

available as single crystals, thus making the determination of the full elastic tensor possible at high pressure.

The electronic and magnetic properties of minerals under extreme conditions of pressure or temperature can also be studied through X-ray emission spectroscopy (XES) in the fluorescence regime. We measured the spin state of iron in the main constituent of the Earth's lower mantle, *i.e.* the iron-bearing magnesium silicate perovskite (Mg,Fe)SiO<sub>3</sub>, by studying the K $\beta$  emission line to pressures exceeding 140 GPa. Geophysical implications for both the anisotropy of propagation of acoustic waves in the Earth's core and the physical properties of the lowermost mantle will be discussed.

**Keywords:** geophysics, inelastic X-ray scattering, high-pressure

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#### Phonon Dispersions in fcc $\delta$ -Pu-Ga by High Resolution Inelastic X-ray Scattering

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The phonon spectra of plutonium and its alloys have been sought after in the past few decades following the discovery of this actinide element in 1941, but with no success. This was due to a combination of the high neutron absorption cross section of <sup>239</sup>Pu, the common isotope, and non-availability of large single crystals of any Pu-bearing materials. We have recently designed a high resolution inelastic x-ray scattering experiment using a bright synchrotron x-ray beam at the ESRF, Grenoble and mapped the full phonon dispersion curves of an fcc  $\delta$ -phase polycrystalline Pu-Ga alloy[1]. Several unusual features including, a large elastic anisotropy, a small shear elastic modulus C', a Kohn-like anomaly in the T<sub>1</sub>[011] branch, and a pronounced softening of the [111] transverse modes are found. These features can be related to the phase transitions of plutonium and to strong coupling between the lattice structure and the 5f valence instabilities. Our results also provide a critical test for theoretical treatments of highly correlated 5f electron systems as exemplified by recent dynamical mean field theory (DMFT) calculations for  $\delta$ -plutonium[2]. Recent work on imaging phonons in Pu-Ga alloys with thermal diffuse scattering[3] will also be discussed.

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[1] Wong J., et al., *Science*, 2003, **301**, 1078. [2] Dai X., et al., *Science*, 2003, **300**, 953. [3] Wong J., et al., *Appl. Phys. Lett.*, 2004, **84**, 3747.

**Keywords:** lattice dynamics, inelastic X-ray scattering, phonon softening

### MS17 NON-COVALENT INTERACTIONS IN CRYSTALS OF SMALL MOLECULES AND MACROMOLECULES

**Chairpersons:** Gautam R. Desiraju, Mariusz Jaskolski

#### MS17.25.1

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#### Multipolar Interactions in Structural Chemistry and Biology

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The past decades of molecular recognition studies have greatly enhanced our knowledge on apolar, ion-dipole, and H-bonding interactions. However, much less attention has been given to the role that multipolar interactions, in particular those with orthogonal dipolar alignment, adopt in organizing a crystal lattice or stabilizing complexes involving biological receptors.

In a recent fluorine scan of thrombin inhibitors to map the fluorophilicity/fluorophobicity of an enzyme active site, we discovered favorable C-F<sub>(ligand)</sub>...C=O<sub>(protein)</sub> interactions, with the F-atom approaching the electrophilic C-atom in a nearly orthogonal way, along the pseudotrigonal axis of the carbonyl unit. The attractive nature of such contacts was subsequently established in model studies.

Using Cambridge structural database (CSD) and protein database (PDB) mining tools, we now have established the generality of these previously rather overlooked interactions. A number of illustrative examples of these interactions found in X-ray crystal structures of small molecules and protein-ligand complexes will be shown to demonstrate their propensity and thus potential importance for both, chemical and biological molecular recognition processes. [1]

[1] Paulini R., Müller K., Diederich F., *Angew. Chem. Int. Ed.*, 2005, *in press*.

**Keywords:** nonbonded interactions, databases, X-ray crystal structure analysis

#### MS17.25.2

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#### Carbonyl...Carbonyl Interactions are Structurally Ubiquitous and Important

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Recent years have seen an increasing interest in intermolecular interactions that are *not* mediated by hydrogen. An early analysis [1] of the Cambridge Structural Database (CSD) identified the isosteric nature of nitro and carbonyl groups in molecular design applications. This prompted further work on dipolar carbonyl-carbonyl interactions that will be reviewed and extended in this talk. In *small organic molecules* it has been shown that CO groups in simple ketones and trans-amides form three main interaction motifs, and that the most frequent sheared-antiparallel arrangement has an attractive interaction energy of ca. -22kJ mol<sup>-1</sup>, competitive with medium-strength H-bonds. In *proteins*, PDB analyses show that CO...CO interactions stabilise  $\alpha$ -helices,  $\beta$ -sheets and  $\beta$ -strands, including the stabilization of the partially allowed Ramachandran conformations of asparagine and aspartic acid. In *organometallics*, we are now studying CO...CO interactions using the CSD. Although compromised by steric hindrance, very significant numbers of CO...CO interactions are observed in M-C=O systems. The antiparallel motif again predominates, and C...O distances are usually shorter than in organic systems, indicative of the stronger dipole in the M-C=O case. Preliminary DFT calculations indicate attractive energies of -20 to -30 kJ mol<sup>-1</sup> for the predominant motif, similar to or stronger than the attractive energies in organic systems.

[1] Taylor R., Mullaley A., Mullier G.W., *Pestic. Sci.*, 1990, **29**, 197-213.

**Keywords:** intermolecular interactions, crystallographic databases, ab initio energy calculations

#### MS17.25.3

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#### Small Molecules and Macromolecules make Contact: Messages from Protein Structures to Atomic Resolution

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Atomic and ultra-high resolution macromolecular crystal structure determination and *ab initio* quantum chemical calculations have become indispensable tools for comprehensive structure interpretation, as they permit acquiring snapshots along the reaction pathway and the assignment of function to the residues involved in catalysis. Fine electronic detail can be visualised and yield valuable information on protein function. The assessment and description of intra- and intermolecular contacts reaches a degree of accuracy which in the past was considered impossible for macromolecules.

The release of geometric restraints and the low coordinate error in atomic resolution protein structures allow the identification of deviations from standard stereochemistry which, at lower resolution, might not have been accounted for. These deviations may occur in intramolecular interactions as well as in intermolecular (protein-ligand) contacts. Quantum chemical calculations, or direct multipole refinement, on these accurate model templates complement the structural data with information beyond the analysis of contact distances. The charge distribution which one can obtain determines the chemical properties and hence characteristics such as substrate