 29) keynote presentation emphasised the importance of 'melting' charge ordered states with an applied magnetic field to obtain colossal magnetoresistance (CMR) effects in manganite perovskites. West (p. 153) described the variation of semiconductivity in Nb-doped CaMnO_3 , and Rosseinsky (p. 160) reported the structure and properties of a tri-layered Mn–Ti perovskite. In the two talks on high- T_c copper oxide superconductors, the use of MgO inclusions to improve the flux pinning in $\text{Bi}_2\text{Sr}_2\text{CaCuO}_8$ (Kazin, p. 168), and the co-existence of magnetism and superconductivity in layered ruthenium copper oxides (McLaughlin, p. 173) were described. The future development of manganite perovskites was discussed; phase separation and the development of low field CMR effects are key issues to be addressed. There is evidence that substituted Ru is present as Ru^{5+} in manganites, leading to the production of Mn^{3+} and hence electron hopping conductivity in $\text{CaMn}_{1-x}\text{Ru}_x\text{O}_3$. In trying to account for the semiconducting properties of $\text{CaMn}_{1-x}\text{Nb}_x\text{O}_{3-y}$ materials, variations of oxygen

content within the samples and grain boundary resistances were considered to be the main problems. Thermopower measurements were suggested to circumvent the grain boundary problem and to assess whether transport is *via* variable range hopping. It was suggested that replacing Ca with La and Na could encourage Mn and Ti to order in the $\text{Ca}_4\text{Mn}_2\text{TiO}_{10}$ Ruddlesden–Popper phase. By contrast, the work of Kazin stressed the need to avoid chemical substitutions to create inclusions of a (Mg,Cu)O secondary phase to pin flux lines within a cuprate superconductor. The possibility of magnetism and superconductivity existing in separate domains within $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ was raised; in reply muon spin rotation experiments were cited as the best evidence that the material is homogenous. $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ exemplifies separate superconducting and magnetic electronic systems co-existing within the same material, whereas in the recently reported UGe_2 the two properties are displayed within the same electronic structure. The chairman, Prof. P. P. Edwards, opened the general discussion by pointing out that the unusual electronic properties of the above materials stem from their proximity to metal–insulator transitions so that electron correlation effects are important. Other contributors added that Kondo-like effects and electronic instabilities such as charge and spin density waves can give rise to unusual transport phenomena around the metal to insulator crossover. The general importance of charge ordered stripes was discussed; their presence in manganites is clear but their role in the superconducting cuprates is still uncertain.

The *Magnetism and Magnetic Materials* discussion chaired by Prof. P. Day covered both fundamental and materials topics. Geometrically frustrated materials were reviewed by Greedan (p. 37), and Wills (p. 179) reported specific results on magnetic order in iron jarosites that exemplify an antiferromagnetic kagome lattice. The synthesis of ferrite materials by two very different routes was described; Jouini (p. 186) used low temperature hydrolyses in polyol media, whereas Parkin (p. 193) employed self-propagating high temperature synthesis. In the discussion of frustrated systems, the need to find new materials that model particular ideal magnetic lattices was a key issue. Recent successes have included spin glasses and ices, but there are still, for example, no materials that satisfactorily model a two-dimensional antiferromagnetic triangular lattice of Heisenberg spin-1/2 ions. Disorder, structural distortions and electron itinerancy have ruled out candidate materials to date. In the discussion of magnetic nanoparticle synthesis in polyols, it was agreed that this mimics hydrothermal conditions, enabling high temperatures to be achieved. The mechanism of the condensation reactions that form the oxides was raised; little is known of this at present. The effect of a magnetic field upon the self-propagating high temperature syntheses was explained by the densification resulting from preorganisation of the loose reactants. No orientation of the reactant particles by the field has been seen, but packing density strongly affects the reaction rate.

The theme of *Materials Synthesis* continued in a session chaired by Prof. M. Jansen. Three papers were discussed. Fundo (p. 200) reported the electroless deposition of Ni films from solution. The high corrosion resistance of the films is due to P, fortuitously incorporated from the solution phase hypophosphite ion. Shen (p. 204) described the use of spark plasma sintering to prepare compact SiN ceramics. The application of this technique to other ceramics such as SiAlONs and oxides was discussed at length. The small size of the heated zone enables rapid heating and cooling rates to be achieved, and ion transport is avoided by reversing the current direction of successive electrical pulses. The hydrothermal growth of crystals of a new fluorophosphate, $\text{Na}_2\text{CoPO}_4\text{F}$, was presented by Ruiz-Valero (p. 208). Determination of the magnetic structure and ion-exchange chemistry was suggested, but this will not be possible until a single phase powder of the material can be prepared.

A range of *Structural Properties* was covered in the final discussion, chaired by Prof. M Alario-Franco. Cava (p. 54) reviewed the use of oxide ceramics as dielectrics for microwave communication devices in a keynote presentation. Subsequent talks described the widespread occurrence of negative thermal expansion in microporous materials (Lightfoot, p. 212), and superhard materials based on crystalline SiC–C solid solutions (Mykhaylyk, p. 217) and on amorphous Si–B–N–C networks (van Wüllen, p. 223). In the discussion of dielectric materials, the need for more fundamental studies (*e.g.* of phonon frequencies) was brought out, and the possibilities of using other

materials than oxides of d^0 transition metals were explored. To obtain large negative thermal expansion materials, the avoidance of extra-framework cations (including H^+) was proposed as being essential. The importance of microstructure in giving superhard materials was discussed. It was felt that high resolution electron microscopy would be useful to see C intergrowths in the SiC–C solid solutions. The use of molecular dynamics simulations of the random inorganic networks complemented the MAS NMR studies.

Prof. J. Etourneau gave the closing summary. He highlighted the range of materials and properties that are now being studied. The abilities of inorganic solids to transport molecules (for catalysis), ions or electrons within themselves, and their responses to external electric and magnetic fields, electromagnetic radiation and mechanical forces have all led to fundamental discoveries and new technologies.

In summary, MD3 served as a ‘snapshot’ of the state of inorganic materials chemistry at the present moment between centuries, illustrating both continuity and change. Perhaps the longest running problems are those of strongly correlated electrons, which still pose considerable difficulties for theory, and allow new phenomena such as CMR in manganites, spin state ordering in $TlSr_2CoO_5$, and coexisting magnetism and superconductivity in layered ruthenium cuprates to be discovered. Change is represented by the expansion of chemistry to cover a variety of length scales from the traditional Å (10^{-10} m) scale of crystal structures to the μm (10^{-6} m) dimensions of photonic crystal lattices. The intermediate ‘meso’ or ‘nano’ scale ($\sim 10^{-8}$ m) featured in many and diverse topics such as mesoporous catalysts, nanoparticles of magnetic oxides, microstructuring of CMR manganites, Li conductors and optical materials, and pinning centres in ceramic superconductors. The future development of inorganic solids with a variety of properties over a range of length scales clearly holds an enormous number of possibilities for the new century.

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