SiMaDes-II

ABSTRACTS

PROGRAMME

All talks will take place in the ILL – Chadwick Amphitheatre

Thursday 31st January 2008

12h20 Lunch

13h00   Registration

13h45   Welcome and opening

Session 1: Liquids (Chairman : G. Cuello)

14h00   L. Hennet   Structure and dynamics of high temperature liquids

14h30   J.-Y. Raty   Structural changes in a high pressure liquid: why sodium melts at room temperature

15h00   V. Cristiglio   The structure of liquid calcium aluminates: a combined neutron diffraction and computer simulation study

15h20   V. Giordano   High-frequency acoustic dynamics of liquid cesium at high-pressure

15h40   J.F. Wax   Simulation of the collective dynamics of liquid Li-Bi alloys

16h00 Coffee

Session 2: Dynamics (Chairman : C. Bichara)

16h30   G. Monaco   Acoustic dynamics of glasses in the mesoscopic range

17h00   N. Jakse   Liquid-liquid phase transition in supercooled silicon

17h30   P. Jund   Ab initio molecular dynamics study of quenching rate on the physical properties of GeS_2 glasses

17h50   C. Otajaques   Unravelling the mechanism of phase change materials: an ab initio MD study

18h10   W. Welnic   Phase change alloys for non-volatile memories - designing new data storage materials from first principles

18h30   E. Lampin   Molecular dynamics simulation of the recrystallization of disordered Si layers

19h00 Dinner- buffet at ILL

Session 3: Silica (Chairman : M. Johnson)

9h00	R. Vuilleumier	First-principle Molecular Dynamics simulation of some natural silica melts
9h30	G. Baldi	Thermal conductivity and THz dynamics in vitreous silica
10h00	C. Massobrio	First-principles molecular dynamics study of liquid and glasses

10:20   Coffee break

Session 4: Molecules, salts (Chairman : C. Massobrio)

10:50	A. Tanguy	Microscale simulations of the mechanical deformation of model amorphous materials
11:20	B. Ruta	High-frequency dynamics in glassy sorbitol
11:50	D. Testemale	Local structure of Fe^{2+} in hydrothermal salt solutions studied by X-ray absorption spectroscopy
12:10	F. D'acapito	The site of metal ions in ion-exchanged metal-doped glasses

12:30   Lunch

Session 5 : Mixed (Chairman : A. Pasturel)

14:00	S. Ispas	First-principles molecular dynamics simulations of silicate glasses upon compression
14:30	F. Fontaine-Vive	Atomistic simulations give new insight into the structure and the work function of thin tungsten films deposited on crystalline high-k oxide
14:50	M. Salanne	Ionic systems: from first-principles to material properties
15:10	G. Bouzerar	Ferromagnetism in diluted magnetic semiconductors
15:30		Open Discussion – A. Pasturel/M. Johnson

16:30   Coffee break

End of the workshop

Liquids

Structure and dynamics of high temperature liquids

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The use of conventional furnaces for studying high temperature liquids can lead to various problems. In particular, the sample can react with the container and become contaminated. Furthermore it is difficult to reach very high temperatures. This has led to the development of containerless techniques and their use at synchrotron and neutron sources for studying the structure and dynamics of molten materials.

Several levitation techniques have been developed by various groups around the world. Our group has chosen to work with aerodynamic levitation associated with CO_2 laser heating. With this method it is possible to design relatively simple and compact devices that can be integrated easily into different instruments at neutron and synchrotron sources.

In this talk, I will give an overview of various x-ray and neutron techniques that we have used for studying the structure and dynamics of high temperature liquids. This will be illustrated by experimental results on different high-temperature liquids.

Structural changes in a high pressure liquid : why sodium melts at room temperature

Jean-Yves Raty[1], Eric Schwegler[2], Stanimir Bonev[3]

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[3]Dalhousie University, Canada

The melting curve of sodium measured in [1] exhibits totally unexpected features under pressure : the melting temperature, Tm, reaches a maximum around 30 GPa followed by a sharp decline from 1000 K to 300 K in the pressure range from 30 to 120 GPa.

In the present study, the structural and electronic properties of molten sodium are studied using first principles theory. With increasing pressure, liquid sodium initially evolves by assuming a more compact local structure, which accounts for the maximum of Tm at 30 GPas. However, at pressure around 65 gigapascals a transition to a lower coordinated structure takes place, driven by the opening of a pseudogap at the Fermi level. Remarkably, the 'broken symmetry' liquid phase emerges at rather elevated temperatures and above the stability region of a closed packed free electron-like metal. The theory explains the measured drop of the sodium melting temperature, down to 300 kelvin at 105 GPas.

[1] Gregoryantz et al., Phys. Rev. Lett. 94,185502 (2005).
[2] JY. Raty, E. Schwegler and S. Bonev, Nature 449 (207) 451

The structure of liquid calcium aluminates:
A combined neutron diffraction and computer simulation study

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Over the past ten years an increasing number of studies on molten materials have been carried out thanks to the development of containerless methods. These techniques allow studies of high-temperature liquids with a very high degree of control. In particular, they eliminate the problems of sample-container interactions and contamination and make it possible to access very high temperatures. The CRMHT has chosen to combine aerodynamic levitation with CO_2 laser heating and has developed various devices for making diffraction measurements at synchrotron and neutron sources [1-3].

From the structure factor S(Q) and the corresponding pair correlation function g(r) obtained with x-ray or neutron diffraction experiments, it is possible to get information on the local structure of liquid materials. But very often the material studied is a polyatomic system and both S(Q) and g(r) are weighted sums of the partial functions for all atomic pairs, so that a single diffraction measurement gives an incomplete representation of the structure.

In order to go further in structural studies, the combination of experimental methods with simulation techniques becomes indispensable. This makes it possible to derive partial S(Q) and g(r) functions for all atomic pairs and to determine reliable structural models to compare with the experimental results. At the ILL we have developed *ab initio* molecular dynamics (AIMD) simulations using the VASP code [4] where interatomic forces are obtained from density functional theory.

We present here a structural analysis of liquid calcium aluminates ($CaO-Al_2O_3$), showing a good agreement between the AIMD simulations and the experimental data.

[1] L. Hennet et al., Appl. Phys. Lett. 83, 3305 (2003)
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High-frequency acoustic dynamics of liquid cesium at high-pressure

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The study of collective excitations in simple metals is a long-standing topic in the Physics of fluids. Relying the density fluctuations studied by inelastic x-ray or neutron experiments to the inter-particle potential has proved to be a particularly challenging task. Several attempts have been made to give a unitary interpretation of the high-frequency acoustic dynamics of the alkali metals.

Scaling features in both static and dynamic properties have been highlighted and linked to two parameters describing the shape of the intermolecular potential, namely the hard-sphere radius σ and the potential well depth ε [1]. However, this study has been so far limited to data collected at the ambient pressure melting point, that is, in conditions of similar packing fraction for all the alkali metals. Only few studies at high temperature have been performed, but in a rather limited density range [2,3] .

In this work we present inelastic x-ray scattering spectra collected on liquid cesium at 500 K and high pressure, corresponding to a density change as large as 40% with respect to ambient conditions. We show that the cited scaling fails in describing systems with a very different packing fraction. However, the high frequency dynamics of liquid alkali metals still follows a universal behavior, even far from melting, once the proper reduced units are used. The relation between σ, ε and the found parameters and their physical meaning are discussed.

[1]   U. Balucani et al., Phys. Rev. A 46, 2159 (1992)
[2]   F. Demmel et al., Phys. Rev. B 74, 184207 (2006)
[3]   W. C. Pilgrim and C. Morkel, J. Phys: Condens. Matter 18, R585 (2006)

Simulation of the collective dynamics of liquid Li-Bi alloys

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Recent inelastic neutron scattering measurements[1] have established the existence of two branches of collective excitations in liquid Li-Bi alloys. In order to highlight the exact nature of the second branch, we have begun a molecular dynamics (MD) study of these systems. The objective is twofold. Firstly, we want to get information about the partial dynamic structure factors, which are hidden in the experimental results. Secondly, we wish to reach q values smaller than the experimentally available ones.

Two main difficulties have to be overcome. The first one is to describe accurately the interactions in these alloys involving atoms with very different valences. The second one is to simulate boxes large enough (to reach small enough q-values) over times long enough (to accumulate sufficient statistics).

Therefore, in our approach, we combine both *ab-initio* and classical MD simulations. The first ones, which accurately describe the interactions are used to determine the densities of the systems since experimental data are lacking. They also provide static structure data considered as a reference to check the validity of the classical ones. Indeed, the required numbers of atoms (about 2000) and the required simulated times (about 100 ps) can only be reached by classical MD.

We will display some results of both static and dynamic structure factors, which illustrate the difficulties typically encountered in any MD study of the dynamical structure of liquid alloys.

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[1] *Evidence for the coexistence of two density fluctuation modes in molten Li30Bi70 as probed by neutron scattering.* L. E. Bove, F. Formisano, E. Guarini, A. Ivanov, C. Petrillo and F. Sacchetti, *EPL* **79** (2007) 16002.

Dynamics

Acoustic dynamics of glasses in the mesoscopic range

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The investigation of the high-frequency acoustic excitations in glasses - as measured by inelastic neutron and x-ray scattering - and of their connection to the universal anomalies in the thermal properties remains a largely debated topic. Different and somehow contrasting views of the nature of these excitations are currently being discussed in the literature. For instance, one interpretation is based on the observation that the high-frequency acoustic dynamics in simulated harmonic glasses shares the same main features as those found in experiments on real glasses [1]. This approach attributes a central role to topological disorder. A different interpretation is based on the observation that both acoustic dispersion and attenuation measured in glasses and in the corresponding poly-crystals are indistinguishable [2]. This result points to the similar nature of the high-frequency excitations in glasses and poly-crystals, and focuses on the role played in the glass by the intrinsic average over all q-directions. A further interpretation is based on the observation that in some glasses the high-frequency acoustic attenuation increases as a power of q - with an exponent of four or larger - up to frequencies corresponding to the Boson peak [3]. This approach focuses on the central role of resonance and hybridization of the acoustic waves with the excess of modes corresponding to the Boson peak. Here, I will discuss the above approaches on the basis of recent inelastic x-ray scattering results on the high-frequency acoustic dynamics of glasses.

[1] G.Ruocco et al., Phys. Rev. Lett. **84**, 5788 (2000).
[2] A.Matic et al., Phys. Rev. Lett. **93**, 145502 (2004).
[3] B.Rufflè et al., Phys. Rev. Lett. **96**, 045502 (2006).

Liquid-liquid phase transition in supercooled silicon

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Despite the occurrence of advanced materials in recent years, silicon still keeps the leadership in semiconductor technology. Most technological applications begin with crystalline silicon wafers elaborated from the melt, and amorphous silicon made from slightly supercooled melts. The properties of normal and supercooled liquid silicon are therefore of importance for the manufacturing process. Unusual behavior of the density in the supercooled liquid states, as deep as 200 K below the melting point, was observed leading researchers to consider plausible the existence of a liquid-liquid transition at even lower temperature, unfortunately out of reach to state-of-the-art experimental facilities. Therefore, the absence of direct evidence from experiments has prompted to look for it using numerical simulations. We have proposed a new mixed approach by combining efficiently classical and first-principles molecular dynamics, giving a strong support to the existence of a transition between a high density liquid to a low density liquid near 1050 K, regardless of a specific empirical interaction model. We were able to clarify the nature of atomic and electronic structures of both the high and low density phase, which were incorrectly described from early classical simulations. Our finding indicates the liquid-liquid transition is accompanied by an enhancement of the local tetrahedral structure and is not characterized by a semimetal to semiconductor transition.

Etude par dynamique moleculaire ab-initio de l'effet de la vitesse de trempe sur les proprietes physiques des verres GeS2

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Le principal objectif de ce travail est l'application des techniques de la dynamique moléculaire ab-initio a l'étude de l'impact de la vitesse de trempe sur les propriétés des verres de chalcogenures (GeS2). Les calculs ont été réalisés en utilisant le code Fireball96 qui repose sur la théorie de la fonctionnelle de la densité (DFT) formulée dans le cadre de l'approximation de la densité locale (LDA).

Des échantillons de GeS2 liquide (2000K) ont été trempes a différentes vitesses de trempe, comprises entre $3x10^{14}$ K/s et $6x10^{12}$ K/s, dans le but d'obtenir des échantillons vitreux a température ambiante (300K). Les propriétés structurales et électroniques des verres ainsi obtenus sont comparées à l'expérience et leur évolution avec la vitesse de trempe est étudiée. Les résultats mettent en évidence la dépendance des propriétés structurales des échantillons vitreux par rapport a la vitesse de trempe (avec l'existence d'une vitesse de trempe limite) mais indiquent que l'existence de zones chargées a l'intérieur de la matrice vitreuse, mise en évidence précédemment, n'est pas remise en cause aux plus faibles vitesses de trempe.

Unravelling the mechanism of phase change materials : an *ab initio* MD study

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Nowadays, thin layers of phase change materials are commonly used in rewritable DVD's and as PC-RAM. The writing process is achieved by a first local melting of the crystalline phase through a laser pulse (DVD-RW), or by Joule heating (PCRAM), followed by a fast amorphization. Reading is then possible thanks to the large differences in optical reflectivity and electrical conductivity between the two phases. The erasing process is achieved through moderate heating of the amorphous phase and recrystallization. Despite their every day use, the internal mechanism responsible for the phase-change behavior of these materials remains controversial and theory is lacking.

Among phase change materials, the $Ge_2Sb_2Te_5$ compound is one of the most successfully used in applications. Currently accepted models [1, 2] are based on X-ray absorption measurements and suppose a complete reorganization of bonds during amorphization, with Ge atoms changing from sixfold to tetrahedral coordination.

In this study, we perform ab initio molecular dynamics simulations of the $Ge_2Sb_2Te_5$ liquid phase at $1073K$ and obtain an excellent agreement with the experimental structure factor. Twenty individual, uncorrelated, liquid atomic configurations are then fully relaxed, both for the ionic and cell degrees of freedom. The relaxed structures are then used as model amorphous structures and their EXAFS signature is positively compared with the experimental spectra. The computed electrical conductivities of the three phases (cubic solid, liquid and relaxed structures) prove to be very different, accordingly with the experiment. As a conclusion, we invalidate the commonly accepted model and show that *Ge* atoms remain mostly octahedrally coordinated in the amorphous phase, with 6 very unequal first neighbors distances.

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Materials, 5 :56, 2006.

Phase change alloys for non-volatile memories - designing new data storage materials from first principles

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In recent years, non-volatile solid state memories have in many applications replaced magnetic hard disk drives. A promising contender for the most popular non-volatile memory - the FLASH random access memory- is the phase change random access memory (PRAM). The PRAM utilizes phase change materials such as the compound $Ge_2Sb_2Te_5$ already successfully employed in rewritable optical data storage. The storage concept of these materials is based on a unique combination of properties: On one side they show a rapid phase transition (~10-100ns) from the crystalline to the amorphous phase upon heating. On the other side this phase transition is accompanied by a fundamental change in the electronic and optical properties between the two phases unknown from common semiconductors such as Si, Ge or GaAs.

In this work we perform *ab initio* calculations to reveal the correlation between changes in the local geometry, vacancy concentration and electronic and optical properties. A comparison between the calculations and experimental data demonstrates the importance of local distortions for the stability of the crystalline state and reveal pronounced changes of the electronic properties upon amorphization. Furthermore optical spectra calculations performed in the Random Phase Approximation explain the profound change in absorption upon amorphization in commercial phase change materials. It is found that the change in the local atomic order induces a change in the overlap of the occupied and unoccupied wave functions. This gives rise to a decrease of the transition matrix elements in the amorphous phase and subsequently to the large change in optical absorption upon amorphization. The results are then applied to design new materials with improved data storage properties.

Molecular dynamics simulation of the recrystallization of disordered Si layers

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Preamorphization of silicon by high dose implantation of heavy ions is a solution for the realization of ultra-shallow p/n junctions. The consecutive recrystallization upon annealing is determining. We will present simulations of this recrystallization by empirical molecular dynamics. Five interatomic potentials published for Si were tested and classified following their ability to handle solid phase or liquid phase epitaxy.

Silica

First-principle Molecular Dynamics simulation of some natural silica melts

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We have performed density functional theory based first-principle molecular dynamics (FPMD) simulations of three natural silical melts: rhyolite, forsterite and anorthite-diopside along with that of a pure silica melt. These chosen magmas represent a wide range of structure formers and structure breakers concentrations. First, we compared structures with experiment and results from empirical potentials developed by two of us (NS and BG) and very good agreement was found. We further studied vibrational properties of the silica melts, including infrared spectroscopy, from the FPMD trajectories. Analysis of the electronic distribution around oxygens through dipoles and quadrupoles defined from maximally localized Wannier orbitals will also be presented.

Thermal conductivity and THz dynamics in vitreous silica

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The dynamic structure factor of vitreous silica is measured by means of inelastic X-rays scattering (IXS) at exchanged wavevectors between 4 and 15 nm^{-1} and at temperatures above and below the glass transition temperature (T_g = 1450 K).

The IXS experiment is complemented by two sets of inelastic neutron scattering (INS) measurements performed at the IN4 and IN6 time of flight spectrometers at the ILL.

The results of a detailed analysis confirm the presence of two excitations in the spectra in the entire explored wavevector region. The lower frequency mode is characterised by its non-dispersive character and is observed in the frequency range of the Boson Peak.

The higher frequency mode is associated to the longitudinal acoustic mode and a positive dispersion is observed, confirming the results of a previous study [1]. The positive dispersion is found to be temperature independent from deeply below to above T_g, indicating the harmonic nature of the dynamics in this high frequency region.

The contribution of the dispersive mode to the thermal conductivity of vitreous silica is then evaluated in the framework of recent theoretical results on the heat transport in disordered systems [2].

The high frequency longitudinal mode observed in IXS is found to be responsible for about one third of the thermal conductivity of the glass at temperatures above 30 K, in the region above the thermal conductivity plateau.

The analysis of the dynamic structure factor obtained by means of IXS and INS and the evaluation of the thermal conductivity give a deeper insight on the nature of the vibrational modes in glasses. The observed modes appear to give a direct contribution to the thermal conductivity, even if the investigated frequency range is located above the Ioffe-Regel limit.

The definition of a pseudo dispersion curve for the modes observed in the dynamic structure factor and the evolution of this quantity to the vibrational density of states are finally examined in the light of these new results.

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First-principles molecular dynamics study of liquid and glasses

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Atomic-scale simulation of liquid and glasses is the ideal complement of experimental probes to gather information on structural properties and their interplay with the chemical bonding features. The predictive power of the first principles molecular dynamics (FPMD) approach rest on its description of the interatomic forces based on a self-consistent determination of the electronic structure. The framework of density functional theory ensures an appropriate treatment of the topological changes occurring as a function of temperature, improving upon approaches based on empirical force fields. We have undergone a series of FPMD studies devoted to the determination of the structural properties for disordered network-forming materials such as $GeSe_2$, $GeSe_4$, $GeSe$, $SiSe_2$ and $SiSe_4$ in their liquid and/or amorphous phases. This talk will report on the most important results of this research effort, in close connection with the interpretation of neutron scattering data. Our motivation is to understand the microscopic origins of intermediate range order in network-forming liquid and glasses. In particular, we seek to establish a connection between the existence of specific structural units and the appearance of the first sharp diffraction peak (FSDP) in the total and in some of the partial structure factors.

The talk will focus on a selection of results extracted for recent published literature (see references). Limitations and advantages of the FPMD approach for the study of disordered systems will be also briefly outlined.

This work has been done in collaboration with A. Pasquarello (EPFL, Lausanne). Calculations on $SiSe_2$ have also involved M. Celino (ENEA, Rome).

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Molecules, salts

Microscale simulations of the mechanical deformation
of model amorphous materials

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We analyse in details the inhomogeneous mechanical response of a model amorphous materials, below the glass transition temperature. The materials we study are described by empirical potentials, and prepared by Molecular Dynamics Simulations from the liquid state. We compare the mechanical response of various model systems: polydisperse Lennard-Jones glasses, Silica glasses (using BKS potentials), and different possible descriptions of amorphous silicon (using Stillinger-Weber, or modified Stillinger-Weber potentials).

We show that the elastic response of all these systems is strongly inhomogeneous. We propose to analyze these inhomogeneities by decomposing the particle displacements into a continuous, inhomogeneous field and the corresponding fluctuations. We then compare the characteristics of the particle displacements in each different systems. Finally, we study the possible relation between the inhomogeneous elastic reponse of the system and its vibrational properties, as well as the localisation of the deformation in the plastic regime.

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High-frequency dynamics in glassy sorbitol

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The study of the vibrational dynamics in glasses is a very active field in Condensed Matter Physics. Indeed, despite of the presence of structural disorder, this class of systems shows a common behavior in the low temperature properties. At about 10 K the heat capacity of glasses exhibits an excess over the Debye expectation [1]. This excess is at the origin of a broad asymmetric peak in the vibrational density of states in the meV energy range, called "Boson Peak" (BP).

The boson peak has been often related to the high-frequency acoustic-like modes [2]. This interpretation is, however, strongly debated. The problem resides in the fact that in the energy range of the BP (1-10 meV) the acoustic branches become more and more ill-defined being the broadening of the excitations of the order of magnitude of the resonance energy itself. Several experiments of high energy resolution inelastic x-ray and neutron scattering have been performed to understand the character of these excitations below and above the boson peak energy, but the "*puzzle*" is still incomplete.

Recent measurements of inelastic x-ray scattering (IXS) on glassy sorbitol ($C_6H_{14}O_6$) have revealed new details on the high frequency dynamics of glasses. The choice of sorbitol resides in the possibility to measure accurately the collective excitations below the BP energy. Indeed recent neutron measurements show that the BP maximum is located at about 5.5 meV at 150 K [3]. Moreover the high fragility of sorbitol, in terms of the Angell's definition [4], leads to an excellent inelastic to elastic integrated intensity ratio in the IXS spectra - this makes the analysis of the IXS data more reliable.

From this data analysis we find the presence of a negative dispersion for the longitudinal acoustic-like excitations in the mesoscopic range: the sound velocity decreases by about 14% at energies well below the Debye energy, where the Debye's theory would predict a constant value. This implies that the Debye continuum approximation breaks down on the nm length scale, i.e. on a scale where it still works well in crystals. The negative dispersion of the longitudinal acoustic-like modes appears below the BP energy and could be related to inhomogeneities in the elastic response at the nano-scale [5]. Furthermore the boson peak seems to correspond to a specific point of the acoustic-like dispersion curve identified by the Ioffe-Regel limit – this limit is defined by the condition that the mean free path of the acoustic wave becomes comparable to its wavelength [6]. A general correlation between the Ioffe-Regel limit and the BP energy has been recently proposed, though it is still under debate [7]. Sorbitol represents the clearest example available to date of a fragile glass where this correlation appears to hold.

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Speciation du fer(II) dans des solutions hydrothermales salines: étude par spectroscopie d'absorption X

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La technique de spectroscopie d'absorption X (EXAFS et XANES) permet de connaître précisément la spéciation des éléments sondés (degré d'oxydation, structure radiale, mais aussi géométrie 3D et information électronique). Nous appliquons cette technique pour étudier la solvatation locale d'espèces métalliques dissoutes dans des solutions aqueuses en conditions élevées de température et de pression, par analyse EXAFS classique et calculs ab initio des spectres XANES (Joly et al., PRB, 2001).

Nous parlerons ici de la spéciation du fer(II) en conditions hydrothermales: pression de 500 bar, température variant de 30 à 500 °C et concentration en chlore (le ligand le plus présent dans les solutions naturelles de la croûte terrestre, les saumures) de 0.5 à 12 M. Dans tout ce domaine du diagramme de phase, nous avons déterminé les quantités relatives et la structure des différentes espèces chlorées, les deux pôles étant l'octaèdre $Fe(H_2O)_6$ et le tétraèdre $FeCl_4^{2-}$. Leur spectres expérimentaux XANES sont représentés sur la figure 1. Connaître la spéciation de ces espèces est essentiel pour la modélisation géochimique des solutions hydrothermales (réactivité eau/roche, stockage du CO_2, etc.).
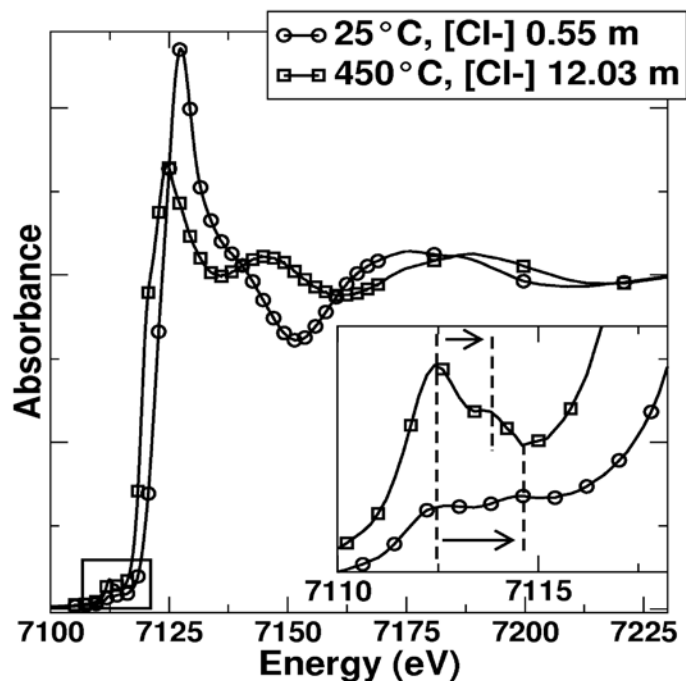

Figure 1: spectres expérimentaux XANES (pre pic dans l'insert) des deux complexes caractérisés comme étant $Fe(H_2O)_6$ et $FeCl_4^{2-}$.

The site of metal ions in ion-exchanged metal-doped glasses

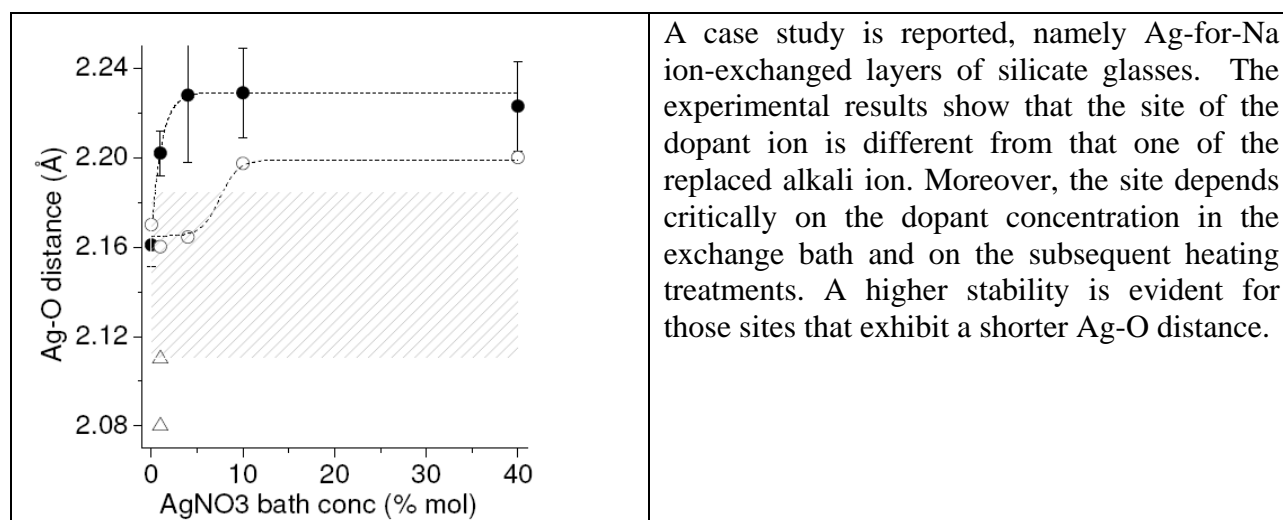**F. D'Acapito[1]**, C. Maurizio[1], E. Cattaruzza[2], F. Gonella[2], E. Ghibaudo[3], J.E. Broquin[3]

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Metal-for-alkali ion exchange is a process that is largely used to dope surface layer of glass with metal ions. The glass is immersed in a bath containing molten salts of the doping atoms and they penetrate in the substrate substituting for alkalis present in the glass via a charge balanced diffusion process. In this way a modification of the optical properties of the doped layer is induced that is useful to fabricate low-loss optical waveguides. We have investigated the site of the metal ions introduced into the matrix by X-ray absorption spectroscopy.

A case study is reported, namely Ag-for-Na ion-exchanged layers of silicate glasses. The experimental results show that the site of the dopant ion is different from that one of the replaced alkali ion. Moreover, the site depends critically on the dopant concentration in the exchange bath and on the subsequent heating treatments. A higher stability is evident for those sites that exhibit a shorter Ag-O distance.

Ab-initio simulation would shed a new light on this subject in particular giving an explanation for the existence of the different sites observed experimentally. From this it could be established a link between microscopical parameter (namely the incorporation site) and the metal diffusivity in the glass.

Mixed

First-principles molecular dynamics simulations of silicate glasses upon compression

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During the last two decades, significant experimental and theoretical effort have been made in order to provide valuable information on the microscopic structure and the vibrational properties of silicate glasses and melts. These systems represent challenging problems of condensed matter physics, glass and earth sciences. In this contribution, we present some microscopic characteristics of a silica glass as well as of a sodium tetrasilicate glass models upon compression. The attention given to these systems is justified by the fact that they can be used as prototypes for more complicated aluminosilicate and hydrous silicate glasses.

The uncompressed glass models were generated by a combination of classical and Car-Parrinello molecular-dynamics simulations.Their structural, electronic and vibrational properties are in agreement with the corresponding experimental results. In order to mimic the effect of pressure the box sizes of the uncompressed models have been rescaled to different sizes in successive steps. The structural as well as the vibrational properties of these glass models upon compression are discussed here.

Atomistic simulations give new insight into the structure and the work function of thin tungsten films deposited on crystalline high-k oxide

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The future of CMOS technology is to replace the silicon dioxide by high-k materials with high dielectric permittivity. In this context, we focused on the properties of the interface between hafnium dioxide and tungsten metal gate. The equilibrium structure of this type of interface is usually constructed by stacking oriented surfaces together, dimensions of the resulting supercell are arbitrarily fixed and ionic positions then relaxed. This convenient approach reveals success for materials having similar crystallographic arrangement and closed cell dimensions. However, it seems to be insufficient for interfaces presenting different crystalline phases and different cell parameters, like a body-centred cubic crystal of tungsten stacking on a monoclinic crystal of hafnium dioxide. Our approach is simpler and more precise since we imitated a pseudo-epitaxial deposit of W atoms on oriented surfaces of m-HfO2 with the help of ab-initio (DFT) annealing simulations. New metallic crystalline phases were revealed which are closed in energy but which present significant different work function in vacuum.

Ionic systems: from first-principles to material properties

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Many modeling problems in materials science involve finite temperature simulations with a realistic representation of the interatomic interactions. These problems often necessitate the use of large simulation cells or long run times, which puts them outside the range of direct *ab initio* simulation. In ionic systems, it is possible to introduce physically motivated model potentials for the interactions, in which additional degrees of freedom provide a 'cartoon' of the response of the electronic structure of the ions to their changing coordination environments and allow the compact representation of many-body contributions to the interaction energy.

These potentials may then be parametrized by fitting the predicted forces and multipoles to a large body of information generated from *ab initio* calculations. The resulting potentials are predictive, of *ab initio* accuracy and have a high degree of transferability between different systems.

Such models were developed for high temperature molten fluorides [1]. LiF-BeF$_2$ mixtures were used as reference systems. Our calculations reproduce a wide range of experimental results [2]: the structure obtained, which is characterized by the formation of complex fluoroberyllate anions at high BeF$_2$ concentration, is in good agreement with spectroscopic results ; the calculated electrical conductivity and viscosity correspond perfectly to the measured ones. The surface tension was determined from simulations of the liquid-vapor system, which revealed important charge separation effects at the interface.[3].

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Ferromagnetism in diluted magnetic semiconductors

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We propose an overview of the magnetism in diluted magnetic semiconductors. In particular, we will show that a two step approach which combines ab-initio calculations and efficient treatment of the effective disordered Heisenberg Hamiltonian is a powerful tool to study the ferromagnetism in disordered magnetic systems. The exchange couplings between magnetic impurities are obtained from ab initio (TB-LMTO) calculations. The disordered Heisenberg Hamiltonian is diagonalized using the self-consistent local RPA (SC-LRPA) which allows treating disorder effects exactly and spin fluctuations within RPA. A comparison with Monte Carlo calculations shows that the semi-analytical SC-LRPA approach is very accurate, reliable and much faster. We will discuss in particular the variation of the Curie temperature with the carrier density and impurity concentration in various materials (GaMnAs, GaMnN, InMnAs, ZnCrTe,…). A detailed discussion of the ferromagnetism in GaMnAs will be provided. It will be shown that the two step approach provides a very good agreement between the calculated and the measured Curie temperature in both as grown and optimally annealed samples. It will be also shown that the widely studied simplified theories (Zener Mean Field) are inappropriate to describe the ferromagnetism in diluted magnetic semiconductors. In contrast, it will be shown that the non perturbative V-Jpd model is able to capture the essential physics. We will see that the theory is very general, allows including the effects of correlation, clustering in the disorder and can be used for the study of very different kind of materials (Manganites, Heusler alloys, d0 materials,….) .