

nitrogen, oxygen, boron, alkali metals, calcium, CaCO₃ and MgCO₃, CO₂ and CH₄ - [1,3-9]), some of which will be presented in this talk.

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Keywords: high pressure, phase transitions, density functional theory

MS.19.2

Acta Cryst. (2008). A64, C42

Theoretical prediction and characterization of high pressure structures and properties of calcium

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This study employed a combination of theoretical techniques to predict the structure and properties of calcium IV and V at high pressures. Structural predictions for calcium in the pressure range 120 – 160 GPa were obtained with a genetic algorithm and with a pseudo-random search method. The X-ray diffraction pattern of the resulting structures are in excellent agreement with recent experimental results. Phonon and electron-phonon calculations were performed with plane-wave density functional methods to investigate the stabilities and potential superconductivity. The proposed structures are both found to be superconducting and the calculated T_c values are close to those observed for Ca-IV and V. Theory indicates a superconducting transition at 25 K for the structures obtained in this study, in excellent agreement with experiment. Analysis of a recent theoretically predicted structure indicates that this structure may be unstable at high pressures

Keywords: *ab initio* calculations, calcium, high pressure studies

MS.19.3

Acta Cryst. (2008). A64, C42

Polymorphism and structural phase transitions in crystals: Computer simulations by metadynamics

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The talk will present the recently developed algorithm for simulation of structural phase transitions in crystals[1,2]. The new approach is based on the general metadynamics algorithm[3] and searches for low-energy pathways leading from one crystal structure to another. It enables also simulation of complex reconstructive transitions with transformation pathways proceeding via several intermediate states, resulting in substantially improved predictive power. The applications of the algorithm will be demonstrated on several systems, with focus on silica[4] and carbon dioxide. We performed an extensive study aimed at investigation of structural transformations in silica and demonstrated that starting from α -quartz it is possible to find nearly all silica polymorphs observed in the range of pressures from zero to several Mbar. We also investigate pressure-induced phase transitions of α -cristobalite [5]. In carbon dioxide we study the interesting mechanisms of transformation of molecular phases to polymeric phases at high pressure. The results demonstrate that the new method is far more efficient than previous ones and for the first time the study of complex structural transformations with many intermediates is within the reach of molecular dynamics (MD) simulations.

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Keywords: polymorph prediction, structural transformations, computer simulation

MS.19.4

Acta Cryst. (2008). A64, C42-43

First-principles calculations of pressure induced magnetic transition in siderite FeCO₃

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Rhombohedral siderite FeCO₃ has been studied by using density functional theory (DFT) with the generalized gradient approximation (GGA). In order to take into account the strong on-site Coulomb interaction U present in FeCO₃, we also performed the GGA + U calculations. We observed a pressure-induced magnetic transition (high spin \rightarrow low spin) at pressures of 15 GPa and 28 GPa, which were underestimated with respect to the experiment, for the GGA and GGA + U calculations, respectively. This phase transition was with a volume collapse of 10% around, also accompanied by an

increase of bulk modulus and a red shift in the optical gap. The electronic density of states (DOS) and charge density calculations revealed that the magnetic transition was due to the pressure-induced Fe 3d electron delocalization.

Keywords: FeCO₃, first-principles, high pressure

MS.19.5

Acta Cryst. (2008). A64, C43

Predicting crystal structures by random searching

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We predict crystal structures by relaxing randomly chosen starting configurations within density functional theory (DFT)[1]. We combine this with constrained searches incorporating knowledge derived from the random searches and other sources. Applications to various systems are described, including hydrogen,[2] silane,[1] and aluminum hydride.[3] Our study of solid hydrogen includes harmonic proton zero point motion and leads to a radical revision of the DFT phase diagram up to 400 GPa. The most stable phases remain insulating to very high pressures, in agreement with experiment, and we find a strong candidate for phase III. We predict that the equilibrium structure of silane is insulating up to about 200 GPa. Our stable structure in the pressure range 50-250 GPa has high symmetry, each Si site is equivalent and each H site is equivalent, and it is held together by electron-deficient three-center-two-electron bonds. This structure has been observed in a recent x-ray diffraction study.[4] For aluminum hydride we find a transition from the insulating low-pressure alpha phase to an insulating layered structure and then to a metallic phase. Our metallic structure has been observed in a recent X-ray diffraction study.[5]

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Keywords: *ab-initio* calculations, high-pressure phase transformations, hydride compounds

MS.20.1

Acta Cryst. (2008). A64, C43

Protein folding dynamics by time resolved SAXS and single molecule fluorescence spectroscopy

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To understand the mechanism of protein folding, the changes in protein compactness in protein folding were investigated by time-resolved small angle X-ray scattering (SAXS). The system is based on the continuous-flow mixing device and the beamline at

SPRING8 designed for X-ray scattering of biological macromolecules (BL45XU-SAXS). By using the device, we observed the folding dynamics of β -lactoglobulin, which forms a burst phase intermediate possessing a significant amount of non-native helices. We characterized that the intermediate is collapsed. Furthermore, the collapse is accelerated in the presence of trifluoroethanol, which increases the helical content of the intermediate. The results suggested that the non-native helix formation is coupled to the collapse in the folding of β -lactoglobulin. To observe the heterogeneity in protein folding, we next developed a new method to detect fluorescence from single molecules. Proteins labeled with a fluorescent dye were injected into a capillary at a low concentration for the observation of one molecule at a time. A laser was introduced into the capillary, and the fluorescence was imaged as traces on EMCCD camera. Thus, the traces reflect the time-dependent changes of the fluorescence signals from single proteins. We monitored the dynamics of yeast iso-1-cytochrome c labeled by Alexa532 at the single molecule level. By analyzing the autocorrelation function of the traces, we could detect characteristic time constants for the fluctuating motions of the sample.

Keywords: small angle X-ray scattering, single molecule fluorescence spectroscopy, protein folding

MS.20.2

Acta Cryst. (2008). A64, C43

XPCS studies of slow, non-diffusive dynamics in glassy soft materials

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For many disordered soft solids such as gels and concentrated emulsions, the solid phase is separated from a fluid state by an ergodic-nonergodic transition that leaves the system in an out-of-equilibrium configuration. Often these out-of-equilibrium materials display a protracted evolution of their dynamical properties that bears resemblance to behavior seen in molecular and polymer glasses. In order to understand these dynamics at a microscopic scale we have investigated such disordered soft solids through x-ray photon correlation spectroscopy (XPCS), a technique uniquely suited for elucidating the nanoscale motions in glassy materials. After a brief introduction to XPCS, the talk will describe our findings from studies on a set of materials that includes clay suspensions, sheared depletion gels, and concentrated nanoemulsions [1-3]. In short, the dynamics we observe are distinct from the cooperative molecular diffusion in liquids near the glass transition. Rather, they are a type of exceedingly slow, non-diffusive motion that can be modeled as strain in response to heterogeneous local stress and that are apparently universal to a range of disordered materials.

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Keywords: XPCS, soft glassy materials, stress relaxation