Advanced Computer Simulation of Materials

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Introduction

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The computer simulation of materials has been going through tremendously exciting changes recently. Two kinds of things are happening. More complex problems are being tackled than was the case a few years ago. But also, completely new kinds of problem are being addressed. The ability to simulate complex real-life problems is certainly due in part to improvements in computer power. Here, both the availability of local distributed hardware and the provision of leading-edge high-performance facilities are playing a major role. The installation of the Cray T3D at Edinburgh in 1994 has been crucial for the vitality of computational science in the U.K. But just as important as bigger computers has been the discovery of new techniques. I am thinking here particularly of the Car-Parrinello method of ab-initio simulation, which has so much expanded the range of problems that can be addressed.

The CCP5 Annual Meeting 1995 provides plenty of illustrations of both kinds of advance – both the importance of improved computer power and the increasing role of ab initio simulation. Indeed, some of the presentations combine the two themes, by reporting ab initio materials simulations performed on the Cray T3D or other high-performance machines. It is a well-worn cliché to talk about a conference giving a 'snap-shot' of the field. But in this case the phrase seems entirely appropriate. The following set of abstracts from the meeting gives a glimpse of what was happening in the advanced computer simulation of materials in late 1995. CCP5 can be proud to be participating in the exciting advances now going on.

Lecture abstracts

Bond Order Potentials: can they bridge the electron-atomistic length-scale gap?

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First principles linear scaling technique: the density matrix approach

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An algorithm for first-principles electronic structure calculations having a computational cost which scales linearly with system size is described. The method exploits the real-space localization of the density matrix, and is related to the technique of Li, Nunes and Vanderbilt. The density matrix is expressed in terms of localized *support* functions, and a matrix of variational parameters $L_{\alpha\beta}$ having finite spatial range. The total energy is minimized with respect to both the support functions and the $L_{\alpha\beta}$ parameters. The method is variational, and becomes exact as the ranges of the support functions and L matrix are increased. The method has been tested on silicon systems containing up to 512 atoms. Some results will be presented, and future developments are outlined.

Monte Carlo simulation of electronic transport in advanced technology semiconductor devices

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Recent developments in semiconductor processing technology have enabled the fabrication of a range of complex device structures. Devices such as the High Electron Mobility Transistor (HEMT) consist of multiple layers of different semiconductor alloys, with minimum layer thicknesses of the order of 10^{-9}m. The active region of such devices has been continually reduced in size, in the quest for high operating speeds and frequencies. State-of-art field effect transistors (FETs) have been fabricated, on both silicon and gallium arsenide substrates, with gate lengths less than 100nm.

An accurate description of such devices requires the development of detailed microscopic models. The most successful approach to date involves the use of a Monte Carlo technique to simulate typical trajectories for an ensemble of electrons within the device. The energy and angle dependences of the electron scattering probabilities are calculated from time-dependent perturbation theory, and scattering events are selected stochastically during the simulation. Scattering by impurities (dopants) and all relevant phonon modes are considered. Consequently, the simulation represents an exact solution of the semi-classical Boltzmann transport equation for the device. The internal electric fields are self-consistently obtained by solving the Poisson equation (usually in two dimensions) on a frequent timestep. The energy band spectrum of the constituent semiconductor(s) can be represented to any desired precision. Usually, a many-valley effective mass scheme is sufficient, but, where high energy phenomena are to be studied, a complete energy band spectrum can be obtained from a pseudopotential calculation.

The purpose of this paper is to explain the key elements of the simulation method, to describe the current state-of-art in this field, and to show results from some of the recent work at Leeds on simulations of ultra-short gate multilayer FETs.

Ab-initio calculation of stacking fault energetics in silicate perovskite

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Extended defects, namely dislocations and stacking faults are a common mechanism for creep in ceramic materials. (Magnesium) silicate perovskite is the major constituent of the Earth's mantle and its creep behaviour at high P and T controls the rheology of convective flow and consequently the motion of tectonic plates on the Earth's surface. Experiments are not practical at mantle pressure and temperature, but computer simulations using quantum mechanical methods based on density-functional theory can provide precise and reliable results irrespective of the extreme conditions.

Dislocations in analogous perovskites such as $CaGeO_3$ dissociate into partials separated by a [110] stacking fault, whose energy and activation energy of formation are an important constraint on the creep process. We have calculated the energetics of the [110] stacking fault in $CaSiO_3$ perovskite including a complete gamma-surface for the [110] shear. At 0GPa and 50GPa the stacking-fault energies are 1.1 and 1.77 J/m^2 respectively and the activation energies for the shear are 1.84 and 3.43 J/m^2.

Investigation of the Si(001) missing dimer defect structure

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At low imaging voltage in STM pictures, single dimer vacancies are highlighted by a bright feature on neighbouring dimers. This contrast disappears at higher imaging voltages. For a number of proposed structures of the single dimer vacancy, *ab-initio* calculations of charge density as a function of energy have been used to simulate STM images. These images show a marked bias voltage dependence, and the low bias voltage images differ markedly between the structures modelled. On this basis, the rebonded structure is identified with the highlighted defects.

Energetic Particle Impacts with Graphite

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This paper will examine the effects of single particle and cluster (C60) impacts with a graphite surface at energies up to keV, by using classical Molecular Dynamics simulations and many-body potentials. It will be shown how single particle impacts can be responsible for bump formation on the graphite surface. These will be compared to experimental observations in the STM. Cluster impacts on the other hand produce waves on the graphite surface which are hexagonal in nature and little sputtering of material occurs at energies up to about 1 keV. The damage to the lattice as a result of these energetic impacts will be examined. Computer-generated simulation videos which illustrate the formation of the bumps and the waves will be shown.

Ab initio molecular dynamics calculations to study catalysis

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Density functional theory (dft) with the local density approximation (lda) was the basis of many solid state calculations, where a lot of experience has been gained. The modern versions of dft especially those using the generalized gradient approximation (gga), have reached (almost) chemical accuracy and thus such dft calculations can be applied to problems of real chemical interest, such as catalysis. The basic concepts for solving such problems are as follows. as a first step one must evaluate the dft and check and improve its form (lda, gga, etc) on small ideal systems of both, solids and molecules.

The ab initio molecular dynamics (md) method was initiated by Car and Parrinello, who started with a lagrangian combining the nuclear and the electronic degrees of freedom, where the forces acting on the atoms are determined within dft but the atomic motion is treated classically. The corresponding equations of motions are solved simultaneously for both, the atoms and the electronic wave functions, using a verlet algorithm. A very efficient implementation of this scheme is the projector augmented wave (paw) method developed

Enantioselective dehydration of butan-2-ol using modified zeolites

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The proton form of zeolite Y was modified with *R*-1,3-dithiane-1-oxide at a loading of one molecule per supercage to create a chiral acid catalyst. The enantiomeric discrimination of this catalyst was demonstrated using the dehydration of the separate enantiomers of butan-2-ol and over the temperature range investigated the *S*-enantiomer was always more reactive. This catalyst system was then studied using computational simulation methods. Molecular dynamics was used to investigate the thermal stability of the modifier molecule in the zeolite. In order to reproduce the experimentally observed thermal stability it was found that the dithiane oxide is probably present as a cationic species. With this model of the active catalyst the butan-2-ol enantiomers were then docked into the structure using a combination of Monte Carlo and energy minimisation techniques. The lowest energy structures for each of the enantiomers of butan-2-ol thus produced had binding energies of 64.7 $kJmol^{-1}$ and 48.3 $kJmol^{-1}$ for the *S*-enantiomer and *R*-enantiomer respectively. This difference in the adsorption of the two enantiomers is considered to be the origin of the enhanced reactivity of the *S*-enantiomer.

The transport of methane through shales

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Natural gas and oil are generated by the geochemical breakdown of dead organisms entombed within compacted sediments, known as source rocks. Unfortunately, it is seldom possible to extract todays commercial hydrocarbons directly from their source sediments. Instead, petroleum geologists must search for pools of oil and gas that have migrated out of low permeability source rocks, and then become trapped within a high permeability reservoir. A detailed knowledge of the diffusion of hydrocarbons through both source and trap rocks is therefore fundamental to petroleum exploration. Molecular dynamics computer modelling can now provide these diffusion data, and establish the microscopic mechanisms involved in hydrocarbon transport. As a first step we have calculated the mobility of methane within the most common group of source and trap rocks, namely clay-rich shales. Data are presented as a function of shale porosity, for burial depths of up to 6km. They show that molecular diffusion within nanometer scale pores is a dominant mechanism for the migration of methane through compacted shales.

Recent Modelling Studies of Molecular Ionic Materials

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Molecular ionic materials present challenges to computer modellers in that their cohesion involves both ionic and covalent interactions, both of which must be accounted for in any potential developed.

The talk will show how a consistent potential model has been used for a range of such materials, with parameters obtained by empirical fitting. The materials studied include carbonates, phosphates, perchlorates and chlorates, where in each case, potentials have been fitted to structural data, and tested by transfer to other materials in the same family. As well as calculating bulk crystal properties, morphologies have been calculated, using both attachment and surface energy approaches. Comparison is made with experimental data, where available.

Finally preliminary results will be presented of modelling studies of ammonium chloride, a molecular cationic material.

Alkali diffusion in alkali silicate glasses

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Molecular dynamics simulations of alkali silicate glasses have revealed a structure consistent with experimental determinations, which in turn are consistent with the modified random network model. Long-time scale molecular dynamics have yielded quantitative measurements of the alkali diffusion and demonstrated the mechanism of ion migration. The results show a pronounced 'mixed alkali' effect similar to that observed experimentally and thus promise to account for the observed behaviour in real glasses.

Dissociation of O_2 on Ag(110)

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The interaction of O_2 with Ag(110) provides a classic example of precursor-mediated dissociation, with a well-characterised molecular state existing between the gas-phase molecule and fully dissociated O atoms. We will present results of a first principles study of this system, based on density functional theory and using a plane-wave, pseudopotential method implemented on a Cray T3D parallel supercomputer. The calculations include full relaxation of the Ag substrate, gradient corrections and spin-polarisation. Results will be presented for the the structure and energetics of the chemisorbed O_2 state and the reaction pathways into and out of this state. The charge transfer from metal to molecule will also be discussed.

Tri-methyl-gallium adsorption on GaAs(001) β(2x4)

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The structure of the GaAs(001)-(2x4) surface has been the subject of considerable controversy. We have fitted tight-binding parameters to Local Density Approximation (LDA) results. Using a linear scaling tight-binding method we have been able to model sufficiently large unit cells to investigate the energetics of dimer row kinking, which provides strong evidence to support the identification of the β phase with the trench dimer model. Having done so, we returned to LDA calculations to investigate the interaction of the important CBE growth precursor tri-methyl-gallium (TMGa) with the surface, in order to identify both the mobile precursor structure and the final bonded structure.

First principles simulation of nanoindentation and Atomic Force Microscopy on silicon surfaces

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Total–Energy pseudopotential calculations, implemented on a massively parallel computer, are used to study the interaction of a tip with a silicon surface in two relevant regimes: close mechanical contact in the nanoindentation experiments, and, weak attractive forces in the AFM operated in the non–contact mode.

In the case of nanoindentation, the goal is to understand the onset and development of plasticity in the indented material. Plastic flow of atoms towards interstitial positions and extrusion of material towards the tip walls, induced by the non-uniform volume strain and stabilized by the adhesive interactions with the tip, are the dominant mechanisms. The delocalization of the charge induced by the stress in the elastically compressed structure triggers these plastic deformations. The adhesive interactions, disregarded in many continuum approaches, are also shown to be responsible for the friction through the induced stick–slip motion of Si atoms along the walls of the tip, the hysteric behaviour observed in the simulations pulling the tip back from different stages of the indentation process, and the recovery of plastic strains during unloading. The onset of irreversible damage is related to the plastic deformation of the second double layer of the silicon slab. The effects of temperature and strain rate on the indentation process are considered by calculating the energy barriers between the different stable structures found in the total–energy diagram and their variation with strain.

The simulations of the non–contact AFM have been motivated by the recent report of atomic resolution images of the Si(111)–7×7 using this technique (F. J Giessibl, Science, 267 (1995) 68). Our results show that the range of operation, the values of the force, and the images determined experimentally, can be understood as a result of the interaction of the tip with the adatoms in the surface. Atomic resolution contrast is enhanced by the interaction between the dangling bonds of the adatoms and the apex atom in the tip. The contrast mechanism is related to the coupling between the tip and the charge transfer modes among the different dangling bonds in the surface.

Clusters, nanostructures and interfaces

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Computer-based modeling and simulations provide deep insights into the structural, dynamical, and mechanical properties of materials and the fundamental mechanisms of materials processes in various phases and degrees of aggregation. In this lecture we discuss computer simulation methodologies, including large-scale classical molecular dynamics (MD), ab-initio Born-Oppenheimer local-spin-0density (LSD) functional MD, and "all-quantum" simulations combining BO-LSD-MD with a path integral quantum mechanical treatment of the nuclei. These methods will be illustrated via investigations of:

- size-evolutionary patterns of materials properties, from molecules to clusters
- protonated water clusters
- fission of charged metallic and molecular clusters

- formation and properties of interfacial solid and liquid junctions
- studies of nano-elastohydrodynamics of complex liquids in lubricated sheared junctions

The importance of combined modelling and experimental studies for characterising semiconductors

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Defects in semiconductors can exist in unexpected structures and exhibit unusual properties dependent on charge state and mode of preparation. In addition, in many cases the defects are not in their lowest energy states but rather in a state of frozen equilibrium. their chemical composition is often unknown along with their crystalline state: ie the number of interstitial versus substitutional components. all this makes *ab initio* modelling extremely difficult. Real progress can come from combined experimental and theoretical investigations and examples of such investigations are presented. The important conclusion is that far from the *ab initio* modeller being able to do away with the experimentalist, the need for close collaboration is stronger than ever.

Chemical Potentials and Defect Energies in Ordered Alloys

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The calculation of defect energies in ordered alloys has been problematic because it is necessary to account for the chemical potentials of the species. These depend on alloy composition and three independent point defect formation energies. This is important for the comparison of energies of grain boundaries of alternative structures, even in the static limit (0 K). A consistent approach to dealing with the problem is described and illustrated by calculations of grain boundaries in NiAl. It is shown how the point defect formation energies determine the relative stability of boundary structures.

Defects and photo-induced processes in ionic nano-clusters

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We have developed a new computer code for studies of defects in clusters and their aggregates in order to model the mechanisms of defect processes in nanometer size clusters and highly dispersed powdered materials used in surface science and catalysis. In this approach a quantum cluster including several tens of ions is embedded in a much larger cluster (nano-cluster) which is treated using interatomic potentials and shell model for ionic polarisation within the GULP computer code. Polarisation of the nano-cluster is produced by an electric field due to ionic displacements and difference in the charge density distribution in the defect area treated quantum- mechanically, with respect to a 'reference system'. The polarisation potential is then included in the elements of the Fock matrix and the whole procedure is repeated until the total energy of the combined system does not change. The reference system may be a relaxed cluster of any form, with or without impurities. It is treated first completely quantum- mechanically to obtain an electronic structure and charge density distribution which is then used to calculate electrostatic interactions in studies of defects in this system. For quantum-chemical calculations we are presently using a semi-empirical technique based on an unrestricted Hartree- Fock method and the CLUSTER computer code. Optical transition energies are calculated using the configuration interaction technique for single excitations. We are currently working on implementation of the GAUSSIAN code within the same approach.

First applications include: i) studies of geometric and electronic structure and optical absorption of (MgO)n clusters (n=32,64,108) as a function of the cluster size and structure of cluster edges (number of steps, kinks and corners); ii) studies of geometric and electronic structure and optical absorption of [Li]0 centres at different positions within these clusters; iii) studies of decomposition of these clusters due to exciton excitation and hole trapping at low- coordinated sites. We suggest an interpretation for the optical absorption and photo-luminescence spectra of highly dispersed MgO. For the hole centres, we have determined the preferred

sites for the trapped holes and [Li]0 centres with respect to the edges and low-coordinated sites of these nano-clusters, and have calculated their optical transitions. We have also developed a new model for photo-induced decomposition of rough MgO surfaces based on exciton trapping and decomposition at low-coordinated sites at the surface.

Defects, interfaces and metastability in compound semiconductors

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The coupling between the electronic and ionic degrees of freedom in compound semiconductors leads to a wealth of interesting phenomena, such as metastable defects, self-compensation and negative-u effects. I present results of first-principles simulations of vacancies, antisites and dopants in these materials, as well as atomic structures and band offsets at planar interfaces. In particular, divacancies and dx/ax centers in GaAs, antisites in GaN and band offsets for interfaces between ZnSe and III-V alloys are discussed.

The ab initio simulation of liquid semiconductor alloys

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In the last few years, dynamical ab initio simulation has become a major tool in the investigation of solids and liquids. This talk will outline the main features of ab initio simulation based on density functional theory and the pseudopotential method, and will show how it is giving important new insights into the structure and dynamics of real liquid semiconductors. Illustrations will be taken from recent work of the Keele group on the liquid alloys Ga/Se and Ag/Se.

Poster Abstracts

MD-Simulation and superhard materials: An empirical potential for Boron Nitride ?

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We discuss an empirical interatomic potential, which could be a promising candidate for MD-Simulations of c-BN thin film deposition. A cluster functional is proposed combining a modified Tersoff potential and a coulombic part. Results of first-principle calculations done by a DFT pseudopotential code are shown and discussed as data base for an optimal parametrization of the proposed potential.

Studies of tRNA^{Asp} Dynamics and Interactions - Part I: Solvated Molecular Dynamics Investigation of the Structuring Effects of Long-Range Hydration Forces on the Anticodon Loop

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A set of six independent 100 psec molecular dynamics trajectories of the fully solvated and neutralized anticodon loop of tRNA^{Asp} [1] were generated using the AMBER force field, SPC/E waters, mobile ammonium counterions and atomic charges from low temperature X-ray data of isolated nucleotides [2] starting from the same initial configuration, but with different initial velocity distributions. The protocol consisted of using a 16Å truncation distance for the electrostatic *solute-solvent* and *solvent-solvent* interactions and no cutoff for the *solute-solute* interactions. This led to an increased stabilization of the structural interactions of the anticodon loop over an earlier set of eight 100 psec simulations using an 8Å truncation distance for the interactions involving the solvent. [3] The results point to the importance of the inclusion of such long-range hydration forces in molecular dynamics. The increased stability of these trajectories allowed us to complete an extended analysis of the dynamical features of some of the main interactions stabilizing this RNA fragment. The observance of C-H ... acceptor hydrogen bonds located in structural strategic sites of the anticodon loop throughout the MD trajectory is presented, as well as dynamical global and detailed structural characteristics of the structure, its solvation, and some pertinent differences observed between the present set and the 8Å set. Additionally the relevance of running multiple molecular dynamics simulations is also discussed.

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[2] Pearlman, D. A., Kim, S. H., *J. Mol. Biol.* **211** , 171-187 (1990)
[3] Auffinger, P., Louise-May, S., Westhof, E. *J. Am. Chem. Soc.,* (1995), in press.

Molecular Dynamics simulations on DEMOS

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The Delft Molecular Simulator (DEMOS) is a special purpose computer designed and build for large scale Molecular Dynamics simulations. It consists of a linear array of processor boards each equipped with a fast 40 MHz i860 RISC processor, and large on-board memory (32 - 128 Mb). Neighbouring boards are able to communicate through an asynchronous inter-processor bus (max 64 Mb per sec), independent of any other board, thus reducing latency to a minimum. Additional communication is handled by a global bus connecting all boards and the host computer, which provides for storage and program control. See figure.

Many potentials used for molecular modelling consist of short-ranged interactions between atoms. This fact can be exploited by linear domain decomposition of the computational box into slices of size larger than the potential cutoff radius. In that situation, only communication between neighbouring processor boards is required, which is extremely fast on DEMOS. In some cases long-range forces like Coulombic interactions are present and special techniques can be applied to handle these interactions correctly and still make use of the parallel architecture of DEMOS.

A molecular dynamics program has been written and is currently used for simulation of solid silicon-germanium superlattices and silicon-oxide structures. Focus is on growth and structural aspects. Preliminary results will be shown.

An Ab Initio Study of the Compressional Mechanisms of Forsterite at High Pressures

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The compressional behaviour of forsterite (Mg_2SiO_4) is of considerable interest to geophysicists since it is the major phase in the upper mantle and interpreting seismic data requires accurate values for bulk moduli. Forsterite is comprised of isolated SiO_4 tetrahedra linked by chains of edge-sharing distorted octahedra occupied by magnesium ions. Experimental data have led to the suggestion that there are discontinuities in the compressional mechanisms at about 8 GPa and 40 GPa. The low pressure change is thought to be due to one of the Mg-O bonds becoming essentially incompressible at about 8 GPa. In order to test this we have performed ab initio LDA calculations using the parallel code CETEP on the Cray T3D at Edinburgh. Extremely good agreement is found between the compressibility of the calculated cell parameters and the experimental data. In contrast to the experiments, however, we find no evidence for discontinuities in compressional mechanism at any pressure up to 70 GPa and suggest that the experimental data has been overinterpreted.

Molecular dynamics simulation of LaF_3 nano-clusters

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A new molecular dynamics code has been used to simulate the behaviour of *in vacuo* LaF_3 nano-cluster (i.e. no periodic boundary conditions). The method is based on a Gear 5th order predictor corrector algorithm with recursive generation of initial variables. Forces are calculated using a Born-like description of an ionic lattice.

Three clusters were simulated, consisting of 160, 552 and 3120 ions respectively. A linear heating rate was applied of 100K per ps starting from clusters equilibrated at 10K. Our interest is in three transitions. The first is at ~1100 K and corresponds to the onset of fast fluorine ion conduction. The second is at ~1600K at which point all clusters melt. Finally at much higher temperature (~4000K) evaporation occurs.

Despite the ionic description of forces, throughout the temperature range we observe short-range structures which are reminiscent of molecular-like behaviour.

An *ab initio* Study of a Σ15 (210)[001] Tilt Grain Boundary in the Transition Metal Dioxide TiO_2.

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The microscopic properties of a high-angle tilt grain boundary in rutile (TiO_2) have been investigated via the density functional pseudopotential approach. Combined electronic and ionic relaxation was performed using self-consistent Conjugate Gradient minimisation of the total energy functional. Optimised pseudopotentials were used for titanium and oxygen, at an energy cutoff of 500eV. The model supercell contained 60 atoms and two grain boundaries. The calculations confirm the stability of the experimentally observed translation state of the boundary. Under stoichiometric conditions, the structure can be characterised by an oxygen sublattice which is mirror symmetric across the boundary. The resulting density of electronic states indicates the presence of interface states spread across the forbidden band gap of the bulk material. The pseudovalence charge density is highly localized on the oxygen ions even in the boundary core. The effect of oxygen loss at the boundary on the atomic and electronic structure has also been investigated. All calculations were performed with the parallel code CETEP (Cambridge-Edinburgh Total Energy Package) running on the Cray T3D at Edinburgh Parallel Computing Centre.

Generation of Amorphous Silicon Structure on Si(110) Surface by a Continuum Monte Carlo Simulation

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A silicon structure is grown on a substrate of a two layer slab of crystalline silicon (110) surface using a semi-empirical potential energy function parametrized for simulating silicon systems. The growth is realized by means of continuum Monte Carlo at 600^0K. Radial distribution functions for the resulting amorphous structure are obtained and compared with experimental curves.

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Parallel Molecular Dynamics simulations of growth and structure of silicon-germanium superlattices

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Most potentials used for modeling of tetrahedral structures of silicon and germanium can be expressed as the sum of short-ranged pair- and triplet-interactions. Parallelization of an MD program using these potentials can be done by dividing the computational box into slices larger than the cutoff distance of the potential. Calculation of the forces in a slice then only requires communication with the two neighbouring slices. The special purpose computer DEMOS in Delft is especially designed and built for this kind of local environment problems which require optimized neighbour-to-neighbour communication (see poster by J. Beckers et al.).

An MD program for two- and three-body interactions has been written and its performance on DEMOS proved adequate. At the moment it is used to simulate the growth and structure of silicon-germanium superlattices (Si_nGe_m) for which the precise growth-mechanisms taking place at the germanium-silicon interfaces are being argued[1,2,3,4]. Preliminary results of the simulations will be shown.

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Molecular Dynamics Simulation studies of antibiotic mediated ion transport

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The selective transport of cations across biological membranes is a process of fundamental importance in cell biology. This transport is facilitated by the presence of small amounts of antibiotics, and broadly two modes of action have been identified involving channels and ion carriers. Valinomycin (VM) is an important example of a carrier antibiotic with high potassium selectivity. For ion carriers three distinct processes appear to be involved. (i) Complexation between the cation and a membrane bound antibiotic, (ii) transport of the complex through the membrane by diffusion or electrophoresis, and (iii) cation release at the membrane interface. Concentration gradients are thus ameliorated by the capture and release of cations on the two sides of the membrane.

We have developed a force field for the Valinomycin and used it to model crystalline phases of both VM and the potassium complex. Both VM and K^+-VM have been studied in water and a non-polar solvent along with the complexation process in free space. We also report large simulations of valinomycin and its potassium complex at a water/membrane interface. The simulations, involving almost 19,000 atomic sites, cover a total of over 500 ps and are used to examine both VM at the interface and the K^+ decomplexation reaction. The calculations demonstrate the feasibility of large scale simulations of complex systems. They were achieved using the recently introduced parallel supercomputing facility at Edinburgh as part of the work of the HPCI Materials consortium.

The studies show uncomplexed VM acts as a surfactant with hydrophobic groups embedding in the membrane while the hydrophilic carbonyl groups hydrogen bond with water. Consequently the conformers VM adopts at the interface are quite distinct from those seen in the solid state or in bulk solution where most experimental measurements are made. In contrast, the K^+-VM complex prefers the membrane interior and adopts a structure close to that seen in the solid state and in non polar solution. It remains embedded in the membrane until the decomplexation process is initiated by water attack through the HyV face. The decomplexation process at the interface is considerably faster than that in pure water and points to the role of the interface itself in the function of carrier antibiotics such as valinomycin.

Predicting growth processes; Atomistic modelling of metal atoms on ionic substrates

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We show that it is possible to use existing methods, well-tested for many other systems, to predict the key energies which determine the growth mode (layer, cluster, etc.) of metal deposited on ionic solids. The results agree well with experiment.

We show further that these energies can be used within a further theory of nucleation to predict the nucleation density and other properties as a function of deposition rate and temperature. In particular, this analysis shows how it is possible that Ag on MgO can form an (observed) metastable layer.

These developments suggest ways to influence the growth mode and morphology of metal on oxide, including the effects of the bulk doping of the oxide and the pre-treatment of the substrate surface, as well as control of deposition rate and temperature.

The approach already allows links to be made between metal morphology and interfacial energies between bulk metal and bulk oxide, though the link is not as simple as sometimes supposed.

The models used have potential for understanding the operation and degradation mechanisms of operating sensors and catalysts.

A parallel conjugate gradient algorithm for ab-initio energy minimization

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The ab-initio molecular dynamics technique evolves simultaneously the ionic and electronic degrees of freedom in time. In the field of solid state physics, this method is now widely used to perform total energy calculations, i.e. to find the electronic ground state and to optimize the ionic geometry of a configuration.

The search for the electronic ground state is most efficiently done by employing a conjugate gradient algorithm. We present the implementation of such an algorithm on a distributed memory parallel computer. Our implementation divides the electronic states over the nodes, so that the gradients can be calculated in parallel (apart from a global summation to obtain the effective local potential).

Once the electronic ground state has been found a variety of interesting properties can be calculated. We will illustrate this for a Si(001) surface with an adsorbed Si dimer.

The ab-initio simulation of the liquid ga-se system

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Ab-initio dynamical simulation has been used to study the liquid Ga-Se system at several different concentrations including Ga_2Se, $GaSe$ and Ga_2Se_3 at the temperature 1300 K. The simulations are based on the density functional pseudopotential technique, with the system maintained on the Born-Oppenheimer surface by conjugate gradients minimization. We present results for the partial structure factors and radial distribution functions, which reveal how the liquid structure depends on composition. An analysis of the valence electron distribution allows us to examine how the chemical bonding depends on the apparent valence of Ga. Our calculations of the electrical conductivity σ using the Kubo-Greenwood approximation show that σ depends very strongly on composition, and is roughly three orders of magnitude lower at the stoichiometric composition Ga_2Se_3 than for pure $\ell - Ga$. We show how this variation of σ is related to the calculated electronic density of states. Comparisons with recent experimental determinations of the structure and conductivity will be presented.

Study of The Pressure Effects on Vibrational Properties of Layered Semiconductors

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The lattice dynamics of layered materials has been found to be different from 3- dimensional covalent crystals because of the coexistence of weak interlayer and stronger intralayer coupling. The weakness of the interlayer cohesion in layered semiconductors makes Raman- and infrared-active vibrations nearly degenerate and induces the very low-frequency optical phonons which are described by the rigid-layer (RL) model. It is expected that these vibrational properties of layered compounds will be affected dramatically under compression while the hydrostatic pressure preferentially enhances the interlayer interaction.

In this poster, the vibrational properties of prototypical layered semiconductors, GeS and GeSe, under pressure have been extensively studied using a combination of first principles calculation and experimental methods. Examination of *ab-initio* calculated phonon eigenvectors shows that the vibrational properties undergo a gradual transition from quasi-two dimensional to three-dimensional character. Also, the breakdown of RL approximation has been found to occur under modest compressions

The liquid Ag-Se system studied by ab-initio simulation

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The ab-initio dynamical simulation of liquids containing transition and post-transition metals presents a major technical challenge, because of the need to include d-electrons explicitly and because of the large basis sets required. We show how recent advances in computer power are making such systems accessible to simulation. We present ab-initio simulations of the Ag-Se system at three concentrations performed on the massively parallel Cray T3D machine. The simulations are performed on systems of 69 atoms at the experimentally interesting temperature of 1300 K, and have a duration of 3 ps, which is enough to ensure statistically reliable results. Results are presented for the partial radial distribution functions and structure factors, and we show that these are in excellent agreement with measured structural data.

Interstitial Carbon Defects in Silicon

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The C_i and $C_s - C_i$ defects in Si exhibit several unexplained properties. In the neutral charge state, the C_i defect possesses two almost degenerate vibrational modes suggesting a trigonal defect in disagreement with the C_{2v} symmetry deduced from several experiments. The B-form of the second defect is believed to consist of a Si interstitial, Si_i, located near a BC site between two C_s atoms, in apparent conflict with the results of PL experiments which show that the C-related vibrational modes are decoupled. The structure and vibrational modes of both defects are analysed using LDF cluster theory. The degeneracy of the modes of C_i is attributed to an almost $\mathbf{D}_{3h}$ structure, with a 3-fold axis along $[01\bar{1}]$. The modes of the di-carbon interstitial lead to a resolution of the long standing problem concerning the almost zero-shifts due to mixed isotopes in the 580 and 543 cm^{-1} local modes observed in PL studies.

Simulation of X-ray Scattering from $C_{10}H_{16}$

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Adamantane ($C_{10}H_{16}$) is an interesting archetypal plastic crystal which has been extensively studied. It undergoes transition from a low temperature ordered phase to a high temperature disordered phase at T=208.6K. The $C_{10}H_{16}$ molecule has tetrahedral symmetry and the orientational disorder in the plastic phase has been interpreted in terms of the distribution of the molecules between two equally preferred orientations.

Our simulation model consists of rigid molecules interacting with an (exp -6) atom-atom pairwise additive potential. We have looked in detail at the dynamics of the adamantane molecules in the plastic phase and have found results in general agreement with previous work [1],[2].

The molecular trajectories generated by our simulation are being used to evaluate the intensity of x-ray scattering from the crystal. Results are being compared with experimental data obtained from energy-dispersive diffuse x-ray scattering measurements made on Station 7.6 at the Daresbury SRS. Using a series of simplified models of the crystal we aim to investigate the relative contributions to the scattering intensity from translational and orientational disorder.

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Studies of $tRNA^{Asp}$ Dynamics and Interactions - Part II: Conserved Interactions in Solvated Molecular Dynamics Simulations of the Thymine Arm

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The thymine arm fragment of transfer RNAs has been shown by chemical probing [1] and NMR [2] to be stable in solution, adopting the same secondary folding pattern as observed in the full tRNA molecule, and is postulated to possess an "intrinsic" tertiary structure. The thymine loop contains several unique tertiary structural motifs including a conserved reverse Hoogsteen ribothymine-adenine base pair, two uracil bulge residues and a U-turn in the phosphate backbone at the base of the loop. In the full tRNA molecule, eight additional potential hydrogen bonds, and two additional stacking interactions are introduced by the intercalation of two guanine residues from the D loop. The dynamical topology of the loop region of the thymine arm of $tRNA^{Asp}$ [3] , and the extent to which the D loop interactions stabilize the tertiary conformation of the loop topology, was studied via solvated molecular dynamics simulations using the AMBER force field, SPC/E waters, mobile ammonium counterions and atomic charges from low temperature X-ray data of isolated nucleotides [4] . A total trajectory of 600 psec constituted of six individual 100 psec simulations starting from the same initial configuration, but with different initial velocity distributions, was generated. Two of the simulations included the two guanine residue fragment of the D loop. The extent of conservation of the hydrogen bonding interactions preserving these structural elements is presented along with global characteristics of the simulations including solvation and counterion behavior.

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Full-potential and pseudopotential calculations on high pressure phases in CuCl.

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The ionic copper halide, CuCl, displays an unusual structural phase transition sequence under pressure. Using neutron diffraction experiments, two high pressure structures were observed. At ambient pressure, CuCl exists in the zincblende structure, while at elevated pressures it assumes the NaCl-type (rocksalt) structure via an intermediate simple cubic structure. This intermediate phase is the binary analogue of the metastable body-centered structure (BC8) seen in the elemental semiconductors Si and Ge. This is the first time this phase has been experimentally observed in a compound semiconductor, although it has been calculated to be a stable phase for the III-V semiconductors also.

Details of ab-initio total energy calculations on these three phases of CuCl will be shown here, using both the full-potential linearised augmented plane wave method (FLAPW) and the pseudopotential method. Band structures and charge densities will be shown for selected phases, along with details of recent work on the other copper halides, CuI and CuBr.

Computer Simulation of the Effect of Molecular Geometry upon the Formation of Nematic and Smectic Phases.

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Recent years have seen an upsurge of interest in ferroelectric and chiral smectic C* phases in liquid crystals. The first example of an achiral anti-ferroelectric phase has been synthesised from which Goodby et al [1] infer that chirality may not necessarily stabilise the formation of a ferrielectric and antiferroelectric phase but that the structure may be stabilised by the biaxial nature of the liquid crystal. Over the last few years computer simulations have demonstrated the success of simple potentials such as the Gay-Berne or hybrid versions [2] in the simulation of smectic phases. However, the Gay-Berne potential is axially symmetric and real mesophases are not uniaxial. The smectic C phase is a tilted analogue of the smectic A and the Wulf theory [3] associates the driving force to tilt the molecules with the molecules having a zigzag rigid central core whilst the McMillan model [4] depends upon the molecules having two large oppositely directed outboard electric dipoles. Two derivations of a generalised form of the Gay-Berne potential to include the effect of two arbitrarily stretched uniaxial gaussians and to include the effect of non-equivalent biaxial particles been proposed [5]. However an alternative route to model the molecular geometry is to employ a multi-site Gay-Berne model. In this work we present preliminary results from molecular dynamics simulations of three-site molecules where each site is represented by a Gay-Berne mesogen spaced so that the repulsive core regions overlap. Various three site models have been compared : a cylindrically symmetric model, a zig-zag model with the central site twisted at an angle to the two end sites and a triangular model with one site displaced longitudinally form the other two. Results indicate a far more extensive nematic region for the triangular model compared with the zig-zag model indicating the importance of the molecular geometry in determining phase transitions.

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Ab-initio Predictions of Omega Phase Stability for Intermetallics of Transition Metal Based Alloys.

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It is well known that the directional nature of the covalent bonding between different atomic species tends to cause intermetallics of transition metal aluminides to be brittle. One strategy for overcoming the brittle behaviour has concentrated on the effect of ternary transition metal additions to intermetallic phases like Ti-Al and Nb-Al in order to induce more ductile alloys with the B2 structure. Unfortunately, it has been found recently that omega phase formation may drastically embrittle the parent B2 phase [1]. It is therefore it is very important to study the stability conditions under which this deleterious phase is likely to occur.

A data base for the theoretical structural trends of 3d and 4d transition metal aluminides has recently been generated using the first-principles Full-Potential Linear Muffin-Tin Orbitals (FP-LMTO) method [2]. Based on this systematic study of the bonding of intermetallics, we have carried out ab-initio calculations of the omega phase in transition metal based systems like Al(Ti, V, Zr, Nb) and Ti(V, Mo, Zr, Nb) and also in the related pure elements. Our calculations have greatly increased the amount of information we have on the microscopic mechanisms of structural B2-Omega transformation. We find that there are three important effects exhibited in this transition: (i)the presence of "soft phonon" modes, (ii) influence of high pressure and (iii) the size factor of the transition metal elements. The calculations have also demonstrated the importance of the omega phase as the most stable phase with 50:50 stoichiometry in NbAl. The predicted curves of the omega phase heats of formation versus an elementary electron/atom ratio are in good agreement with experimental data obtained from the measured diffuse omega peak shift versus e/a. As a result of these calculations, we are now able, for the first time, to make realistic calculations of the phase diagrams of useful intermetallic ternary alloys based on Nb3Al and TiAl for structural applications.

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Potential for a Novel Muon Experiment - Simulation Results

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Predicted results for a novel muon spectroscopy experiment are described. The results come from static and dynamic *ab initio* density functional calculations of ethanal + muonium, using the PAW technique [1]. The potential binding sites for the muonium are evaluated, along with the associated (stretching) vibrational frequencies and the Einstein coefficients for the vibrational transitions. These vibrational frequencies occur in the near IR, and so are well separated from other vibrational frequencies and also from any electronic transitions

This opens up the possibility of a new form of muon spectroscopy. If these vibrations were to be optically excited, then the resulting change in the environment of the muon should be detectable in the μSR signal.

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The Interaction of the SO_2 Molecule with the TiO_2 Surface

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Ab initio calculations have been used to study the structure of the TiO_2 (110) surface in which surface oxygen has been replaced with sulphur, and to obtain preliminary estimates for the energy of reaction of the O2 and SO_2 molecules with the reduced surface. The work is motivated by experimental work which shows that SO_2 reacts very readily with the reduced TiO_2 surface. According to ultraviolet photoelectron spectroscopy (UPS) measurements, the reaction leads to the incorporation of sulphur into the surface crystal structure. The calculations are based on density functional theory and the pseudopotential method, and have been performed with the CETEP code on the Daresbury Intel parallel computer.

Model study of $[Li]_0$ -centres in MgO nano-clusters

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A common model in the study of surface defect sites is that of an infinite surface hosting the defect area. In cases of practical relevance (catalysis), however, one rarely encounters these extended low-index surfaces; rather the assumption of nano-clusters seems more appropriate. In this present study we follow this idea by embedding a quantum-mechanically treated cluster (QM-cluster) into a nano-cluster, which in turn is treated in the framework of interatomic potentials and the shell model for ionic polarisation (for technical details see also the paper by A. L. Shluger et. al., this meeting)

In the application to a $[Li]_0$-centre in MgO, clusters of various sizes have been tested to study the quality of the suggested model. The formation of a pair of substitutional Li and an electron hole localized on the adjacent oxygen anion was studied both in the bulk and on the surface of the nano-cluster. Cubic clusters $(MgO)_{64}$, $(MgO)_{108}$ and dimers of $(MgO)_{64}$ were used to model these situations. Geometric and electronic structure were determined as well as optical absorption properties.

In the study of the cubic clusters, a clear tendency of the hole to localize on the corner is established. Comparison with analog cases in a stepped dimer of two cubic clusters show, that the presence of the second cluster has little influence on the results obtained from the single cluster. There are, however, new possible sites arising from the presence of the step, namely at the bottom of the step. They are compared to the cases existing in the simple cubic model.

Chemical Modelling of Glassy Polymer and Composites with Flexible Bond Angles

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Molecular Mechanics Computer Simulation was applied to modelling of polymer glasses, i.e. the produced model structures represent minimum energy configurations. Atatic polypropylene was used as model polymer. Macroscopic density at -40 °C was guaranteed by three dimensional periodic boundary conditions. Unlike former works on this subject a model which includes not only torsion angles as degrees of freedom but bond angles too, was develloped. Both macroscopical and structural properties were examined. Structural properties like mean square of end-to-end distances were obtained directly by the minimum energy configuration. Elastic constants, internal pressure and thermal expansion coefficient were computed by deforming the originally simulated model structure. The results were compared with those of other model computations and experimental data. The method described above was also applied to polymer-graphite-systems. Results for structural and thermodynamic properties of the interface were shown.

Defects on the 90° Partial Dislocation in Silicon

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Simulations of the motion of defects of the 90° partial dislocation in Si are carried out using the Tersoff interatomic potential. Low energy paths corresponding to the motion of kinks, antiphase defects (APDs) and kink-APD complexes are found using a conjugate gradient elastic band method. This method gives the coordinates of the atoms as well as the energy of the system along the path and in this way we obtain the migration energy of these defects (energy at the saddle point configuration). The results obtained are a first step towards understanding the changes in the electronic structure associated with dislocation motion and the dependence of the mechanical properties of Si on its electronic structure.

Theoretical Studies of Implanted Muons in Organic Magnets

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Wholly organic ferromagnets are a new class of materials of great potential interest, but the early examples exhibit only very weak magnetic order at very low temperatures [1]. In these circumstances, muon spin rotation μSR is among the most sensitive sources of information about the magnetic structure and interactions on a molecular scale [2]. However, interpretation of the μSR data is complicated because of the large number of binding sites made possible by the relatively complicated molecular structure.

We have performed semi-empirical and *ab initio* density functional calculations of the electronic and molecular structure of muonium incorporated into the organic ferromagnets *para* -nitrophenyl α-nitronyl nitroxide (*p*-NPNN), 3-quinolyl nitronyl nitroxide (3-QNNN) and *para* -pyridyl nitronyl nitroxide (*p*-PYNN). We find evidence for a wide variety of possible muon binding sites including sites in the conjugated ring systems of the materials as well as in the nitronyl nitroxide group. Our calculations also suggest the formation of local triplet electronic states near the muon within the spin-1/2 magnetic system.

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Full structural relaxation using density-functional theory

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The widely-used `CASTEP` and `CETEP` codes have been modified to allow full structural relaxation, enabling the unit cell to be optimised as well as the ionic positions. The equilibrium structure of complex triclinic crystals can now be found automatically. Further development will allow constant-pressure molecular dynamics simulations, offering the possibility of observing phase transitions.

Simulations are performed with a constant number of plane waves, to ensure that no charge is lost, but if the supercell changes then so will the energy of the highest plane wave, effectively altering the energy cutoff. A Pulay correction to the stress and total energy has thus been used: the practical implementation of this technique and the limitations to its use are discussed. We further modify the Parrinello–Rahman Lagrangian to work with the strain rather than the supercell vectors, to preserve the symmetry of the supercell.

Examples of simulations with cell relaxation are given, illustrating the applications and restrictions of the code, and explaining the choice of box mass and timestep. Further refinements to the code are suggested.

Dynamical instabilities in a-quartz and a-berlinite: A mechanism for amorphization

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Elastic instabilities have been used to explain the occurrence of amorphization in both α–quartz (SiO_2) and α–berlinite ($AlPO_4$). However, there is a dynamical instability at (1/3,1/3,0) in the Brillouin zone preceding the elastic instability for both structures which implies that distortion of a 3x3x1 supercell will form a more stable crystal structure. Simulations of distorted supercells of size 3x3x1 resulted in the collapse of the structures below the elastic instability pressures for both α–quartz and α–berlinite. A subtle difference between them was that the eigenvectors for phosphorus were smaller than those of silicon or aluminium and on 'amorphization' the PO_4 units in α–berlinite remained completely intact with only the aluminium changing coordination. This resulted in amorphization around the PO_4 units with no P-O-P links formed and a return to a crystalline phase on the release of pressure for α–berlinite, which was not found in the simulations of α–quartz.

Computer Simulation in the Physics of Contact Melting Phenomena

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Contact melting (CM) is a phenomenon at the interface of two heterogeneous bodies that occurs at a lower temperature than the melting point of each component. CM is the first-order transition with its specific distinctive indications, mechanisms and kinetics. Detailed studies of the contact melting phenomenon highlight the contact melting nature and allows wide application of the phenomenon in various technologies. Computer simulation is a powerful new technique that enable us to investigate the contact melting for the model system without cumbersome experiments. It allows us to obtain a connection between macroscopic CM phenomena and its microscopic characteristics, and dynamical properties of the constituent components, such as: the ion radius, the potentials of interactions in the system, the dynamic structure factor, the diffusion factor and other characteristics of the microstructure of the system.

In this paper the scientific software for the simulation of contact melting phenomena was developed. The software includes the direct Molecular Dynamic (MD) simulations and numerical solutions of the Nernst-Plank (NP) equation. In the MD experiments the data on ion coordinates and other results can be displayed on a monitor in the graphic form. The programs can be used for calculations of the mean square displacements, the diffusion coefficients, the radial distribution functions, the normalized velocity autocorrelation functions, and the contact melting temperature. The method was applied for the analysis of the KBr - NaBr, NaI - KI, NaI - NaCl and other typical ionic systems. The numerical solutions of the NP equations allows us to calculate the concentration distributions of ions in the melt. Investigations were conducted for different double nitrate, nitrite and alkali-halide systems.

From the Molecular Dynamics analysis the result was obtained that the form of the first maximum of the partial radial distribution functions are non-symmetrical, it means that the effects of anharmonicity are dominant in this region. The mean square displacements of Na and Cl ions in the NaCl-RbCl system grows faster than in the NaCl-KCl system and in the NaCl one component system. The calculated diffusion coefficients are sensitive to the CM temperature and can be used for its valuations. The mobility of ions in CM depends on the interface and arrangements of ions in the contacting crystal lattices. Local domains, consisting of mobile ions, of the size of 2 nm can be observed during a time of 10 ps. It reflects the appearance of the liquid phase in the interface. The results of the numerical calculations of the NM equations show a strong dependence of the interdiffusion coefficient on the concentration, on the external fields and on the charge of the diffusing ions. The results obtained lead to the elaboration of the methods for the control of the contact melting process and allows us to predict optimal conditions for the contact melting in practice.