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MS–09.01.05 COMPUTER SIMULATION OF MICRO-POROUS SOLIDS by R.A.Jackson, Department of Chemistry, Keele University, Staffordshire, STS 5BG, UK

Computer Simulation is now well–established as a means of calculating the structural and other properties of microporous solids, including zeolites, ALPOs and germanates. The specific method that will be described is lattice energy minimisation (R.A.Jackson and C.R.A.Catlow, Mol Sim, 1988,1,207–224), which calculates equilibrium structures and lattice properties, and which has been applied to a wide range of materials from each of these categories. Crucial to the success of this technique is the availability of good quality interatomic potentials, and current progress in this area will be discussed. Applications will be described to the following problems: (i) framework modeling, (ii) relative stabilities of frameworks, and (iii) location of non–framework cations. Comparison with experimental data will be given where possible. Finally, future developments in the field will be discussed.

MS–09.01.06 FIRST-PRINCIPLES STUDIES OF PRESSURE-INDUCED PHASE TRANSFORMATIONS. By John S. Tse, Dennis D. Klug and Yvon Le Page, National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Recent advances in theoretical methodologies and improvement in computational technologies have enabled accurate prediction of the structure and properties of crystals from first principles methods. The emergence of molecular dynamics and of *ab-initio* total energy methods has greatly aided the fundamental understanding of the stability of crystal structures and has led to the development of new materials. Recently, known pressure-induced transformations in ice, α-quartz, α-berlinite and rutile have been successfully reproduced by our group, employing classical constant-pressure molecular dynamics calculations with realistic empirical potentials derived from quantum-mechanical calculations, or using *ab-initio* quantum total energy calculations. In particular, the theoretical results distinguish between the contrasting behaviour in isostructural α-quartz and α-berlinite under pressurization, and provide detailed mechanisms for the amorphization process and the memory effect. One of the advantages of first principles methods is the ability to study structures and properties of crystals under conditions not easily amenable to experimental studies. Novel high pressure (~ 100 GPa) structures for silica and rutile have been revealed from our studies. Since under extreme conditions, the empirical potentials may no longer be applicable, the electronic properties of the system must be treated in a self-consistent manner. Recent implementation of the Car-Parinnello techniques allows one to perform parameter-free molecular dynamics simulations. This method has now been applied to the study of the stability of the recently predicted high pressure phases of silica and rutile.

MS–09.01.07 PHYSICAL CHEMISTRY OF THE AGEING OF SILICAGEL by R.A. van Santen*, Schuit Institute of Catalysis, Eindhoven University of Technology, Department of Chemical Engineering, 5600 MB Eindhoven, The Netherlands

SAXS studies of silicagel formation enable the *in situ* study of aggregation and ageing processes. Aggregation can be analysed in terms of changes in elementary particle size, fractal dimension as well as radius of aggregation.

Cluster aggregation computer simulations can be applied to analyse the consequences of different aggregation and ageing models. Two ageing processes have been identified. At relatively high silica concentration initially gels of a fractal dimension 2.2 are formed. Ageing occurs by dissolution and non-uniform distribution of silicagel building units results. The fractal dimension decreases to 1.8.

At low concentrations initially a gel also of fractal dimension on 1.8 is formed. However, this gel has a uniform distribution of elementary particles. Ageing now occurs by internal reorientation processes of the silica particle chains resulting in a fractal dimension of 2.1. NMR relaxation spectroscopic studies as well as X–ray microsopic data will be shown to support the ageing mechanisms as deduced from computer simulated aggregation processes.

PS–09.01.08 ON THE USE OF FORCE CONSTANTS IN SIMULATED ANNEALING REFINEMENT
D. TranQui

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Simulated annealing technique has shown to be an efficient procedure for refinement of protein and macromolecule crystal structure, specially in the case where the starting model is approximately known (Brunger, A.T., Kurian, J. and Karplus, M. ,1987, Science, 235. 458-460; Fujinaga, M., Gros, P. and Gunsteren W.F., 1989, J. Appl. Cryst. 22, 1-8).

In addition, due to its high convergence radius, this method is able to generate atomic-position shifts, up to 4Å and sometimes more, and/or large flipping moving the structure into the correct orientation: such large changes which necessarily involve jumpings over energy barrier are usually beyond the convergence radius of conventional standard least-squares procedure. It is also commonly recognized that simulated annealing refinement reduces substantially the need of human interventions during the structure refinement stage.

However, it is well known that simulated annealing refinement sometimes suffers serious drawbacks, even it was apparently applied following to the appropriate protocole. Thus, in the course of refinement of a ferredoxin from *Clostridium Acidurici*, (TranQui, D., Meyer J., Moulis J.M., Sieker, L and Jesior, J.L. to be published) a metalloprotein which harbours in its polypeptide chain two inorganic [4Fe-4S] clusters, we have obtained, whatever the starting points used, an unreasonable departure of the [4Fe-4S] geometry from the cubane-like structure. This is due to the fact that the minimizer tends to compensate the unproper force constant of covalent bond Fe-Sγ (Sγ of Cysteine) in tearing the internal bond lengths bond angles of [4Fe-4S] clusters. Finally, this unwanted effect was corrected in assigning two different constant values: $k_{0,1}$ and $k_{0,2}$ for

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(Fe-S) (S is an inorganic sulfur) and (Fe-Sγ) bonds, respectively. The $k_{0,i}$'s were allowed to dynamically fluctuate as a function of the clusters distortion.

The concept of fluctuating constant force was generalized to other atoms and could be used to predict the molecular structure of "small molecule" and mineral compounds, provided the topology of the structure was known. In the case of inorganic compounds the Lennard-Jones potential was replaced by Born-Mayer (Born, M. and Mayer, J.E., Z. Phys. 75 1932, 1) or by Keating, P. N.(Phys. Rev. B2, 1966, 637) type potential. The contribution of electrostatic energy and Coulomb stress tensor which were omitted in the dynamic calculations were compensated by lattice energy (Evans, M., Ann. Phys. , Leipzig, 64 (1921) 253; Bertaut, E.F., 1952, J. Phys. Rad. 13, 499-505).

Details of this method are described and results of two attempts of ab-initio structure determinations are also reported in this paper.

PS-09.01.09 FLEXI-CRYSTALLOGRAPHY
A. L. Mackay, Dept. of Crystallography, Birkbeck College, (University of London).

Nodal surfaces, defined by wave vectors in reciprocal space, equipotential surfaces, defined by point charges in real space, and periodic minimal surfaces, 'soap-film' elements lying smoothly across the asymmetric domains in given crystallographic symmetry groups, are exact mathematical objects which may be of physical significance and which can help with the visualisation of significant structure at a level above that of single atoms. They are two-dimensional manifolds, with local metrics different from the Euclidean metric of the planar sheets of orthodox crystallography, and are of use in the development of the flexi-crystallography of the 'soft matter' proposed by de Gennes and in crystal chemistry generally.

PS-09.01.10 CRYSTAL AND ELECTRONIC STRUCTURE OF KF.2H$_2$O. By A. Preisinger*, M. Zottl, K. Mereiter, Ph. Dufek, K. Schwarz* and P. Blaha, Technische Universität Wien, Austria. W. Paulus, CEN Saclay LLB, France.

Simple hydrates have been studied extensively in literature. We have chosen KF.2H$_2$O as a model system for a hydrate in an ionic solid in order to study the effects of hydrogen bonds. In this study we combine experiments and electronic structure calculations in order to investigate this system.
Single crystals were grown from solution and were investigated by X-ray and neutron diffraction. The crystal data are: space group Pmc2$_1$ with Z=2 and a=4.083(1), b=5.184(1), c=8.831(1) Å. Neutron refinement converged at R=0.020 for 320 reflections.

Table 1. Positional and thermal parameters for KF.2H$_2$O from neutron diffraction data.

	x/a	y/b	z/c	$B_{eq}[Å^2]$
K	0.5000	0.3879(3)	0.0000	2.20(1)
F	0.0000	0.0969(2)	0.1093(2)	2.38(1)
O(1)	0.5000	0.2032(3)	0.7110(3)	2.76(1)
O(2)	0.0000	0.2918(3)	0.3969(3)	2.74(1)
H(1)	0.3127(3)	0.1003(3)	0.6804(3)	3.56(1)
H(2)	0.0000	0.2268(4)	0.2938(3)	3.58(1)
H(3)	0.0000	0.1414(4)	0.4616(3)	3.60(1)

The crystal structure consists of $K^{(2+4)}$ and $F^{(2+4)}$ octahedra. The water molecule with O(2), H(2) and H(3) lies in the (100)-plane and the two hydrogens point nearly towards the neighbouring F⁻ (Fig.1), while the oxygen of this water molecule has two K⁺ ions as nearest neighbours, where these four ions form a tetrahedron. The other water molecule has a similar coordination. The three types of distances K-F, K-O and hydrogen-bonded F-O are 2.72, 2.73-2.82, and 2.72-2.75Å, respectively.
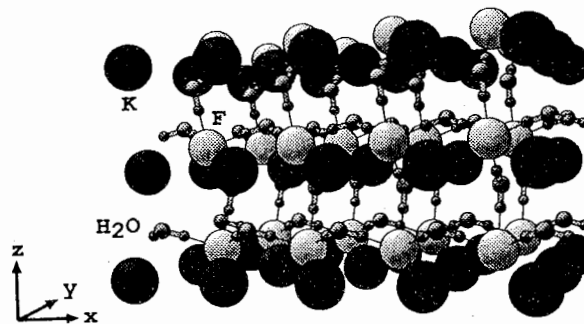

Fig.1 Crystal structure of KF.2H$_2$O

In the theoretical study we determine the energy band structure by taking the structural data of the neutron experiments and perform full-potential linearized augmented plane wave (LAPW) calculations using the WIEN code (P.Blaha, K.Schwarz, P.Sorantin, S.B.Trickey, 'Computer Phys.Commun. 1990, 59, 399), where we treat exchange and correlation effects by the local density approximation. We obtain the density-of-states, which can be partly related to the corresponding MO diagram of a free water molecule by means of electron density plots. In order to study the polarization of the water molecule and its hydrogen bond, we calculate the density of a hypothetical reference system, in which we keep the water molecules in their positions as in the hydrate, but remove all K⁺ and F⁻ ions. The difference density between the true and the reference system indicates an increase of the lone pair densities due to a polarization by K⁺, but a reduced density near the hydrogen atoms which is caused by the hydrogen bonding to F⁻. The interaction with K⁺ is mostly electrostatic, while that with F⁻ has an additional covalent contribution.

PS-09.01.11 DODAF SIMULATION OF ELECTRONIC STRUCTURE OF LOW SYMMETRY CRYSTALS DOPED WITH TRANSITION METAL IONS. By V. S. Goroshkoff and E. G. Noda, Department of Physics, Zaporozhye State University, Ukraine.
In a contrast to the usual unrestricted Hartree-Fock (HF) method known as DODS, another variational "different orbitals for different angle functions" (DODAF) method is developed and used for calculations of electronic structure and spectra of transition metals in ionic crystals.