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09.01 – Computer Simulation of Inorganic Crystal Structures

MS-09.01.01 COMPUTER MODELLING OF INORGANIC CRYSTALS by C.R.A.Catlow*, The Royal Institution, 21 Albemarle Street, London W1X 4BS, UK

Computer simulation techniques are now playing a major role in modelling and increasingly predicting the structures and properties of inorganic materials. This introductory lecture will review the main techniques used in the field, including both quantum mechanical methodologies based on force fields. Recent applications will be described in the fields of microporous crystal structures and high T_c superconductors.

MS-09.01.02 COMPUTER SIMULATION AND CRYSTAL STRUCTURE PREDICTION by C.M.Freeman* and J.M.Newsam, BIOSYM Technologies Inc, 9685 Scranton Road, San Diego CA 92121, USA

We describe techniques for predicting and solving crystal structures based on simple interatomic interaction potentials and powder diffraction data. Computational methods have traditionally commanded a central role in the solution and refinement of crystalline structures. Similarly computer simulation procedures, which commonly draw on crystallographic findings, have established an important position in the rationalization of the physical properties of the condensed phases of matter. The parallel evolution of computational crystallography and computer simulation has led to a distinct overlap between the two fields. Recently procedures have been described which exploit the standard techniques of computer simulation in combination with hybrid potential energy functions to yield structures which are sterically and experimentally plausible. These real space techniques have been especially useful in the investigation of microcrystalline framework structured materials for which powder diffraction may be the sole experimental possibility. In contrast to traditional refinement procedures (which have tended to use rapidly convergent but locally biased least squares methods), the analogy with physical simulations, has prompted the use of simulated annealing as an optimization method in the majority of studies. Metropolis Monte Carlo or Molecular Dynamics based annealing procedures provide significant 'searching' capabilities framework structured solids, condensed metal oxides and molecular crystal structures will be described. *Acknowledgement: The Biosym Catalysis and Sorption Project is supported by a consortium of industrial, academic and government institutions.*

MS-09.01.03 THE BOND VALENCE MODEL by I.D.Brown*, Institute for Materials Research, McMaster University, Hamilton, Ontario, Canada

The bond valence model is an essentially chemical approach to the problem of the description and simulation of inorganic crystal structures. Its particular strengths are its simplicity, the chemical insights it provides and its modest computing

requirements. Its weakness is that it does not give energies and cannot be easily used to explore non-equilibrium conditions. The model assumes that the valence (formal charge) of an atom is distributed as equally as possible, between the bonds that it forms, each bond having a certain valence associated with it. The valence of a bond, which can be precisely calculated using two network equations, correlates well with its length, making it possible to predict the bond geometry of most crystals to within a few picometres providing that the bond topology is known. These bond lengths, or the network equations used to derive them, can be used as part of the cost function in a simulated annealing study.

Predicting the topology of the bond network is more difficult, but the concepts of Lewis acid and base strength, these being *a priori* estimates of the valence of the bonds formed by the cation and anions respectively, permits the local bond topology to be predicted. Expanding this into an infinite bond network is, as yet, an unsolved problem. Mapping the infinite bond network into Euclidian space places constraints on the geometry which are not always equations described above. In these cases, the structure, if it forms, will be strained. The bond valence model allows one to explore the ways in which this strain may be relieved (e.g., by altering oxidation states, adding interstitial atoms or varying the lengths of other bonds) and allows one to predict, at least qualitatively, many of the chemical and physical properties of the material.

MS-09.01.04 CALCULATION OF THE CRYSTAL STRUCTURE AND THERMODYNAMIC PROPERTIES OF OXIDES AND MINERALS USING FREE-ENERGY MINIMISATION TECHNIQUES by Stephen C.Parker* and Alison Wall, School of Chemistry, University of Bath, Claverton Down, Bath, UK

The aim of this work is to develop reliable simulation techniques which can predict the structural and physical properties of oxides and minerals at varying minimisation, in which the structural parameters are varied until the configuration with lowest energy is achieved. An important development is that lattice dynamics are employed to calculate the vibrational behaviour and hence the thermodynamic properties including heat capacities and free-energies. Early studies have shown that this approach can model the elasticity, heat capacity and thermal expansion of the Mg_2SiO_4 polymorphs under ambient conditions with a high degree of reliability. We have extended the range of applications in two ways. Firstly, to simulate the relative stability and elasticity of a range of minerals at varying pressures to infer the equations of state and phase diagrams. We shall illustrate this work by describing the predicted phase stabilities of magnesium silicate pyroxenes for which there is still considerable experimental uncertainty. Secondly, to predict whether the minor elements including iron, calcium and aluminium in a magnesium silicate assemblage form a solid solution with the major mineral phases or from distinct new mineral structures. The success achieved to date shows that with reliable interatomic potentials these techniques provide a valuable link between the atomistic and thermodynamic behaviour of minerals.