Mineral Physics with Computation and Experiment

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1 Workshop Details

1.1 Details

Timing
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Location of the activity
CECAM
46 allée d’Italie
69007 Lyon
France

1.2 Description

No description provided

2 Requested Support

ESF

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CECAM workshop Report

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4 Presentation List

Benchmarking for mineral simulations

Michele Warren

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Abstract

Workshops such as this one illustrate well the abundance and diversity of research groups and simulation methods for computational mineralogy. As the number of methods increase it has become increasingly hard to make meaningful comparisons between them. Since extensive testing of new codes or methodologies can be very resource intensive, it rarely extends to the larger unit cells and demanding electronic structures typically required for minerals.

The quantum chemistry community have for many years used a set of molecules to define benchmarks for their codes, in order that codes may be tested and approximations compared. We have started to explore the possibilities for a similar benchmarking methodology for mineral simulations. One promising possibility is to use emerging e-science tools to facilitate collection and comparison of results from different codes and contributors.

Some initial plans and questions are presented, with the intention of stimulating debate about how this initiative could be most useful to computational mineralogists and most appealing to code developers. A possible set of minerals and types of simulation outputs, devised at a previous CECAM meeting, will be presented so that they can be reviewed in the light of continuing developments. The overall aim is to obtain a better understanding of how methodology affects results in mineral simulations, which mineral properties are hardest to calculate accurately and which factors have the greatest effect.

Chemical reaction between iron and oxides at core-mantle boundary

Leonid Dubrovinsky

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Abstract

Studying of chemical reactions in the megabar pressure range, and temperatures exceeding 2000 K is not a trivial task. The amount of reacted material is very small (in the order of a few wt. percent, or, in absolute values, in the order of 10-10 g). Despite high temperatures, spatial temperature distribution across the pressure chamber is not homogeneous. The material can be partially, or completely lost when the cell, containing the recovered sample, is opened. Combination of different modern analytical techniques (synchrotron based X-ray powder diffraction, Mössbauer and Raman spectroscopy, SEM, ATEM, etc.) allows the elucidation of major trends in the behavior of the geophysically and geochemically important metal-oxide (Fe-SiO2, Fe-Al2O3, MgO-FeO, Fe-MgSiO3, for example) systems at pressures and temperatures of the Earth's deep interior. Methodological aspects of investigation of chemical reactions in DACs and in large volume apparatus are also considered.

First-principles calculation of stable isotopes fractionation

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Abstract

Quantitative modelling of isotope fractionation is a key-problem in geochemistry. Difficulties to extract information from empirical data, as well as the experimental impossibility to access fields of low temperature for kinetic reasons, justify the quest for alternative approaches to this problem. In this context, the study of hydrogen fractionation in the kaolinite/water system is a fundamental issue, for this system is used as a low-temperature geothermometer, whereas experimental data are limited to temperatures above 170 degrees Celsius. Equilibrium isotopic fractionation is a thermodynamic property which is determined by the vibrational properties (phonons) of the system. Within a simplified approach, the isotopic fractionation can be extracted from the knowledge of the vibrational energy levels of the material. This path has been explored by several authors, using experimental vibrational informations to calculate isotope fractionation factors. Their calculations were mostly based on semi empirical models.

In our work, we go beyond this phenomenological approach and use ab-initio computational methods to determine the vibrational properties and, thus, the isotopic fractionation. Beyond the choice of a particular approximation to deal with a specific system, the ab initio methods have proved to be successfull in many areas of research in which they are nowadays commonly used, such as molecular spectroscopy, or semiconductor physics. Standard ab initio methods (total energy calculations) can be used to obtain the phonon properties at the center of the Brillouin zone of a crystal. More sophisticated techniques, such as the density functional perturbation theory approach (DFPT) are required to compute the dynamical matrix in any point of the Brillouin zone, and thus to obtain the complete phonon dispersion. This information is then used to calculate the free energy of a material of given isotopic composition. Equilibrium isotopic fractionation is related to differences in the free energy of materials of different isotopic composition. Selected examples of stable isotope fractionation in the system quartz, kaolinite, water will be presented.

Multiscale modelling of crystal growth from solution

Julian D. Gale

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Abstract

Crystal growth is an important process since it determines the size, shape and in some cases the purity of the crystallites of a material. Similarly this can impact on the properties of the system. Ideally we would like to be able to control the crystal growth process so that in some cases we can produce large single crystals of high quality and in other instances to suppress the formation, as is the situation for mineral scale. The formation of a crystal from solution is a complex process that represents a significant challenge to computational methods. Often the critical nucleus size can be too large for atomistic simulation and the growth process can be slow on the timescales accessible too. Consequently, no single theoretical method is suitable for tackling all aspects of crystal growth and so a multiscale approach is required. In this presentation, we will demonstrate how the combination of atomistic molecular dynamics and kinetic Monte Carlo simulation can be used to model the growth of a crystal at length and timescales comparable to those seen experimentally [1]. The molecular crystalline solid urea will be used as a first case example to illustrate the technique. Subsequently, the extension of this work to

simulate the growth of molecular ion containing minerals, such as barite, will be discussed [2]. Results will be presented that highlight the critical role that the solvent plays during surface growth and how it can determine the morphology of mineral crystallites.

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Modelling defects in minerals

Kate Wright

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Hydrogen bonding in minerals

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Ab initio calculations of lattice friction in minerals

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Atomistic simulations of frustrated magnetic ordering in the ilmenite-hematite solid solution

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Abstract

The magnetic ordering behaviour of ilmenite-rich (⟩ilm90) ilmenite-hematite solid solutions is being studied via Monte Carlo simulation. The low-temperature, ilmenite-rich part of the ilmenite-hematite phase diagram exhibits complex magnetic properties, with antiferromagnetic, paramagnetic, superparamagnetic and spin glass regions present. In particular, not much is known about the spin glass region, other than the fact that it is related to frustration between the ilmenite and hematite ordering schemes. The main purpose of the simulations is to try to gain insight into what could be happening in this region.

We use a pair interaction model Hamiltonian for the magnetic interactions between iron cations in both 2+ and 3+ oxidation states. This Hamiltonian restricts the orientation of spins to the basal plane but allows their magnitudes to vary according to the rules for a spin-S system (i.e. 2S+1 values from -S to +S). The values of interaction parameters are mostly obtained from experimental measurements and in some cases are tuned to reproduce correctly particular magnetic phenomena (e.g. the metamagnetic transition in pure ilmenite, Kato et al. 1982).

We perform simulations starting in both hematite-like (ferrimagnetic) and ilmenite-like (antiferromagnetic) configurations, to examine the preference for a particular configuration at a particular composition. Our simulations reproduce quite well the observed magnetic phase boundaries described by Ishikawa et al. (1985), e.g. decreasing ilmenite Neel temperature with decreasing ilmenite content. At ilm90 the hematite-like ordering is preferred, and around ilm94-96 there is definite competition between ilmenite-like and hematite-like ordering, until the system settles into ilmenite-like ordering at ilm100. The competition between ordering schemes is clearly reminiscent of spin glass behaviour, although further investigation is required because of the problems of performing Monte Carlo simulations at low temperature.

So far, our simulations have been performed at zero field and using the relatively simple Hamiltonian discussed above. We have also recently begun to perform simulations using a Heisenberg Hamiltonian (in which magnetic spins may take up any orientation, and there is a uniaxial anisotropy term indicating the orientational preference of spins), and also with the capability of cooling in a magnetic field. We envisage that these improvements will be useful in trying to elucidate further the properties of the ilmenite-hematite spin glass.

This research is supported by the European Science Foundation (ESF) under the EUROCORES Programme EuroMinScI, through contract No. ERAS-CT-2003-980409 of the European Commission, DG Research, FP6.

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High-energy X-ray scattering: Probing nano-crystalline and amorphous materials at high-pressure

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Abstract

Studies of the structural response to compression are important for the interpretation of macroscopic properties of materials and as a test of theoretical models. The anomalous compression and phase transition behavior of nanocrystalline materials at high pressure and the compression mechanisms and phase transitions in amorphous solid and liquid materials are examples for compelling problems, that require reliable structural data for their solution. The use of quantitative pair distribution function analysis has been proven to be a valuable method for developing and testing structural models for nanocrystalline and amorphous materials. However, measuring the total elastic scattering of a sample at high pressure, which is necessary for pair distribution function analysis, is technically very difficult. Recently, we have developed a methode whereby a high energy X-ray beam and a diamond anvil cell can be used to collect data from a sample at high pressure, suitable for pair distribution function analysis. In addition to the technique itself, several examples from nanocrystalline, glasses, and liquids at high pressure will be presented.

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DFT calculations with WIEN2k

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Abstract

Density functional theory (DFT) is frequently used to study the electronic structure of solids. The choice of exchange-correlation potentials can affect the results. The linearized augmented plane wave (LAPW) method plus the use of local orbitals [1] is the basis for the WIEN2k code [2] that is used worldwide (see www.wien2k.at) to simulate materials. This program package is one among the most accurate versions for DFT calculations. It is an all-electron, full-potential scheme which can include relativistic effects. The solutions of the corresponding Kohn-Sham equations lead to the total energy, the energy bands, the corresponding electron densities, from which the chemical bonding can be analyzed. The results allow to go from the electronic structure to (mechanical, electrical, optical or magnetic) properties of various solids. The electric field gradient (EFG) can also be obtained which is sensitive to the anisotropy of the charge distribution at a nuclear site. The total energy determine the relative stability of various phases and the forces allow the calculation of phonons by the direct method, so that structural instabilities or phase transitions can be investigated Some of these features will be illustrated in some detail for Y2Nb2O7 in the pyrochlore structure [3].

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Metadynamics simulations of structural phase transitions in crystals: the case of silica

Roman Martonak
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Abstract

Silica is the main component of the Earth's crust and is also of great relevance in many branches of material science and technology. Its phase diagram is rather intricate and exhibits many different crystalline phases. The propensity to amorphization and the strong influence on the outcome of the initial structure and of the pressurization protocol indicate the presence of metastability and large kinetic barriers. As a consequence theory is also faced with great difficulties and our understanding of the transformation mechanisms is still very sketchy despite a large number of simulations. Here, we introduce a novel and much improved version of the metadynamics method which finally brings simulations in close agreement with experiments. We unveil the subtle and non-intuitive stepwise mechanism of the pressure-induced transformation of 4-fold coordinated alpha-quartz into 6-fold coordinated stishovite at room temperature. We also pre-

dict that upon compression 4-fold coordinated coesite will transform into the post-stishovite alpha-PbO2 phase. The new method is far more efficient than previous ones and for the first time the study of complex structural phase transitions with many intermediates is within the reach of molecular dynamics (MD) simulations. This insight will help designing new experimental protocols capable of steering the system towards the desired transition.

References

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Superspace methods for structural description

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Abstract

The superspace formalism was introduced in the 1970s to treat aperiodic structures (Wolf, 1974; Janner and Janssen, 1977). Since then it has been successfully applied to the analysis of modulated phases, composite crystals and quasicrystals, whose lost periodicity in three dimensions

is regained by embedding the crystal structure into a higher dimensional space. While the application of this formalism to aperiodic structures can be nearly considered routine, a recent development has shown the usefulness of the approach to obtain, under certain circumstances, a unified description of families of compounds with varying composition (Boullay et al, 2002; Elcoro et al, 2003). In most cases, these compounds exhibit long-period structures whose size and symmetry depend on composition. The real structures can be described as a three-dimensional section of a virtual, periodic, (3+d)-dimensional structure, with a unit cell determined by an average structure common to all the members of the family. A single superspace motif (atomic domains) generates the different orderings of atoms (or vacancies) through modulation functions for the occupation with a wave vector fixed by composition. The analysis of various experimental cases of structures with one- and two-dimensional orderings has shown that the superspace motifs can be constructed following simple rules, and yet successfully predict atomic orderings for any composition.

This method has thus a high potential for the systematization of systems with a large variability in chemical composition like most minerals. Moreover, the approach shows great promise for the prediction of possible structures and, above all, ordering schemes, which can be deduced using the symmetry relationships between the higher-dimensional superspace group and the possible three-dimensional space groups derived by superspace sections. This is one of the research topics of the ESF-Eurominsci project ”ORION” (Ordering of ions in minerals).

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Are there Hydrogen Bonds in Brucite?

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High-Pressure Nitrides: computation of phase diagrams and transformations

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Abstract

Advances in instrumentation of diamond-anvil-cells and multi-anvil-cells provided the environment for recent chemical syntheses of novel nitride compounds at high-pressure/high-temperature conditions. Motivated by the simultaneous discovery of spinel-type silicon nitride by experimental and computational methods [1] we set out to study more binary nitride compounds of main-group elements and transition metals [2,3].

To access the full metal-nitrogen phase diagram at elevated temperatures and high pressure, hence, to locate the thermodynamical equilibrium between several nitrides upon nitridation of a given metal M, entropy effects of nitrogen are the dominant source for the difference between enthalpy dH and free enthalpy dG for any given pressure. To solve this obstacle we propose an explicit scheme to include the fugacity of nitrogen based on thermochemical data [4].

The combination of first-principle and thermochemical calculations let us predict the synthesis of a new high-pressure phase of Ta3N5 at about 27 GPa. Synthesis of WN2 becomes feasible at about 45 GPa. Moreover, the scheme is easily applied to phase diagrams of noble metal nitrides.

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Advanced interatomic potentials for large scale simulations of minerals and melts

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Abstract

Geomaterials (minerals, melts, fluids) are often composed of three or more different chemical components and usually possess a rather complex atomic structure. They are the building blocks of our planet and hence their properties need to be studied to understand processes at the Earth's surface or in the Earth's interior. This includes not only properties of single phases in a wide range of pressure and temperature but also dynamical processes, such as mechanical deformations, structural phase transformations, melting and crystallization processes etc. In recent years, theoretical methods have been developed to model geomaterials on the computer. Electronic structure calculations are regarded as the most general and accurate of these techniques. However, they are computationally expensive and still limited to rather small or perfect systems. Classical interatomic potentials provide a more effective description of the atomic interaction but their application is usually restricted to a narrow range of materials and thermodynamic conditions. The limitations of these interatomic potentials often arise from deficiencies of the models themselves and/or from the way the potential parameters are optimized. It would be highly desirable to find a systematic way to construct transferable interaction potentials for geomaterials that are applicable to a wide range of minerals and melts in a wide range of pressure and temperature. Ideally, one would like a database of potential parameters to be used for atomistic modeling of oxides and silicates. In this talk, a set of advanced interaction potentials for the Ca-Mg-Al-Si-O system is assessed in terms of transferability. The model has been derived from physical considerations and parameterized solely by reference to electronic structure calculations. First, the ability of the model to reproduce thermoelastic properties of minerals included in the potential development is assessed. Then the transferability of the model to other minerals is checked. Finally, the model is applied to study the atomic structure and transport properties of melts. Besides predicting melt properties (density, structure factor, etc.) that are in excellent agreement with experimental data, the simulation provides insight into the relation between structural changes and the anomalous behavior of transport properties (viscosity, diffusivity) with pressure and composition.

Theory of Iron at High Pressure and Temperatures

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Abstract

We have used a variety of first-principles techniques to study the thermoelasticity and structure of iron at high pressures and temperatures, including under conditions of the Earth's core. Full-potential linear response lattice dynamics computations using the full-potential Linearized muffin tin orbital (FLMTO) method with the PBE generalized gradient approximation have been performed as a function of compression and shear strain for bcc, hcp, and fcc iron for pressures over 400 GPa. For each volume and lattice strain, the phonon frequencies were computed from first-principles. The quasiharmonic free energies as a function of temperature is then obtained from the frequencies along with the static lattice total energy. We also performed particle-in-a-cell (PIC) computations to obtain anharmonic contributions, which were found to be small. A full set of thermomechanical properties were derived from the free energies. Seismic velocities agree with free oscillation values for the inner core for a temperature of about 6500K. Below 50 GPa, magnetism becomes important for hcp-Fe. A multiscale model is used to obtain finite temperature contributions from magnetism to the properties, which are significant near the Curie temperature for bcc. Generally very good agreement is found with experimental quantities, although there are systematic shifts in moduli from experiment, so that an improved density functional is desirable. Nevertheless, the predicted dynamic compression of iron is in good agreement with experiment, and computed core properties should be good constrains on core properties.

Carbonia: the amorphous silica-like carbon dioxide

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Abstract

Among the group IV elements only carbon forms stable double bonds with oxygen at ambient conditions and, at variance with SiO2 and GeO2, the non molecular single-bonded crystalline form of CO2, phase V, only exists at high pressure. Similarly, the amorphous forms of SiO2 (a-silica) and GeO2 (a-germania) are well known at room conditions. In this presentation I will report about the synthesis of an amorphous, silica-like form of carbon dioxide, a-CO2 or "a-carbonia". This material, which is non molecular has been described so far only as a result of first-principle simulations. The onset of the transformation to the non molecular amorphous phase of carbon dioxide was obtained by compressing the molecular phase III of CO2 between 40 and 48 GPa at room temperature. Infrared spectra measured at temperatures up to 680 K show the progressive formation of C-O single bonds and the simultaneous disappearance of all molecular signatures. Furthermore, state-of-the-art Raman and synchrotron x-ray diffraction measurements on temperature quenched samples confirm the amorphous character of the material. Comparison with vibrational and diffraction data for amorphous silica and germania, as well as with the structure factor calculated on the a-CO2 sample obtained by first-principle molecular dynamics5, shows that a-carbonia is structurally homologous to the other group-IV dioxide glasses. We therefore conclude that the class of archetypal network-forming disordered systems as a-silica, a-germania, a-Si, a-Ge, and water, must be extended to include a-CO2.

Heat transfer in olivine single crystals and upper mantle rocks

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DFT calculations for the environment

Emilio Artacho
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Abstract

The biosphere represents a harder challenge for first-principles simulations than deeper Earth's environments: infested by weak interactions, liquids and organic matter, it seems hopeless and better suited for direct observation and empirical potentials. There are however questions posed by processes happening in our environment that would benefit from first-principles insights, and it is worth exploring and pushing the frontier of what first-principles methods can achieve in this context. I will present our efforts along three different lines (time permitting): wet surfaces towards soil adsorption processes, irradiated ceramics towards synthetic rocks for nuclear waste disposal, and adsorption on cloud particles. Our (little) progress will be described along with the many problems encountered.For the wet systems, the first-principles description of water itself has undergone several crises in the last three years, from the huge viscosities found in GGA water to the claim that liquid water is filamentous in nature, and that all simulations so far (empirical or ab initio) are fundamentally flawed. After discussing our present understanding of the matter [1,2], I will present our studies on the adsorption of chlorinated organic pollutants onto pyrophyllite. It represents the end member of clay minerals that is hardest to simulate due the hydrophobic character of its most common surface, the interactions being dominated by weak forces and easily masked by basis-set superposition errors. In the case of radiation damage in ceramic materials to host nuclear waste, substantial progress has been achieved with empirical potentials. An important question remains unanswered which could be important for the understanding and prediction of the durability of these materials: to what extent is the electronic heating by the decay processes altering the interatomic interactions that resist the damage? It is not a trivial question, since the velocities of some of the heavy ions in decay processes are intermediate, i.e. in a regime where their energy is transmitted to both electrons and nuclei. We are trying to get a handle on this with the help of TD-DFT calculations.

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Experiments on liquids at high-pressure in Earth's sciences

Chrystele Sanloup
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Abstract

Liquids of geophysical interest range in three main compositional classes: silicate melts, molten Fe and Fe-alloys, and H2O/CO2 fluids. Both static and dynamic experiments on these geomaterials will be reviewed, with an emphasis on *in situ* X-ray synchrotron based techniques. An advantage of in situ observations is that complications due to quench effects can be avoided. Physical properties such as the density, viscosity, and the local structure of liquids can now be experimentally determined for a wide range of compositions, mostly using large-volume presses but recent advances have been done using laser-heated diamond-anvil cell techniques. The evolution of the local structure of liquids can provide information on the partitioning of elements between melts. Understanding the partitioning of elements for instance between silicate and Fe-based melts, and measuring their solubility is essential to understand the chemical composition of Earth's reservoirs as well as their formation. Another example is the evolution of miscibility gaps with increasing P-T conditions. Miscibility gaps are widespread among geophysically relevant liquids (silicate/H2O fluids, liquid Fe-alloys, silicate/Fe melts), different experiments tackling these issues will be presented.

Synthesis and characterization of the noble metal nitrides

Eugene Gregoryanz
The University of Edinburgh, United Kingdom

Polymorphism in molecular systems at high pressure

David Allan
The University of Edinburgh, United Kingdom

Abstract

Molecular materials contain a rich spectrum of interaction types - from the relatively weak van der Waals interaction, through the more moderate ionic bond and hydrogen bond, to the relatively strong covalent bond - and as these interactions depend strongly on intermolecular distance, high-pressure provides a powerful means of altering their relative hierarchy of strengths. A systematic study of molecular systems at high pressure is rewarding, therefore, as competition between the various interaction types causes phase transitions, including glass formation, and effects melting, crystal solubility and nucleation. Over the past few years, we have been conducting a series of studies on the high-pressure crystal structures of a variety of molecular systems including: organic materials, such as simple functional compounds, pharmaceutical compounds, amino acids, peptides, and more recently proteins; along with inorganic materials, such as the oxoacids and their hydrates. All of these systems have been studied, principally, with single-crystal x-ray diffraction techniques where the crystals have been grown from either the melt or from solution within the diamond-anvil cell. The more usual approach requires the crystals to be cut to the correct size prior to their loading into the cell. However, on subsequent pressure increase, a first-order structural phase transition could shatter the crystal or the kinetic barrier for the transition may be sufficiently large that the crystal remains trapped in a metastable structure. The in situ growth of single-crystals, although it can often prove to be experimentally challenging, overcomes both of these fundamental difficulties and the high-pressure equilibrium phase can usually be obtained. We have used DFT calculations to follow on from these

high-pressure studies to, principally, provide additional structural information if, for example, the positions of the weakly scattering hydrogen atoms could not be obtained by experiment. In addition, the calculations allow us to determine the relative energies of the observed structural phases and, in some cases, to establish the comparative strength of the hydrogen bonding. A number of examples will be presented.

Predicting the isotopic fractionation in geological systems

Bruno Reynard
ENS Lyon, France

Abstract

The isotopic fractionation in geological systems is used for various purposes such as reconstructing the origin of the matter that forms the solar system (supernovae, metallicity, nuclear processes, ...), inferring the conditions of formations of rocks or biogenic minerals (temperature, interactions with fluids, pH, ...), evaluating environmental processes in the past (biological productivity in oceans, element cycles, shock effect during meteoritic impacts ...). I review some aspects of the experimental progresses made over the last few years for understanding mass dependent and mass independent isotopic fractionation, and discuss the required degree of sophistication of theoretical predictions for useful combination with experiments and applications to natural systems.

Thermal Conductivity from Atomistic Simulations

Sandro Scandolo
The Abdus Salam ICTP, Italy

Abstract

The thermal conductivity of minerals is a crucial parameter to understand and model the dynamics of the Earth's interior. I will review recent attempts to calculate the thermal conductivity of solids using atomistic simulations, trying to emphasize virtues and weaknesses of the various approaches, and illustrating strategies for the grand challenge of calculating thermal conductivities from first principles.

Single crystal to polycrystalline physical and mechanical properties; the link between the laboratory, seismology and geodynamics of the Earth's mantle

David Mainprice
Laboratoire de Tectonophysique, Université Montpellier II, France

Abstract

The mechanical and physical properties that govern the geodynamics of the Earth's interior can now be investigated by numerical and laboratory experiments at in situ high pressure and temperature conditions. The pertinence of new mineral physics data at the sample scale (crystal, polycrystal) to geodynamics can be evaluated by comparison with geophysical observables, such as seismic, electrical or thermal properties of the Earth. The physical properties of crystal

can conveniently be represented by tenors and this representation can be directly used for polycrystals for volume-weighted properties (e.g. elasticity). At the high temperature and pressure conditions of the Earth's interior crystals deform by dislocation glide which is controlled by mineral dependant properties (symmetry, structure, mechanical resistance, glide planes and directions), environmental factors (T, P, chemical activities..) and the deformation regime (simple shear, axial compression..). Deformation by dislocation glide results in polycrystalline samples acquiring a crystal preferred orientation (CPO), which is a non-uniform distribution of crystal orientations in the sample reference frame. The symmetry and intensity of the CPO is dependent on the all the factors that effect dislocation glide, hence CPO is a sensitive indicator deformation conditions. If the mineral has anisotropic properties (e.g. elasticity) then a sample deformed by dislocation glide with a CPO will also have anisotropic properties (e.g. seismic). Experimental techniques are currently available to deform samples at in situ conditions of the Earth's mantle and even the Earth's core. Most of these techniques use the power of synchrotron radiation to measure some deformation parameters in situ. The D-DIA apparatus can explore the PT range of the upper mantle, the multi-anvil apparatus the transition zone, and the laser heated diamond anvil cell the lower mantle and core. Atomic modelling has made a major impact on the elastic properties of minerals at high pressure and more recently high pressure and temperature currently inaccessible for direct experimental measurement of the elastic tensors. Very recently atomic modelling has been applied to dislocation motion in minerals at mantle conditions. Using glide systems determined from experiments or atomic modelling as a starting point for visco-plastic self-consistent (VPSC) modelling the CPO of minerals for any deformation regime can be predicted. Combining CPO and single crystal elasticity tensors a model for seismic anisotropy can be compared with seismic observations and the implications for geodynamics accessed.

Obtaining phase coexistence conditions and phase diagrams from atomistic

Eduardo Hernandez
Institut de Ciencia de Materials de Barcelona (ICMAB-CSIC), Spain, Spain

Abstract

In this presentation I will discuss a series of novel atomistic simulation techniques which aim at making the calculation of free energies, coexistence conditions, and ultimately entire phase boundaries (and hence also phase diagrams), more efficient. In particular I will discuss the techniques known as adiabatic switching, reversible scaling and dynamical Clausius-Clapeyron integration. Examples illustrating the computational efficiency of these techniques will also be presented; specifically I will show results for the melting temperatures of a series of fcc metals, the calculation of the phase diagram of Si, and finally I will also discuss the case of the melting line of Na.

An integrated ab-initio and experimental approach to structure and spectroscopy

Keith Refson
CCLRC Rutherford Appleton Laboratory, United Kingdom

Abstract

Vibrational spectroscopy by infrared, raman or neutron techniques is a sensitive probe of the crystalline environment. However its scope is limited by selection rules, instrumental range and more profoundly by the absence of direct structural information. Traditional practice has used analogues and rules of thumb to perform mode assignment. Ab-initio lattice dynamics by contrast is based on the quantum-mechanical formalism of density functional theory and yields not merely the full range of mode frequencies but the associated eigendisplacements. A combined ab-initio and experimental approach allows an unambiguous mode assignment of an experimental spectrum even in uncommon cases where analogues are not available. Furthermore it describes the structure-property correlation, adding insight to the measurement.
I will discuss methods of computing lattice dynamics ab-initio, and show some applications where the link to experimental spectroscopy has proved fruitful. These will include mineral systems, hydrogen storage materials and the application to high-pressure phase transitions. I will also discuss challenges to the theory, notably anharmonicity where future developments are needed.

Mineral Physics and Geosciences: Opportunities within the ESF

Bernard Avril
European Science Foundation (ESF), France

Abstract

The European Science Foundation (ESF, www.esf.org) – a European organization serving 78 national agencies from 30 countries and their scientific communities – aims at creating a common platform to advance European research and explore new directions for research in Europe in a global context. Several multidisciplinary activities in the fields of Life, Earth and Environmental Sciences (ESF-LESC) and of Physical and Engineering Sciences (ESF-PESC) are of high relevance to the most advanced studies of minerals (e.g., under extreme conditions or in complex interactions with the geosphere or the biosphere). Recent progress in the use of physics-based experimental techniques and of atomistic computer simulation makes it possible to study mineral properties and behaviour through an unprecedented effort. At the same time, measurements of many minerals properties are now feasible in a wide range of natural, environmental conditions. Through a series of specific, targeted activities, ESF contributes to help the European scientific community integrating many emerging theoretical, computational and experimental approaches in order to answer complex questions in mineral sciences / geosciences. This presentation details the portfolio of those present and future ESF activities of direct interest to the scientific community involved in the workshop entitled “Mineral Physics with Computation and Experiment”.

5 Program

Day 1: June 19 2006

Session : 1 Challenges from the Earth
10:00 to 10:30 : Welcome

10:30 to 11:30 : Presentation
Experiments on liquids at high-pressure in Earth's sciences
Chrystele Sanloup

11:30 to 12:00 : Coffee Break

12:00 to 13:00 : Presentation
Advanced interatomic potentials for large scale simulations of minerals and melts
Sandro Jahn

13:00 to 14:30 : Lunch Break

14:30 to 15:30 : Presentation
Predicting the isotopic fractionation in geological systems
Bruno Reynard

15:30 to 16:30 : Presentation
First-principles calculation of stable isotopes fractionation
Merlin Mé heut

16:30 to 17:00 : Coffee Break

17:00 to 18:00 :

Day 2: June 20 2006

Session : 1 Minerals under extreme conditions
09:00 to 10:00 : Presentation
Synthesis and characterization of the noble metal nitrides
Eugene Gregoryanz

10:00 to 11:00 : Presentation
High-Pressure Nitrides: computation of phase diagrams and transformations
Peter Kroll

11:00 to 11:30 : Coffee Break

11:30 to 12:30 : Presentation
Obtaining phase coexistence conditions and phase diagrams from atomistic
Eduardo Hernandez

12:30 to 14:00 : Lunch Break

14:00 to 15:00 : Presentation
Metadynamics simulations of structural phase transitions in crystals: the case of silica
Roman Martonak

15:00 to 16:00 : Presentation
High-energy X-ray scattering: Probing nano-crystalline and amorphous materials at high-pressure
Lars Ehm

16:00 to 16:30 : Coffee Break

16:30 to 17:30 : Presentation
Chemical reaction between iron and oxides at core-mantle boundary
Leonid Dubrovinsky

17:30 to 18:30 : Presentation
Theory of Iron at High Pressure and Temperatures
Ronald Cohen

Day 3: June 21 2006

Session : 1 Structure and bonding
09:00 to 10:00 : Presentation
DFT calculations with WIEN2k
Karlheinz Schwarz

10:00 to 11:00 : Presentation
Hydrogen bonding in minerals
Bjoern Winkler

11:00 to 11:30 : Coffee Break

11:30 to 12:30 : Presentation
Are there Hydrogen Bonds in Brucite?
Kersti Hermansson

14:00 to 15:00 : Presentation
Polymorphism in molecular systems at high pressure
David Allan

15:00 to 16:00 : Presentation
Superspace methods for structural description
Alberto Garcia

16:00 to 16:30 : Coffee Break

16:30 to 17:30 : Presentation
Carbonia: the amorphous silica-like carbon dioxide
Federico Gorelli

Day 4: June 22 2006

Session : 1 Defects and interfaces

09:00 to 10:00 : Presentation
An integrated ab-initio and experimental approach to structure and spectroscopy
Keith Refson

10:00 to 11:00 : Presentation
DFT calculations for the environment
Emilio Artacho

11:00 to 11:30 : Coffee Break

11:30 to 12:30 : Presentation
Modelling defects in minerals
Kate Wright

12:30 to 14:00 : Lunch Break

14:00 to 15:00 : Presentation
Thermal Conductivity from Atomistic Simulations
Sandro Scandolo

15:00 to 16:00 : Presentation
Heat transfer in olivine single crystals and upper mantle rocks
Benoit Gibert

16:00 to 16:30 : Coffee Break

16:30 to 17:30 : Presentation
Atomistic simulations of frustrated magnetic ordering in the ilmenite-hematite solid solution
Erika Palin

Day 5: June 23 2006

Session : 1 Defects and interfaces

09:00 to 10:00 : Presentation
Multiscale modelling of crystal growth from solution
Julian D. Gale

10:00 to 11:00 : Presentation
Ab initio calculations of lattice friction in minerals
Philippe Carrez

11:00 to 11:30 : Coffee Break

11:30 to 12:15 : Presentation
Benchmarking for mineral simulations
Michele Warren

12:15 to 12:30 : Presentation
Mineral Physics and Geosciences: Opportunities within the ESF
Bernard Avril

12:30 to 12:45 : Closing word

6 Organizer's report

6.1 Conclusions.

Conclusion 1: Breadth of discussion.
The workshop contributions consisted of talks addressing experimental and theoretical approaches to solve relevant problems in the Earth Sciences. Six talks mainly described state-of-the-art of experiments (C. Sanloup, D. Mainprice, E. Gregoryanz, L. Ehm, L. Dubrovinsky, B. Winkler, D. Allan). Four talks were primarily aimed at presenting recent developments of theoretical aspects (K. Schwarz, K. Hermansson, A. Garcia, R. Martonak) while atomistic modelling to solve a diverse range of problems in ⟩ Mineralogy was at the center of the remaining contributions (S. Jahn, E. Palin, K. Wright, P. Carrez)
There were additional contributions addressing projects relevant to the Mineral Physics community (e.g. discussion of the 'Benchmarking initiative' by M. Warren; funding opportunities on a European level by B. Avril from the ESF) and a discussion by some participants on the 'Cyberinfrastructure' initiative.

Conclusion 2: format of workshop.
It is a hallmark of the 'Mineral Physics' series of workshops that contributions are about 60 min long, that discussions during and after the talk are open, that every participant is required to present a contribution and that participants are strongly encouraged to stay for the duration of the whole workshop. This format, while initially considered unusual by some, was appreciated by all at the end of the workshop due to the insight gained during debates and the level of detail that could be presented, thus enabling further small-group discussion thereafter.

Conclusion 3: need for continuing funding.
The enthusiastic response of the various funding agencies is a clear sign of the quality of the workshop. We had more applications than we could accpet and obviously there is a demand for such workshops, both in the experimental Mineral Physics community, where people need to learn about state-of-the art modelling approaches, in the developers community, where there needs to be awareness of what the relevant problems are and what accuracy is required to really solve relevant problems, and in the computational Mineral Physics community to understand how advances in both computational and experimental approaches can advance mineral physics. The CECAM workshop have been instrumental in coordinating computational Mineral Physics science in Europe, and one tangible outcome was the successful proposal for an ESF EUROCORES EuroMinScI.

Conclusion 4: local organisation and role of CECAM.
Funding for the workshop was obtained from CECAM, Psi-k, COST and through the ESF-EUROCORES EuroMinScI, and in the case of the first three, administered to a large degree by CECAM. Funding levels were sufficient to contribute significantly to travel and subsistence

costs of all participants, including those coming from the US and Australia. CECAM is the ideal organisation to hold such meetings, overwhelmingly due to the outstanding support of Emmanuelle Folzer and Emilie Betrand.

Conclusion 5: carrying the science forward.
In the spirit of the CECAM workshops, most of the talks discussed work in progress, and outlined research directions for the future. Each talk had a long Q&A session (at least 5-10'), which was occasionally very heated. The list of "hot" topics, i.e. of topics where discussion has been particularly heated, includes i) the developments of accurate empirical potentials for atomistic simulations; ii) the prediction of OH stretching modes in minerals, an important ingredient to model water incorporation in the mantle; iii) the determination of the dominant contribution (lattice vs radiative) to the thermal conductivity of minerals

6.2 Recommendations.

Recommendation 1 It is hoped that CECAM realizes the importance of Mineral Physics meetings, where atomistic modellers, code developers and experimentalists meet AND identify areas both for fruitful collaboration and for which further development is needed.
Hence it is strongly recommended that this series, in which 4 workshops have been held in 1997, 2000, 2004, and 2006, is continued in 2008.

Recommendation 2 The format of the workshop, with its very limited number of participants all of which have to contribute, extended contributions, and open atmosphere is the basis of the usefulness of these workshops to the participants. It is therefore recommended that future organizers of workshops in this series are allowed to maintain this format, and that no demand is placed on them to enlarge the number of participants.

Recommendation 3: future funding. The conference series was initiated under the scientific (and partially financial umbrella of the ESF Psi-k network. The Psi-k network will expire in 2007, and will therefore not be able to support the series in 2008. It is therefore important that other funding agencies continue to provide financial and intellectual support to the series. The EuroMinSci programme is a very welcome addition in this respect. It is therefore recommended that CECAM continues to help the community find funding sources, as it has done in the past, e.g. by their links to the COST and other european programmes.

Recommendation 4. The local organisation of the workshop by CECAM staff has been perfect. This has also been the case in the past. The recommendation can therefore only be, that this support is available in its current form to the scientific organizers of future workshops.

The evolution of this workshop series over the last years has shown that from a scientific standpoint, it is important to ensure that the scientific themes covered in the workshop can be continued with some continuity in the future. We thus recommend that the organizers of the 2008 edition be chosen within the scientific community that contributed to the success of the 2006 edition.

7 Key references

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[7] L. Ehm, P. Dera, K. Knorr, B. Winkler, A. Krimmel and P. Bouvier *Crystal structure of the Chevrel phase SnMo6S8 at high pressure*, Physical Review B **72** 014113 (2005)