

# High Pressure and Synchrotron Radiation Satellite Workshop

## Workshop on High Pressure and Synchrotron Radiation

February 8-10, 2006

### Aim of the workshop

The workshop will focus on recent advances in science at high pressure at third generation synchrotron sources. This meeting will be aimed a variety of experiments using synchrotron-sourced techniques, including XRD, EXAFS, inelastic x-ray scattering, Compton scattering and Mössbauer spectroscopy of crystalline, liquid or amorphous samples. We aim to delineate the state-of-the-art in these wide-ranging techniques and to establish future directions. It will also deal with the rapid progress made in the theoretical interpretation of the experimental results.

The workshop will consist of approximately 20 invited presentations with ample time reserved for questions and discussion and a poster session.

### Organisation

The workshop is co-organised by people from three groups from the Experiments Division reflecting the different domains of use of high pressure.

- **Michael Hanfland** and **Mohamed Mezouar**, ESRF, *Materials Science Group*
- **Michael Krisch** and **Ulrich Ponkratz**, ESRF, *High Resolution & Resonance Scattering Group*
- **Sakura Pascarelli**, ESRF, *X-ray Absorption & Magnetic Scattering Group*

### Administrative coordinators

- **Myriam Dhez**
- **Ute Ramseger**

### Venue

[CNRS Grenoble Auditorium](#)

# High Pressure and Synchrotron Radiation Satellite Workshop

Workshop on High Pressure and Synchrotron Radiation

February 8-10, 2006

## Programme

Wednesday February 8th, 2006		
13:00	<b>Registration</b>	
14:00	<b>Welcome</b>	
<b>Session 1: Earth Science</b> <b>Chairman: Wilson Crichton</b>		
14:15-15:00	Synchrotron radiation as a probe of earth's deep interior	<b>Jay Bass</b> University of Illinois at Urbana-Champaign, USA
15:00-15:30	Post perovskite	<b>Motohiko Murakami</b> Tokyo Institute of Technology, Japan
15:30-16:00	MgSiO <sub>3</sub> post-perovskite phase P-V-T equation of state	<b>Nicolas Guignot</b> ESRF, France
16:00-16:30	<b>Coffee break</b>	
16:30-17:00	Nuclear resonant spectroscopy in the laser-heated DAC diamond anvil cell	<b>Wolfgang Sturhahn</b> Argonne National Laboratory, USA
17:00-17:30	Solubility of minerals in HP-HT aqueous fluids: an <i>in situ</i> synchrotron X-ray fluorescence study	<b>Isabelle Daniel</b> Univ. Claude Bernard, France
17:30-18:00	Ferropericlase at high pressures: probing structural and electronic properties at synchrotron and in-house facilities	<b>Innokenty Kantor</b> Universität Bayreuth, Germany
18:00-19:00	<b>Poster session with aperitif</b>	
19:15	<b>Bus departure to downtown Grenoble</b>	

Thursday February 9th, 2006

**Session 2: Materials Science and Chemistry**  
**Chairwoman: Giuliana Aquilanti**

09:00-09:45	Chemistry at extreme conditions: from geosciences to synthesis of new materials	<b>Leonid Dubrovinsky</b> Universität Bayreuth, Germany
09:45-10:15	Hydrogen and hydrogen - containing materials studied by a combination of synchrotron and neutron techniques	<b>Igor Goncharenko</b> CEA-CNRS, France
10:15-10:45	New insights on the possible crystalline structure of the metallic $\zeta$ phase of solid oxygen	<b>Serge Desgreniers</b> University of Ottawa, Canada
10:45-11:15	<i>Coffee break</i>	
11:15-11:45	Novel extended phases of molecular triatomics	<b>Choong-Shik Yoo</b> Lawrence Livermore National Lab., USA
11:45-12:15	Carbonia: the amorphous silicalike carbon dioxide	<b>Federico Gorelli</b> University of Florence, Italy
12:15-12:45	Stability and phase transitions under high pressure in silicon clathrates	<b>Pierre Toulemonde</b> Univ. Claude Bernard, France
12:45-14:00	<i>Lunch at the CNRS restaurant</i>	
14:00-14:30	Polymorphism and metastable phenomena in liquid Sn under pressure	<b>Angela Trapananti</b> ESRF, Grenoble
14:30-15:00	High-pressure synchrotron X-ray scattering of oxides with a nano-scaled local structure	<b>Jens Kreisel</b> ENS de Physique de Grenoble, France
15:00-15:30	<i>Coffee break</i>	
<b>Session 3: Hard Condensed Matter</b> <b>Chairwoman: Monica Amboage</b>		
15:30-16:00	Pressure-induced collapse of strong ferromagnetism in $YCo_5$ - a pressure induced electronic topological transition	<b>Helge Rosner</b> MPI, Germany
16:00-16:30	Modulated structures in group VIa elements at high-P and high-T	<b>Clivia Hejny</b> The University of Edinburgh, UK
16:30-17:00	Pressure-driven structural distortion and band gap closure in transition-	<b>Ingo Loa</b> MPI, Germany

	metal perovskites	
17:00-17:30	Lattice dynamics at ultra-high pressures: Quantification of phonon energies using high-resolution inelastic x-ray scattering	<b>Daniel Farber</b> Lawrence Livermore National Lab., USA
17:30-18:00	Bonding changes in compressed superhard graphite	<b>Wendy Mao</b> ( <i>not confirmed</i> ) The University of Chicago, USA
<b>18:00-19:00</b>	<b>Poster session</b>	
<b>19:15</b>	<b>Bus departure to the restaurant</b>	
<b>20:00</b>	<b>Workshop dinner</b>	
<b>Friday February 10th, 2006</b>		
<b>Session 3: Hard Condensed Matter (continued)</b> <b>Chairman: Gyorgy Vankó</b>		
09:00-09:45	Superconductivity in molecular solids at high pressure	<b>John Tse</b> Univ. of Saskatchewan, Canada
09:45-10:15	Resonant X-ray magnetic scattering under hydrostatic pressure: pressurised magnetic order in Co doped CeFe <sub>2</sub>	<b>Pascale Petronella Deen</b> ESRF, France
<b>10:15-10:45</b>	<b>Coffee break</b>	
10:45-11:15	Magnetic properties of the Eu-monochalcogenides at extreme pressures	<b>Kirsten Rupprecht</b> Universität Paderborn, Germany
11:15-11:45	Lattice dynamics of cerium metal around the $\gamma \leftrightarrow \alpha$ transition by inelastic X-ray scattering	<b>Alexandre Beraud</b> ESRF, France
11:45-12:15	Combined XAS and XMCD studies under pressure of iron and iron based compounds	<b>Olivier Mathon</b> ESRF, France
12:15-12:30	Conclusions	
<b>12:30</b>	<b>Lunch at the CNRS restaurant</b>	

# Synchrotron radiation as a probe of earth's deep interior

BASS J.

Geology Dept, University of Illinois, 1301 W Green St., Urbana, IL 61801 USA, jaybass@uiuc.edu

The previous decade has witnessed a number of discoveries that have greatly altered our view of the Earth's deep interior. Major advances have come in two areas: the first is our ability to observe fine details of Earth's interior structure and properties, and the second is in our ability to interpret those observables in terms of the most basic properties, such as chemical composition, mineralogy (or crystal structure), thermal structure, and the presence of solid versus liquid phases (or both) at great depth. Much of the progress in Earth observation has been in the area of seismology, which is now capable of mapping out the fine-scale structure of the interior in terms of acoustic wave velocities. These are some of the most basic clues we have on the variations of chemistry and temperature that are responsible for the density variations that drive convective motions in Earth's mantle and core, and power the plate tectonic activity that we see on the surface of our planet.

Synchrotron radiation plays an essential and ever-expanding role in the interpretation of the observed properties of the Earth, particularly the deepest levels of the Earth from which we have no actual samples and which we cannot directly probe. The high intensity of tightly focused synchrotron x-rays are allowing the identification of new solid phases at ever-increasing pressures on smaller samples. Moreover, the high-energy resolution of synchrotron x-rays now makes it possible to utilize inelastic scattering techniques for a new generation of high-pressure experiments. Two examples would be the determination of acoustic velocities of samples at high pressure (which is of primary importance for geophysical investigations), and electronic phase transitions (which bear on the geochemical and thermal properties of the mantle). In this talk we review some of the recent Earth observations that have stimulated mineral physics research, major questions about the Earth's interior, and synchrotron-based methods that are being used to address forefront issues in studies of the deep Earth. Some examples are the compositional dependence of acoustic wave velocities in the abundant phases of Earth's deep interior (such as silicate perovskite in the lower mantle, and iron alloys the core), acoustic wave anisotropy, and the properties of silicate melts under high-pressure-temperature conditions. We also present some recent efforts to combine Brillouin scattering with synchrotron x-ray diffraction for simultaneous measurement of sound velocities (by Brillouin spectroscopy) and density. This combination of methods may play a critical role in the determination of absolute pressure scales and the more accurate measurement of pressure in diamond cell experiments.

# MgSiO<sub>3</sub> post-perovskite phase P-V-T equation of state

GUIGNOT N.<sup>1</sup>, ANDRAULT D.<sup>2</sup>, MORARD G.<sup>1</sup>, BOLFAN-CASANOVA N.<sup>3</sup> and  
MEZOUAR M.<sup>1</sup>

<sup>1</sup> ESRF, 6 Jules Horowitz, BP 220, 38043 Grenoble Cedex, France

<sup>2</sup> IMPMC, 140 rue de Lourmel, 75015 Paris, France

<sup>3</sup> Laboratoire Magmas et Volcans, 5 rue Kessler, 63038 Clermont-Ferrand Cedex, France

The recent discovery of a new MgSiO<sub>3</sub> high pressure polymorph ([1][2]) has a huge impact on our understanding of the structure and dynamics of the deep Earth. This phase with Cmc<sub>2</sub>m CaIrO<sub>3</sub> type-structure, and now commonly named post-perovskite phase, is produced from Pbnm-perovskite MgSiO<sub>3</sub> in the 110-125 GPa pressure range ([3]). This roughly corresponds to the depth of appearance of Earth's D'' layer. This lowermost part of the lower mantle is the probable destination of a non negligible part of downwelling subducted slabs, the probable source of superswells and mantle plumes, and the site of chemical exchanges with the core, all of this being ruled by the very steep temperature gradient near the core-mantle boundary. It displays very complex seismic signatures, mainly due to a high lateral heterogeneity and shear-wave splitting ([4]). Knowing that (Al,Fe)-MgSiO<sub>3</sub> perovskite phase is the major constituent of the lower mantle, it is mandatory to clarify what are the effects of the post-perovskite phase production, i.e. the Clapeyron slope dP/dT of the transition and of course the post-perovskite phase elastic properties. It is therefore necessary to provide precise data on the post-perovskite phase compressibility at D'' layer pressure and temperature conditions. The new ID27 beamline facilities of ESRF (Grenoble) were used to collect in-situ high temperature angle-dispersive x-ray diffraction spectra at high pressure. After a short presentation of the experimental setup, details on MgSiO<sub>3</sub> post-perovskite phase P-V-T equation of state will be provided.

## References

- [1] - Murakami, M., et al., *Science* **304**, 855-858, (2004)
- [2] - Oganov, A.R. and Ono, S., *Nature* **430**, 445-448, (2004)
- [3] - Ono, S. and Oganov, A.R., *Earth Planet. Sci. Lett.* **236**, 914-932, (2005)
- [4] - S. Stackhouse, J. P. Brodholt, J. Wookey, J. -M. Kendall and G. D. Price, *Earth Planet. Sci. Lett.* **230**, 1-10, (2005)

# Nuclear resonant spectroscopy in the laser-heated diamond anvil cell

STURHAHN W.

Advanced Photon Source, Argonne National Laboratory,  
9700 South Cass Ave, Argonne, IL 60439, USA

The introduction of nuclear resonant scattering techniques to third generation synchrotron radiation facilities around the world has been very successful over the last decade. New opportunities for the study of vibrational and magnetic properties of condensed matter have opened up for research areas like biophysics, geophysics, and nanoscience. In particular, the determination of the vibrational density of states with nuclear resonant inelastic x-ray scattering (NRIXS) and the study of valences and magnetic properties with synchrotron Mössbauer spectroscopy (SMS) provided remarkable results [1].

In this contribution, we discuss the combination of nuclear resonant spectroscopy with diamond anvil cell technology and its impact on the scientific area of geophysics. We will briefly address the specifics of NRIXS, a method that uses probe nuclei with suitable resonances to measure the vibrational density of states, and SMS for the determination of valences, spin states, and magnetic ordering analogous to conventional Mössbauer spectroscopy. Both methods are very sensitive to small amounts of material and take advantage of the high brilliance of synchrotron radiation, which makes micrometer-sized x-ray beams with high intensity possible. These properties together with the isotope selectivity allowed NRIXS and SMS investigations on materials under pressures in the Mbar regime using diamond anvil cells and Laser heating [2-4].

Even though  $^{57}\text{Fe}$  has spawned the largest interest so far, we will review the selection of other suitable nuclear resonances that could become important for future applications. Nuclear resonant spectroscopy methods, which include NRIXS and SMS, continue to evolve with the development of new instrumentation, the improvement of synchrotron radiation sources, the increased diversity in nuclear resonant methods, and the synergy with other experimental techniques like x-ray diffraction, inelastic x-ray scattering, and x-ray fluorescence analysis. We will identify different evolutionary branches and speculate about their potential impact on the experimental realizations and the applications of nuclear resonant spectroscopy.

This work is supported by the U.S. DOE-BES, Office of Science, under Contract No. W-31-109-Eng-38.

## References

- [1] – W. Sturhahn, *J. Phys.: Condens. Matter* **16**, S497, (2004)
- [2] – J.-F. Lin, W. Sturhahn, J. Zhao, G. Shen, H.-k. Mao, R. J. Hemley, *Geophys. Res. Lett.* **31**, L14611, (2004)
- [3] – J. Zhao, W. Sturhahn, J.-F. Lin, G. Shen, E. E. Alp, H.-k. Mao, *High Press. Res.* **24**, 447, (2004)
- [4] – J.-F. Lin, W. Sturhahn, J. Zhao, G. Shen, H.-k. Mao, R. J. Hemley, *Science* **308**, 1892, (2005)

# Solubility of minerals in HP-HT aqueous fluids: an *in situ* synchrotron X-ray fluorescence study

DANIEL I.<sup>1</sup>, SANCHEZ VALLE C.<sup>2</sup>, REYNARD B.<sup>1</sup>, MARTINEZ I.<sup>3</sup>,  
SIMIONOVICI A.<sup>1</sup>

<sup>1</sup>Laboratoire de Sciences de la Terre, UMR 5570 CNRS - ENS Lyon – Université Claude Bernard Lyon 1, France.

<sup>2</sup>Dpt of Geology, University of Illinois at Urbana Champaign, IL, USA.

<sup>3</sup>Laboratoire de Géochimie des Isotopes Stables, UMR 7047 CNRS – IGGP - Université Paris 7, France.

CO<sub>2</sub>-rich saline aqueous fluids are liberated into the mantle when the altered oceanic crust is subducted, leading to the important geochemical phenomena of mantle wedge metasomatism and arc magmatism. To better understand these processes, knowledge of mineral-fluid equilibria and mineral solubility in HP-HT crustal fluids is thus required.

We report here *in situ* measurements on the solubility of strontianite (SrCO<sub>3</sub>) and GeO<sub>2</sub>-rutile at P (up to 6.6 GPa) and T (up to 400°C) relevant for cold subducted slabs. The composition of the fluid surrounding the crystal, loaded in an externally heated diamond-anvil cell, was analysed *in situ* by monitoring the X-ray fluorescence of Sr<sup>2+</sup> and Ge<sup>4+</sup> cations, respectively, until chemical equilibrium was reached. Experiments were carried out at the ESRF (ID22 beamline) using a high-resolution monochromatic beam (2×5 μm<sup>2</sup> and 18 keV), and a collection geometry at 30° from the transmitted beam.

This results in quantitative analysis of the solution down to the 20 ppm level. In the case of strontianite, kinetic data of the dissolution reaction showed instantaneous equilibration times at 400 °C. Measured dissolution rates are essentially compatible with a first-order reaction mechanism and allow to retrieve the activation energy (E<sub>A</sub>) for the dissolution of SrCO<sub>3</sub> at HP-HT conditions. Taking into account activity coefficients, measured Sr<sup>2+</sup> concentrations are used to determine the solubility constant (K<sub>s</sub>) of SrCO<sub>3</sub> at HP-HT conditions, allowing further thermodynamic modelling of carbonate dissolution.

In the case of GeO<sub>2</sub>-rutile, we observed a gradient of the Ge concentration in the fluid. Hence, on the top of solubility measurements, it also allows to calculate the diffusion coefficients of Ge in high P-T aqueous fluids. This experiment thus shows the suitability of the SXRF technique for the *in situ* study of elemental diffusion in aqueous systems under high P-T conditions. Such data are essential for the modeling of diffusive transport of elements and its influence on the growth and dissolution of minerals.



# Ferropericlase at high pressures: probing structural and electronic properties at synchrotron and in-house facilities

KANTOR I., DUBROVINSKY L., MCCAMMON C.

Bayerisches Geoinstitut, Universität Bayreuth, D-95440 Bayreuth, Germany

Ferropericlase (Mg,Fe)O with ~20% of Fe is one of the main constituents of the Earth's lower mantle (second in abundance after (Mg,Fe)SiO<sub>3</sub> perovskite). Its properties and stability field are therefore important for geophysical and geochemical models of the Earth's deep interior. The MgO end member of this solid solution has no phase transitions up to at least 200 GPa [1]. In contrast, there are several structural and electronic transformations in FeO at high pressures: it transforms from the cubic NaCl structure to a rhombohedrally distorted one and further to a hexagonal NiAs-like structure [2]. Several electronic transitions are also known to occur in FeO: a magnetic ordering transition from paramagnetic to antiferromagnetic and a high- to low-spin transition [3]. If any of these transformations were to occur in ferropericlase, its physical properties would be changed significantly.

We present a combined X-ray diffraction, X-ray absorption and conventional Mössbauer spectroscopic study of (Mg<sub>0.8</sub>Fe<sub>0.2</sub>)O up to 105 GPa. Based on multiple experimental techniques we clearly established the presence of two transitions in ferropericlase: rhombohedral distortion at ~35 GPa [4] and spin transition that occurs in the 55-102 GPa pressure range. These results change our understanding of high-pressure properties of ferropericlase: the spin transition is so broad that there would be no discontinuities in any physical properties associated with spin crossover, but only smooth changes. At the same time a structural transition in ferropericlase could result in a minor seismic waves velocity discontinuities.

## References

- [1] - T. S. Duffy, R. J. Hemley, H. K. Mao, Phys. Rev. Lett. **74**, 1371, (1995)
- [2] - Y. Fei and H. K. Mao, Science **266**, 1678, (1994)
- [3] - M. P. Pasternak, R. D. Taylor, R. Jeanloz, X. Li, J. H. Nguen, and C. A. McCammon, Phys. Rev. Lett. **79**, 5046, (1997)
- [4] - I. Kantor, L. Dubrovinsky, C. McCammon, A. Kantor, S. Pascarelli, G. Aquilanti, W. Crichton, M. Mattesini, R. Ahuja, V. Urusov, Phys. Chem. Minerals: DOI 10.1007/s00269-005-0052-z, (2006)

# Chemistry at extreme conditions: from geosciences to synthesis of new materials

DUBROVINSKY Leonid, DUBROVINSKAIA Natalia, KANTOR Innokenty,  
KURNOSIV Alexandr, KUZNETSOV Alexei  
Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany

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-SiO<sub>2</sub>, Fe-Al<sub>2</sub>O<sub>3</sub>, MgO-FeO, Fe-MgSiO<sub>3</sub>, 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.

# Hydrogen and hydrogen - containing materials studied by a combination of synchrotron and neutron techniques

GONCHARENKO I.\* & LOUBEYRE P.<sup>1</sup>

\*Laboratoire Léon Brillouin C.E.A.-C.N.R.S., C.E.A. Saclay, 91191 Gif-sur-Yvette, France

<sup>1</sup>Département Physique Théorique et Applications, C.E.A., 91680 Bruyères-le-Châtel, France

Hydrogen and hydrogen – containing materials exhibit many fascinating physical phenomena associated with quantum nature of hydrogen atoms in solids. A combination of synchrotron and neutron scattering techniques is the most powerful tool to study crystal structure and phase transitions in these systems. New pressure techniques, allowing to perform neutron and X-ray experiments on the same sample in the same thermodynamical conditions had been developed. The technique is suitable for both powder and single-crystal experiments.

We report our recent work on crystal structure of quantum broken-symmetry phase (BSP) in solid deuterium at pressures above 20 GPa [1]. Since discovery in 1980s by indirect optical probes, the crystal structure of the high pressure phases in solid hydrogen and deuterium had been subject of many speculations. Contrary to the most of theoretical predictions, our results suggest a *Pa3*-type local order and an incommensurate modulation in the BSP.

At the end, prospects for combined X-ray and neutron studies in the “light” hydrides such as AlH<sub>3</sub> are discussed, including a possibility of new stable (or quasistable) phases having potential interest for applications.

## Reference

[1] - I. Goncharenko & P. Loubeyre, *Nature* **435**, 1206 (2005)

# New insights on the possible crystalline structure of the metallic $\zeta$ phase of solid oxygen

DESGRENIERS Serge<sup>1,2</sup>, WECK Gunnar<sup>2</sup>, and LOUBEYRE Paul<sup>2</sup>

<sup>1</sup>Institut de physique Ottawa-Carleton, université d'Ottawa, Ottawa Canada. K1N 6N5

<sup>2</sup>DIF/DPTA, CEA 91680 Bruyères-le-Châtel, France

Solid oxygen has been shown, unlike nitrogen and hydrogen, to undergo a transition to a metallic state at a room temperature at 96 GPa [1,2]. The electronic transition to the metallic phase ( $\zeta$ -O<sub>2</sub>) is accompanied by a structural transition [3]. Weck *et al.* [4] have shown, by X-ray diffraction of single crystals, the displacive nature of planes of O<sub>2</sub> molecules initiated as the  $\varepsilon$ - $\zeta$ -O<sub>2</sub> transition takes place. Goncharov *et al.* [5] have reported a discontinuity of the Raman-active O<sub>2</sub> stretching vibration wavenumber, beyond the  $\varepsilon$ -O<sub>2</sub>/ $\zeta$ -O<sub>2</sub> phase boundary starting at 103 GPa, as an evidence that the  $\zeta$ -O<sub>2</sub> phase, although clearly molecular, is not isostructural to the  $\varepsilon$ -O<sub>2</sub> as speculated from earlier powder X-ray diffraction results [3]. To further elucidate the nature of the  $\zeta$ -O<sub>2</sub> phase, we have undertaken a study of dense solid oxygen under the best hydrostatic pressure conditions. In this presentation, we report recent results of X-ray diffraction and Raman spectroscopy experiments performed on single crystals of oxygen imbedded and oriented differently in solid helium, studied across the  $\varepsilon$ -O<sub>2</sub> to  $\zeta$ -O<sub>2</sub> phase line and beyond, to pressures close to 140 GPa. The successful growth of individual single crystals of oxygen in helium was based on the very low miscibility of liquid O<sub>2</sub> in liquid He at 450K and 22.5 GPa at a concentration of 2.5 mol % of O<sub>2</sub>. Under those conditions and upon cooling or pressure increase, the phase segregated liquid oxygen transformed into the pure solid  $\varepsilon$ -O<sub>2</sub> phase, resulting in good quality single crystals. Pressures were calculated using the calibrated spectral shift of the ruby luminescence R-lines, well resolved at all pressures. X-ray diffraction images recorded from single crystals in the  $\zeta$ -O<sub>2</sub> phase, in different orientations, indicate most likely a crystalline structure different from that of the  $\varepsilon$ -O<sub>2</sub> phase. The  $\zeta$ -O<sub>2</sub> phase is characterized by the occurrence of a significant lattice plane stacking fault arrangement resulting in large Bragg peak shifts. Furthermore, our Raman spectroscopic results indicate, in agreement with those published [5], a significant decrease of the O<sub>2</sub> stretching vibration wavenumber at 103 GPa with respect of that extrapolated from the  $\varepsilon$ -O<sub>2</sub> phase and, in addition, the appearance of a second Raman-active line at a wavenumber slightly above the former. The increase of pressure induced a gradual splitting between the stretching vibration wavenumbers in the  $\zeta$ -O<sub>2</sub> phase.

## References

- [1] - S. Desgreniers, Y. K. Vohra, and A. L. Ruoff, J. Phys. Chem. 1990, **94**, 1117-1122.
- [2] - K. Shimizu *et al.*, Nature, 1998, **393**, 767-769.
- [3] - Y. Akahama *et al.*, Phys. Rev. Lett., 1995, **74**, 4690-4.
- [4] - G. Weck, P. Loubeyre, and R. Le Toullec. Phys. Rev. Lett., 2002, **88**, 035504/1-4.
- [5] - A. F. Goncharov, E. Gregoryanz, R. J. Hemley, and H-k. Mao. Phys. Rev. B., 2003, **68**, 100102/1-3.

# Novel Extended Phases of Molecular Triatomics

YOO C-S., IOTA V., PARK J., CYNN H.

Lawrence Livermore National Laboratory, Livermore, California 94551

Application of high pressure significantly alters the interatomic distance and thus the nature of intermolecular interaction, chemical bonding, molecular configuration, crystal structure, and stability of solid. With modern advances in high-pressure technologies, it is feasible to achieve a large (often up to a several-fold) compression of lattice, at which condition material can be easily forced into a new physical and chemical configuration. The high-pressure thus offers enhanced opportunities to discover new phases, both stable and metastable ones, and to tune exotic properties in a wide-range of atomistic length scale, substantially greater than (often being several orders of) those achieved by other thermal (varying temperatures) and chemical (varying composition or making alloys) means.

There are numerous theoretical and experimental results demonstrating that simple molecular solids transform into nonmolecular phases at high pressures and temperatures, ranging from monatomic molecular solids such as sulfur, phosphorous and carbon to diatomic molecular solids such as nitrogen, carbon monoxide and iodine, to triatomic molecules such as ice, carbon dioxide and carbon disulfide, and to polyatomics such as methane and cyanogen, and aromatic compounds. In this paper, we will focus on the pressure-induced phase transitions observed in a few molecular triatomics: first reviewing the transformations in two isoelectronic linear triatomics, carbon dioxide and nitrous dioxide, and then discussing about their outstanding issues and periodic analogies to carbon disulfide and silicone dioxide.

This work was performed under the auspices of the U.S. DOE by the Univ. of Calif., LLNL under contract No. W-7405-Eng-48. The authors acknowledge invaluable uses of beamtimes at the ESRF and the APS which made the present study possible. We also recognized the experimental contributions from other collaborators including M. Nicol, H. Kolhmann, S. Carlson, T. LeBihan, M. Mohammad, and D. Hausermann.

# Carbonia: the amorphous silicalike carbon dioxide

GORELLI F.

University of Florence, Italy

Among the group IV elements, carbon is the unique that at ambient condition forms stable double bonds with oxygen. In contrast to the cases of  $\text{SiO}_2$  and  $\text{GeO}_2$  the nonmolecular tetrahedral crystalline form of  $\text{CO}_2$ , phase V, only exists at high pressure. Similarly, while the amorphous phases of  $\text{SiO}_2$  (a-silica) and  $\text{GeO}_2$  (a-germania) are well known and stable at room condition, the amorphous, nonmolecular, phase of  $\text{CO}_2$ , although predicted by ab-initio simulations, had not yet been discovered. Here we report on the synthesis of amorphous, silica-like, carbon dioxide. The non molecular amorphous phase of carbon dioxide, a- $\text{CO}_2$ , that for similarity with other amorphous oxide of the group IV we will call a-carbonia, was attained by compressing molecular phase III above 47 GPa at room temperature. In situ infrared spectra, measured with raising temperature up to 680 K, probe the progressive formation of C-O single bonds and the simultaneous disappearing of the molecular signatures. State-of-the-art Raman and synchrotron x-ray diffraction measurements on the temperature quenched sample show the amorphous character of this material. The comparison with vibrational and diffraction patterns of amorphous silica and germania, shows that a-carbonia is homologous to those glasses. The static structure factor of a- $\text{CO}_2$  has also been calculated by ab initio techniques, reproducing the main features of the experimental pattern. These findings do extend the scenario of archetypal network-forming disordered systems such as a-silica, a-germania, a-Si and a-Ge, and water.

## Stability and phase transitions under high pressure in silicon clathrates

TOULEMONDE P.<sup>1</sup>, MACHON D.<sup>1</sup>, MERLEN A.<sup>1</sup>, SAN MIGUEL A.<sup>1</sup>  
 AMBOAGE M.<sup>2</sup>, AQUILANTI G.<sup>2</sup>, MATHON O.<sup>2</sup>, PASCARELLI S.<sup>2</sup>, ITIE, J.-P.<sup>3</sup>  
 McMILLAN P.F.<sup>4</sup>

<sup>1</sup>LPMCN, Université Claude Bernard Lyon-1 and CNRS, Villeurbanne, France,

<sup>2</sup>ESRF, Grenoble, France, <sup>3</sup>IMPMC, Paris, France and Synchrotron SOLEIL, Gif-sur-Yvette, France,

<sup>4</sup>Department of Chemistry, University College London, London, United Kingdom.

Silicon clathrates are nanostructured cage-like materials that allow for high intercalation. As a consequence, their physical properties are depending on the nature of the guest atom trapped in the Si<sub>20</sub>, Si<sub>24</sub> and Si<sub>28</sub> cages constituting their covalent sp<sup>3</sup> network. In this work, the high-pressure properties of different type of silicon clathrates (type-I M<sub>x</sub>Si<sub>46</sub>, type-II M<sub>x</sub>Si<sub>136</sub>...) have been studied by X-ray diffraction (ESRF, ID30 and ID09) and X-ray absorption spectroscopy (ESRF, ID24 and BM29). The case of type-I Ba<sub>8</sub>Si<sub>46</sub> [1] and the effect of the substitution of the guest - or host - atoms were particularly investigated [2].

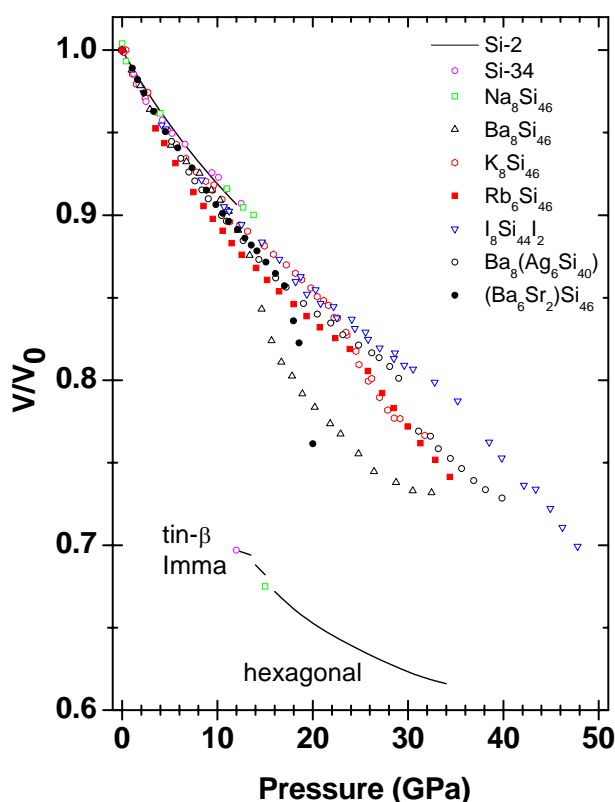


Figure 1: Relative volume as a function of pressure in type-I and type-II silicon clathrates.

First of all, it is shown that the clathrate structure has a pressure stability domain up to 4 times bigger than the Si-diamond one.

Secondly, we observed that clathrates intercalated with light atoms (Na) or empty clathrates give rise to a 1st order phase transition. For large atoms (K, Rb, Cs, Sr, Ba) in the cages, an original phase transition is found, i.e. a 2nd order transition based on an isostructural volume collapse. Rietveld analysis of the Ba<sub>8</sub>Si<sub>46</sub> XRD data shows the homothety of the contraction of the host lattice after the structural transition (~ 11.5-14 GPa).

EXAFS at the Ba K-edge demonstrates that the Ba atom is at the center of cages, with a precision of 0.3 Å, at least up to the volume collapse pressure. Finally, the position of the Ba L3-edge shows a jump at about 5 GPa demonstrating a change of hybridization of the Ba-5d electrons. This change is associated to the disappearance of low energy Raman modes [3].

### References

- [1] - A. San Miguel, A. Merlen, P. Toulemonde et al., *Europhysics Letters* **69** 556, (2005) and ref. therein.  
 [2] - A. San Miguel and P. Toulemonde, *High Pressure Research* **25**, 159 (2005).  
 [3] - T. Kume et al., *Phys. Rev. Lett.* **90** 155503 (2003).

# Polymorphism and metastable phenomena in liquid Sn under pressure

TRAPANANTI A.<sup>\*</sup>, DI CICCO A.<sup>1</sup>, DE PANFILIS S.<sup>\*</sup>, FILIPPONI A.<sup>2</sup>

<sup>\*</sup>European Synchrotron Radiation Facility, Grenoble (France)

<sup>1</sup> CNISM-INFN and Dipartimento di Fisica, Università di Camerino, Camerino (Italy)

<sup>2</sup> CNISM-INFN and Dipartimento di Fisica, Università dell'Aquila, Coppito (Italy)

Polyamorphism, the property of liquids and glassy systems of transforming between different structures in response to the pressure and the temperature, has been proposed and discussed for a variety of systems.

This is a fundamental phenomenon with strong interdisciplinary implications ranging from earth and planetary science to chemistry and material science. However, very few experiments have been performed so far, especially for simple substances.

Within this contribution, we report about new experimental results on liquid and undercooled tin under high-pressure obtained by combining x-ray absorption spectroscopy (XAS) and x-ray diffraction.

The interest in liquid Sn stems from the possible occurrence of liquid-liquid phase transitions which have been related to the soft-core interaction potential often used to describe not-simple liquid metals, such as Sn, Bi, Ga or Ge. In addition, discontinuities of volume, heat capacity and electric resistivity have been reported for Sn in a rather narrow interval of the pressure- temperature phase diagram.

We investigated Sn at high-pressure up to 4 GPa and temperature up to 700 K by a combination of experimental techniques such as x-ray absorption spectroscopy, fixed energy x-ray absorption temperature scans and energy scanning x-ray diffraction.

We show that crucial properties like undercooling limit and local structure change upon application of pressure. In particular, above a critical pressure ( $\approx 2$  GPa) the undercooling limit of liquid tin is drastically reduced by preferential nucleation of the liquid into a solid phase (Sn-III) stable only at much higher pressures ( $\approx 3$  GPa). This phenomenon is accompanied by a gradual change of the local structure, analyzed on the basis of a three-dimensional structural model compatible with XAS data. The picture emerging from this study of liquid Sn is that of a liquid composed of tetrahedral and close-packed configurations, where the latter dominate at high pressures leading to preferential nucleation toward a phase of higher coordination (Sn-III) as the pressure increases.

No evidence for a definite liquid-liquid phase transition was found, but a clear experimental proof of a drastic change in the nucleation properties at high pressures, accompanied by a change of the short-range local geometrical ordering of the liquid has been provided.



# High-pressure synchrotron X-ray scattering of oxides with a nano-scaled local structure

KREISEL J.<sup>1</sup>, BOUVIER P.<sup>2</sup>, DKHIL B.<sup>3</sup>, CHAABANE B.<sup>1,2</sup>

<sup>a</sup> Lab. Matériaux et Génie Physique, CNRS, ENS de Physique de Grenoble, France, kreisel@inpg.fr

<sup>b</sup> LEPMI, CNRS, ENSEE Grenoble, France

<sup>c</sup> SPMS, CNRS, Ecole Centrale Paris, France,

Many of the remarkable physical properties observed in ABO<sub>3</sub>-type oxides are related to materials with an *intrinsic* nano-scaled local structure, where the different regions are characterized by competing chemical, structural and/or physical properties. One of the major challenges in the analysis of the nano-scaled oxides is the experimental access to the local properties, which is often at best a difficult task. The presence of a nano-scaled structure is characteristic of so-called relaxor ferroelectrics (relaxors), materials that have attracted considerable attention since the recent discovery of ultrahigh strain and giant piezoelectric properties in relaxor-based single crystals [1].

New approaches to the detailed characterization of nano-structured materials are clearly of interest since they will provide improved understanding which in turn should lead to the possibility of tuning of local properties to create new functional materials with superior properties. Furthermore, a fundamental understanding of nano-scale features of materials including a good knowledge of the local structural properties is also an important prerequisite for promising *ab initio* calculations.

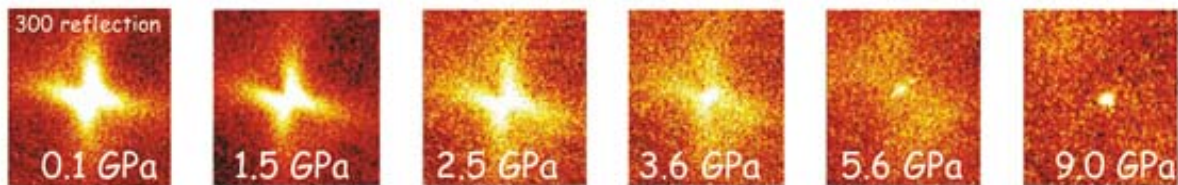


Figure 1: Pressure-dependent evolution of the diffuse scattering around the (300) reflection in PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub>

Motivated to understand in detail the local structure of relaxors we have extended our laboratory Raman scattering investigations [2-3] by high-pressure X-ray scattering studies at the ESRF synchrotron source [4-6]. Here we present results obtained for the model relaxors PbMg<sub>1/3</sub>Nb<sub>2/3</sub>O<sub>3</sub> (PMN) and Na<sub>1/2</sub>Bi<sub>1/2</sub>TiO<sub>3</sub> (NBT) which will be discussed within the framework of relaxors in a more general manner.

Our results show namely that an external pressure of several GPa (as can be met in thin films) alters fundamentally the structural and polar properties in relaxor ferroelectrics on the short- *and* long-range. A particular interesting observation is the suppression of the relaxor-characteristic X-ray diffuse scattering with pressure (see Figure [5]) which points to a pressure-induced crossover from short-to-long-range order.

## References

- [1] - S. E. Park, and T. R. Shrout, J. Appl. Phys. **82**, 1804 (1997)
- [2] - J. Kreisel, A.M. Glazer, P. Bouvier, G. Lucazeau, Phys. Rev. B **63**, 174106 (2001).
- [3] - J. Kreisel, B. Dkhil P. Bouvier, J.M. Kiat, Phys. Rev. B **65**, 172101 (2002)
- [4] - J. Kreisel, P. Bouvier, B. Dkhil, *et al.* Phys. Rev. B **68**, 014113 (2003),
- [5] - B. Chaabane, J. Kreisel, B. Dkhil, P. Bouvier, M. Mezouar, Phys. Rev. Lett. **90**, p. 257601 (2003)
- [6] - P.E. Janolin, B. Dkhil, P. Bouvier, J. Kreisel, P.A. Thomas, Phys. Rev. B (accepted, 2006)

# Pressure-induced collapse of strong ferromagnetism in YCo<sub>5</sub> – a pressure induced electronic topological transition

ROSNER H.<sup>1</sup>, KOUDELA D.<sup>2</sup>, SCHWARZ U.<sup>1</sup>, HANDESTEIN A.<sup>2</sup>, HANFLAND M.<sup>3</sup>,  
OPAHLE I.<sup>2</sup>, KOEPERNIK K.<sup>2</sup>, KUZ'MIN M.<sup>2</sup>, MUELLER K.-H.<sup>2</sup>, MYDOSH J.<sup>1</sup>,  
RICHTER M.<sup>2</sup>

<sup>1</sup> Max-Planck-Institut für Chemische Physik fester Stoffe, Nöthnitzer Straße 40, 01187 Dresden, Germany

<sup>2</sup> Institut für Festkörper- und Werkstoffforschung, P.O. Box 270116, 01171 Dresden, Germany

<sup>3</sup> ESRF, BP220, 38043 Grenoble, France

Isomorphic lattice collapse under pressure is a rare phenomenon, usually related to a change of chemical valence. The most famous examples are samarium sulfide and cerium metal. They are cubic under ambient conditions and collapse isomorphically under pressure, with about 15% volume reduction<sup>1,2</sup>. In SmS the electronic transition is ascribed to a change of valence. The collapse in Ce is connected with altering contributions of the 4*f*-electrons to the chemical bonding, though details are still debated<sup>3,4</sup>. In contrast, the investigated YCo<sub>5</sub> is obviously a compound with a stable valence. We have found that an entirely new type of isomorphic transition occurs in the hexagonal metallic compound YCo<sub>5</sub> under hydrostatic pressure of 19GPa. Here, the volume collapse is driven by magnetic interactions and can be characterized as a first-order Lifshitz<sup>5</sup> or electronic topological transition. This is shown in a combined investigation using ab-initio electronic structure calculation and high-pressure x-ray diffraction. Our studies prove the existence of a bistable bonding state due to magnetoelastic interaction.

## References

- [1] - Bridgman, P. W.. *Proc. Am. Acad. Arts Sci.* **76**, 55 (1948), *Proc. Am. Acad. Arts Sci.* **62**, 207 (1927).
- [2] - Chatterjee, A., Singh, A. K. & Jayaraman, A. *Phys. Rev. B* **6**, 2285 (1972).
- [3] - Haule, K. et al. *Phys. Rev. Lett.* **94**, 036401 (2005).
- [4] - McMahan, A. K., Held, K. & Scalettar, R. T., *Phys. Rev. B* **67**, 075108 (2003).
- [19] - Lifshitz, I. M., *Sov. Phys. JETP* **11**, 1130 (1960).

# Modulated structures in group VIa elements at high-P and high-T

HEJNY C.<sup>1</sup>, FALCONI S.<sup>2</sup>, LUNDEGAARD L.F.<sup>2</sup>, McMAHON M.I.<sup>2</sup>

<sup>1</sup> Mineralogisches Institut, Universität Heidelberg, Germany.

<sup>2</sup> School of Physics and Centre for Science at Extreme Conditions, University of Edinburgh, UK.

Incommensurately (IC) modulated structures in elements at high pressures have recently been shown to be a well established and frequently encountered phenomenon [1]. The group VIa elements S [2], Se [3] and Te [4] have non-composite IC modulated structure with superspace group  $I'2/m(0q0)s0$ . In Te the single phase IC Te-III is stable from 4.5 to 29.2GPa, single phase IC Se-IV above 41GPa, and single phase IC S-III above 95GPa. Sulphur was measured at ESRF on ID09 and is the first element with an incommensurately modulated structure above 100GPa.

Te-III is known to be stable over a wide pressure range at 300K. New high-P high-T measurements performed at ESRF on ID09 study the stability of this modulated phase at elevated temperatures (Fig. 1) as well as the T-dependence of the incommensurate wavevector  $q$ .

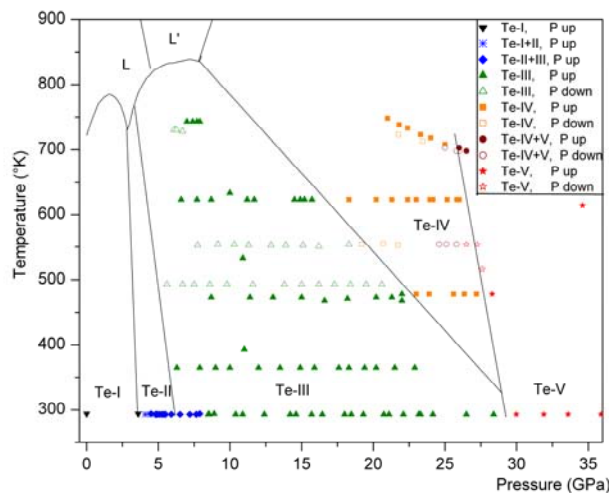


Fig. 1: Phase diagram of Te up to 35GPa and 900K showing measured data points. The melting curve and phase boundaries between the two liquid phases and between the Te-I  $\rightarrow$  Te-II phase boundary are taken from [5]. The Te-III  $\rightarrow$  Te-IV and Te-IV  $\rightarrow$  Te-V phase boundaries were determined from the first appearance of the higher-pressure phase on pressure increase.

## References

- [1] - M.I. McMahon and R.J. Nelmes, *Z. Kristallogr.* **219**, 742 (2004).
- [2] - C. Hejny, L.F. Lundegaard, S. Falconi, M.I. McMahon, M. Handland, *Phys. Rev. B* **71**, 020101 (2005).
- [3] - M.I. McMahon, C. Hejny, J.S. Loveday, L.F. Lundegaard, M. Handland, *Phys. Rev. B* **70**, 054101 (2004).
- [4] - C. Hejny and M.I. McMahon, *Phys. Rev. Lett.* **91**, 215502 (2003).
- [5] - V.V. Brazhkin, R.N. Voloshin, S.V. Popova, A.G. Umnov, *J. Phys. Condens. Matter* **4**, 419 (1992).

# Pressure-driven structural distortion and band gap closure in transition-metal perovskites

LOA I.<sup>1</sup>, SYASSEN K.<sup>1</sup>, WANG X.<sup>1</sup>, ROTH H.<sup>2</sup>, and LORENZ T.<sup>2</sup>

<sup>1</sup>Max-Planck-Institut für Festkörperforschung, D-70569 Stuttgart, Germany

<sup>2</sup>Universität zu Köln, II. Physikalisches Institut, D-50937 Köln, Germany

Orbital ordering, fluctuation, and excitation phenomena in transition metal perovskites have been investigated in recent years both experimentally and theoretically. In this context, rare-earth titanates with three nearly degenerate  $3d(t_{2g})$  orbitals, which are occupied by a single electron, have been of particular interest. We address here the question of how robust the orbital ordering is in  $\text{YTiO}_3$ , and show that it may possibly be tuned by the application of hydrostatic pressure. By means of synchrotron x-ray powder diffraction we investigated structural details of  $\text{YTiO}_3$  up to 30 GPa. Marked changes in the distortion of the  $\text{TiO}_6$  octahedra were observed at around 10 GPa, indicating the possibility of an orbital reorientation. In addition to the structural aspects, we have studied the pressure-induced charge delocalization and metallization in  $\text{YTiO}_3$  and other perovskites by synchrotron infrared micro-spectroscopy in the mid- and far-infrared spectral ranges. The optical band gap shifts in  $\text{YTiO}_3$  and  $\text{LaMnO}_3$  under pressure were determined quantitatively. The combined results on the structural, orbital and electronic changes under pressure give new insight into the physics of these materials.

This work was performed in collaboration with Y.-L. Mathis, B. Gasharova, and D. Moss (ANKA, Karlsruhe, Germany); M. Amboage and M. Hanfland (ESRF, Grenoble, France); O. K. Mel'nikov and A. Ya. Shapiro (Russian Academy of Science, Moscow, Russia).

# Lattice dynamics at ultra-high pressures: Quantification of phonon energies using high-resolution inelastic x-ray scattering

FARBER Daniel L.\*, ANTONANGELI Daniele\*†, KRISCH Michael†,

BADRO James\*‡, FIQUET Guillaume‡, OCCELLI Florent\*

\*Earth Science Division, Lawrence Livermore National Laboratory, 7000 East Avenue, Livermore, CA 94550, USA and Department of Earth Sciences, University of California, Santa Cruz.

†European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France

‡Institut de Minéralogie et de Physique des Milieux Condensés, UMR CNRS 7590, Institut de Physique du Globe de Paris, Université Paris VI, 4 Place Jussieu, 75252 Paris Cedex 05

Traditionally, experimental determination of phonon energies away from the zone center was solely the domain of inelastic neutron scattering. While our understanding of many physical properties was greatly enhanced by the large body of neutron studies performed from the 1960's to the present, the restrictions on sample size imposed by the technique relegated the achievable information to low or at most moderate pressures (~10 GPa). However, with the advent of third generation synchrotron sources and the construction of ID 16 and ID 28 at the ESRF for inelastic x-ray scattering experiments (IXS), these limitations have to a great degree been overcome.

Over the past few years our group has focused a large experimental and theoretical effort on quantifying the vibrational energies in transitional metals at high-pressures and high-temperatures. Our interest in the high-pressure properties of these elements is motivated both by their importance as constituents in the cores of many planetary bodies as well as by the rich variety of intriguing phenomena displayed by their lattice dynamics at room pressure. IXS has addressed a number of phenomenological problems of great importance, such as the nature of the acoustic anisotropy of the Earth's inner core, by direct measurements on the high-pressure hcp-phase of iron, as well as by proxy experiments on cobalt. We have also pursued more general studies of condensed matter at high-pressure important for the understanding of many fundamental physical properties. Indeed, with the application of pressures approaching 100 GPa, we are able to perturb the energy of condensed systems on the order of ~1 eV. Thus, performing lattice dynamics measurements under these conditions allows us to probe systems that have undergone fundamental changes the energetics of the chemical bonds. Such experiments have now begun to shed light on important magneto-elastic interactions, electron-phonon coupling and have the singular potential to provide critical data on the newly observed elastic perturbations across pressure induced spin-transitions.

Finally, we note that the state of the art with respect to synchrotron beamlines has come so far over the past few years, that in most cases we are no longer limited by the IXS beamlines. In fact, from the high-pressure experimental side, IXS experiments at high-pressure routinely require state of the art experimental capabilities from the standpoint of sample preparation and sample environment. In the case of transition metals, the development of the techniques for the production of small (~30  $\mu\text{m}$  x 20  $\mu\text{m}$ ), high-quality, single-crystal disks as well as novel new diamond anvil cells accommodating either large angular apertures or stable high temperatures have been at the core of our ability to make lattice dynamics measurements at extreme conditions.

# Bonding changes in compressed superhard graphite

MAO W. L., MAO H. K. \*, ENG P.<sup>1</sup>, KAO C. C.<sup>2</sup>, SHU J. F. \*, HEMLEY R. J.\*

Los Alamos National Lab

\*Geophysical Lab

<sup>1</sup>University of Chicago

<sup>2</sup>Brookhaven National Lab

Inelastic x-ray scattering spectroscopy (IXSS) or x-ray Raman was used to study the near K-edge structure of carbon at high pressure. IXSS reveals that at approximately 17 GPa, half of the  $\pi$ -bonds between graphite layers convert to  $\sigma$ -bonds while the other half remain as  $\pi$ -bonds in the high-pressure form. The x-ray diffraction pattern of the high-pressure form is consistent with a distorted graphite structure in which bridging carbon atoms between graphite layers pair and form  $\sigma$ -bonds, while the non-bridging carbon atoms remain unpaired with  $\pi$ -bonds. The high-pressure form is superhard, capable of indenting cubic diamond single crystals with potential materials science application. The resulting work finally solved the mystery of what happens to cold-compressed graphite, a problem that had puzzled scientists for nearly four decades, and demonstrates the potential for studying the near K-edge structure of low-Z materials at extreme conditions.

# Superconductivity in molecular solids at high pressure

TSE J.S., YAO Y.

Department of Physics, University of Saskatchewan, Saskatoon, S7N 5E2, Canada

Recently it was proposed that hydrogen rich metal alloys may be high temperature superconductors [1]. It was pointed out that the high pressure metallic phases of Group IVa hydrides are potential candidates. Following this suggestion, the optical properties of  $\text{SiH}_4$  have been examined up to 218 GPa by experiment [2]. The results strongly suggest an insulator-metal transition at 80 GPa. Motivated by the experimental finding, theoretical electronic structure calculations were performed to explore possible high pressure phases of Group IVa  $\text{SiH}_4$  and  $\text{SnH}_4$  hydrides. Starting from ambient structures, First-Principle molecular dynamics simulations were used to identify stable high pressure polymorphs. The crystal structure, electronic and vibrational properties and the possibility of superconductivity behaviour in these novel high pressure structures will be presented and discussed.

## References

[1] - N. W. Ashcroft Phys. Rev. Lett. **92**, 187002 (2004)

[2] - A.L. Ruoff, L. Sun, C. Zha and G. Stupian, AIRAPT, Proceedings, Karlsruhe (2005)

# Resonant x-ray magnetic scattering under hydrostatic pressure: pressurised magnetic order in Co doped CeFe<sub>2</sub>

DEEN P. P.<sup>1</sup>, PAOLASINI L.<sup>1</sup>, BRAITHWAITE D.<sup>2</sup>, KERNAVANOIS N.<sup>3</sup>,  
LAPERTOT G.<sup>2</sup>

<sup>1</sup> European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France

<sup>2</sup> CEA Grenoble, SPSMS, CEA, F-38054 Grenoble, France.

<sup>3</sup> Institut-Laue-Langevin, BP156, F-38042, Grenoble, France.

Pressure is an important experimental parameter that can provide, via perturbation, information on the origin of the ground state. In strongly correlated electron systems such perturbations can result in changes that are manifested in the electronic behaviour and thus leads to very useful information. The technique of resonant x-ray magnetic scattering has been highly productive in the field of strongly correlated electron systems yet, to date, it has been impossible to probe the pressure, temperature phase space. A new pressure set-up on ID20, the resonant scattering beamline of the ESRF, is able to provide in-situ pressure and temperature variation to study the resonant x-ray magnetic scattering (RXMS) amplitudes in strongly correlated electron systems [1,2]. This is exemplified by a study on cobalt doped CeFe<sub>2</sub>

The cubic Laves phase CeFe<sub>2</sub> is a rarity among the cubic laves phase RareEarthFe<sub>2</sub> family with the lowest Curie temperature  $T_c = 230$  K and the smallest saturation moment. Inelastic neutron scattering experiments reveal a coexistence of antiferromagnetic fluctuations in the ferrimagnetic ground state and these results show that the system is close to an antiferromagnetic instability [3]. Doping CeFe<sub>2</sub> with Co stabilises the antiferromagnetic state below  $T_N = 69$  K for 7 %

with a rhombohedral crystallographic distortion. Via RXMS and neutron diffraction it was shown that the antiferromagnetic ground state of the doped sample has a non-collinear magnetic structure on the Fe sites. This is interpreted in terms of a competition between antiferromagnetic and ferrimagnetic excitations due to the frustration of the Fe non-collinear sublattice [4].

The application of hydrostatic pressure on cobalt doped CeFe<sub>2</sub> reveals a great sensitivity to this external parameter. For a 7 % doped system  $T_N$  is greatly enhanced reaching 130 K at 2 GPa. In contrast applying 1.6 GPa on a 10 % doped sample reduced  $T_N$  to 37 K from  $T_N = 75$  K for 0.15 GPa. These results contradict recent work by Koyama *et al.* which found an increase in  $T_N$  with pressure at this doping level [5]. We shall remove the ambiguity between these two results and show that the application of pressure in CeFe<sub>2</sub> systems is analogous to doping. Thus these results open up the possibility to study an antiferromagnetic quantum critical point within a ferromagnetic state.

## References

- [1] N. Kernavanois Rev.Sci.Instr. **76** (2005) 083909
- [2] P. P. Deen J. Phys. Condens. Matter **17** (2005) S3149
- [2] L.Paolasini et. al. Phys.Rev.B **58** (1998) 12117.
- [3] L.Paolasini et. al. Phys.Rev.Lett **90** (2003) 57201.
- [4] H. Fukuda et al. Physica B **346** (2004) 187.



# Magnetic properties of the Eu-monochalcogenides at extreme pressures

RUPPRECHT K.<sup>1</sup>, LEUPOLD O.<sup>2</sup>, PONKRATZ U.<sup>1,3</sup>, WORTMANN G.<sup>1</sup>

<sup>1</sup>Department Physik, Universität Paderborn, 33098 Paderborn

<sup>2</sup>HASYLAB, DESY, 22607 Hamburg

<sup>3</sup>ESRF, 38043 Grenoble Cedex

The divalent Eu-chalcogenides EuX (X = O, S, Se, Te) are well-known model substances for Heisenberg magnetism because of the spin-only  $J = S = 7/2$  4f-moment of the Eu<sup>2+</sup>-ions and their simple NaCl structure. The variation of the magnetic ordering temperatures with pressure has been intensively studied in the NaCl phases up to 30 GPa using <sup>151</sup>Eu-Mössbauer and neutron spectroscopy [1, 2], delivering important information on the pressure dependence of the magnetic exchange interactions.

Here we present for the first time systematic studies on EuO, EuS, EuSe and EuTe in their CsCl-type high-pressure phases up to 120 GPa using the <sup>151</sup>Eu nuclear forward scattering (NFS) technique developed at the ESRF, where the present studies as well as previous studies on other Eu systems were performed [3]. The NaCl to CsCl phase transitions occur around 45, 20, 15 and 12 GPa for EuO, EuS, EuSe and EuTe, respectively. The samples were pressurized in a special diamond anvil cell designed to fit into the cryomagnet at ID22N. At each pressure we measured NFS spectra from 4 K up to 300 K to determine the magnetic ordering temperature  $T_M$ , the saturation magnetic hyperfine field  $B_{hf}$  and the isomer shift  $S_{IS}$  with respect to an applicable Eu reference absorber. The results on EuTe in the CsCl phase are already published [3].

In the CsCl-type high-pressure phases of EuSe, EuS and EuO we observe a further strong increase of the ferromagnetic ordering temperatures  $T_C$ , reaching 300 K at 77 GPa for EuSe, 295 K at 120 GPa for EuS and 165 K at 75 GPa for EuO. For EuS the pressure dependent slope of  $T_C$  denotes a saturation at the highest pressure in a strongly mixed valent state. In the case of EuO we found at even higher pressures a strong decrease of  $T_C$  to 110 K at 92 GPa, a behaviour resembling that of EuO around 30 GPa in the NaCl phase [1]. This behaviour points to the onset of a mixed-valent state in CsCl-type EuO, which is also reflected by the isomer shift and the variation of  $B_{hf}$ .

We discuss the present results in conjunction with models developed for magnetic and mixed-valent Eu systems, for instance for Eu metal at high pressures [4].

Work supported by the BMBF (grant no 05 KS4PPB/4)

## References

- [1] - M.M. Abd-Elmeguid and R.D. Taylor, Phys. Rev. B **42**, 1048, (1990)
- [2] - I.N. Goncharenko and I. Mirebeau, Phys. Rev. Lett. **80**, 1082, (1998) and cited references
- [3] - O. Leupold, K. Rupprecht, G. Wortmann, Structural Chemistry **14**, 97, (2003)
- [4] - J. Röhler, Handbook of the Physics and Chemistry of Rare Earth, **Vol. 10**, 523, (1987)

# Lattice dynamics of Cerium metal around the $\gamma \leftrightarrow \alpha$ transition by inelastic X-ray scattering

BERAUD A.<sup>\*</sup>, KRISCH M.<sup>\*</sup>, FARBER D.<sup>+</sup>, ANTONANGELI D.<sup>+</sup>, ARACNE C.<sup>+</sup>,  
ZARESTKY J.L.<sup>o</sup>, MCQUEENEY R.<sup>o</sup>

<sup>\*</sup> European Synchrotron Radiation Facility (Grenoble, France)

<sup>+</sup> Lawrence Livermore National Laboratory (Livermore, USA)

<sup>o</sup> Iowa State University (Oak Ridge, USA)

Cerium displays an extremely rich and varying behavior under different thermodynamic conditions of temperature and pressure with at least five allotropic forms. The most spectacular transition occurs at a pressure of 8 kbar and 300K between the gamma (low pressure) and alpha (high pressure) phases with a strong volume change of 15% [1]. The current theories suggest that this structural instability is directly linked with the electronic properties of cerium, with the 4f electron being at the border between localisation and itinerancy. Previous measurements of the phonon dispersion of gamma-Ce had shown an unusual softening of the transverse acoustic branch along the [111] and [110] (<110> polarization) directions, which involve the elastic constants C11 and C12, thus explaining the decrease of the bulk modulus with increasing pressure. We performed the first measurements of the longitudinal branches in the gamma and alpha phases close to the transition on the IXS beamline ID28 of the ESRF. We confirmed the anisotropy of the phonon evolution under pressure, with a complex behaviour of the phonon branch in direction [100] (softening with pressure, followed by a hardening close to the transition) and [110] that shows a different behaviour between zone boundary (softening up to the transition) and the rest of the branch (hardening after the transition). With these observations, we open the door to a better understanding of the underlying electronic mechanisms in cerium.

## References

- [1] - D.G. Koskenmaki and K.A. Gschneider, Jr. in Handbook on the Physics and Chemistry of Rare Earths, edited by K.A. Gschneider, Jr. and L. Eyring (North-Holland, Amsterdam, 1979), Vol. I, p. 337
- [2] - B. Johansson, I.A. Abrikosov, M. Alden, A.V. Ruban, and H.L. Skriver; Phys. Rev. Lett. 74, 2335 (1995)

# Combined XAS and XMCD studies under pressure of iron and iron based compounds

MATHON O.<sup>1</sup>, BAUDELET F.<sup>2</sup>, DECREMPS F.<sup>3</sup>, ITIE J.-P.<sup>3</sup>, NATAF L.<sup>3</sup>,  
PASCARELLI S.<sup>1</sup>, POLIAN A.<sup>3</sup>

<sup>1</sup>European Synchrotron Radiation Facility, B.P. 220, F-38043 Grenoble Cedex, France, <sup>2</sup>Synchrotron SOLEIL, B.P. 48, F-91192 Gif-sur-Yvette Cedex, France, <sup>3</sup>IMPMC, 140, rue de Lourmel, F-75015 Paris, France

X-ray Absorption Spectroscopy (XAS) and X-ray Magnetic circular dichroism (XMCD) performed simultaneously is a powerful technique to investigate condensed matter properties under high pressure. The high sensitivity of XMCD allows us to follow the magnetic transition and to correlate it to the local structure followed by XAS. Thus, we can obtain simultaneous information on the magnetic state and on the structural properties of the system (both determined under the same thermodynamic conditions) by probing the same volume of the sample.

These experiments have been performed on ID24, the energy dispersive beamline. The high flux, the beam stability, the highly focusing optics and the use of a quarter wave plate to produce circularly polarized X-rays, make this beamline particularly suited for combined XAS/XMCD high pressure measurements with a Diamond Anvil Cell (DAC) [1]. In particular, the small focal spot on the sample (about 5 by 5  $\mu\text{m}^2$  FWHM at the Fe-K edge) is an important factor to decrease the effect of pressure gradient inside the experimental volume of the DAC.

The Iron  $\alpha$ - $\varepsilon$  phase transition case is a good example to illustrate the possibility of combined XAS/XMCD on an energy dispersive beamline [2]. Under the application of an external pressure, Iron undergoes a transition around 13 GPa from the bcc  $\alpha$  phase to the hcp  $\varepsilon$  structure, with the loss of its ferromagnetic long range order. Despite many experimental and theoretical investigations, the mechanism of this phase transition is still not clear. We took advantage of the combination of the two techniques to probe simultaneously the structure and the magnetic state. The magnetic and structural transitions are sharp, both are of first order and the pressure domain of the transition is about 2.4 GPa  $\pm$  0.2 GPa. Our data seems to indicate that the magnetic transition slightly precedes the structural one, suggesting that the origin of the instability of the bcc phase in Iron with increasing pressure could be attributed to the effect of pressure on magnetism.

Investigation of the invar effect on Iron based alloys like  $\text{Fe}_3\text{C}$  [3],  $\text{Fe}_3\text{Pt}$  and  $\text{Fe}_{0.64}\text{Ni}_{0.36}$  will be also presented. These experiments confirm the  $2\gamma$ -state model in terms of gradual population of a low spin-small volume state at the expense of a high spin-large volume state under pressure. Only some results obtained on  $\text{Fe}_{0.64}\text{Ni}_{0.36}$  diverge curiously from this model, suggesting that the preparation and the magnetic history of the sample seems to be of crucial importance.

## References

- [1] – O. Mathon, F. Baudelet, J.-P. Itié, S. Pasternak, A. Polian and S. Pascarelli, *J. Synchrotron Radiat.* 11, 423 (2004).
- [2] – O. Mathon, F. Baudelet, J.-P. Itié, A. Polian, M. d'Astuto, J.-C. Chervin and S. Pascarelli, *Phys Rev Lett* 93, 25503 (2004).
- [3] – E. Duman, M. Acet, E. F. Wassermann, J.-P. Itié, F. Baudelet, O. Mathon and S. Pascarelli, *Phys. Rev. Lett.* 94, 077502 (2005).