2015 IUCr High-Pressure Workshop

September 12th - 15th, 2015

Brazilian Synchrotron Light Laboratory (LNLS)
CNPEM Campus – Campinas, Brazil

pages.cnpem.br/hpworkshop

BOOK OF ABSTRACTS

Ministry of
Science, Technology
and Innovation

CNPEM - Campus Map

- 🟦 **LNLS – Main Building**
- 🟦 **LNLS – Storage Ring Building**
- 🟥 **LNLS – Red Building**
- 🟪 **LNLS – Magnets Building**
- 🟪 **LNLS – Factory and Control Building**
- 🟩 **CTBE**
- 🟦 **LNBio**
- 🟧 **LNNano**
- 🟨 **Administration Building**
- 🟫 **Warehouse**
- 🟪 **Restaurant**
- ⬛ **Guest House**

Summary

Event website: ***pages.cnpem.br***/***hpworkshop***/

Presentation

2015 IUCr High-Pressure Workshop

The primary focus of the meeting is the recent scientific advances in high pressure techniques. Presentations will cover a variety of subjects in and related to high-pressure crystallography, including crystal structures, phase transitions and their kinetics, new materials synthesis, Earth and planetary science, soft and biological matter, physical and chemical properties, theory and computation, as well as technique developments for high-pressure studies at synchrotron, neutron and laboratory-based facilities.

This workshop is a continuation of The International Union of Crystallography (IUCr) Commission on High Pressure workshop series, first established in 1996, followed by workshops at the ESRF (1997), APS (‘98), SPring-8 (‘00), in Orsay (‘01), Berkeley (‘03), Saskatoon (‘04), Dubna (‘06), Oxford (‘07), Harbin (‘09), Gatlinburg (‘10), Mito (2012) and most recently in Hamburg (2013).

This year the workshop will be held at the **Brazilian Synchrotron Light Laboratory (LNLS)** in Campinas/Brazil, where several high pressure experiments are being performed in the current beamlines and are planned to be implemented in an ultra-low emittance synchrotron source called **Sirius** currently under construction.

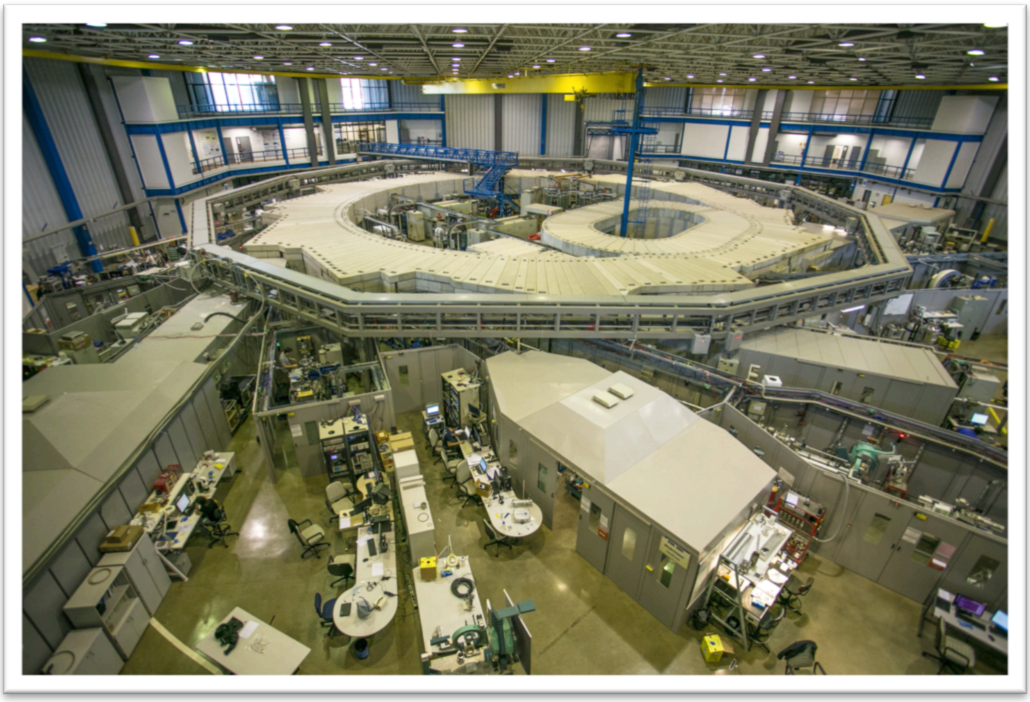
The event will be held just after the 1st LACA Meeting, promoted by the Latin American Crystallographic Association (LACA) jointly with the 22nd SBC meeting (Sociedade Brasileira de Cristalografia), and right before the 25th RAU (LNLS Annual Users Meeting), promoted by LNLS from September 16th to 17th.

This proximity will enhance the combined participation to all events, as well as the exchange of ideas and experiences from the participants with complementary backgrounds.

CNPEM: A cutting-edge research center

Welcome to the Brazilian Center for Research in Energy and Materials (CNPEM), a world-class center for development of science, composed by four laboratories: Brazilian Synchrotron Light Laboratory (LNLS), Brazilian Biosciences National Laboratory (LNBio), Brazilian Bioethanol Science and Technology Laboratory (CTBE) and Brazilian Nanotechnology National Laboratory (LNNano).

Located in Campinas (SP), CNPEM is a private nonprofit organization qualified by the Ministry of Science, Technology and Innovation (MCTI), whose laboratories have open facilities to the scientific and industrial communities across the country and abroad.



Current LNLS synchrotron light source available at the CNPEM Campus, in Campinas, Brazil

Brazilian Synchrotron Light Laboratory (LNLS)

As part of CNPEM, the **Brazilian Synchrotron Light Laboratory (LNLS)** is responsible for operating the only synchrotron light source in Latin America, providing high brilliant light from infrared to X-rays for the analysis of organic and inorganic materials.

Designed and built with Brazilian technology, LNLS was inaugurated in 1997 and, since then, it offers unique conditions to the progress of synchrotron techniques at this region. Today, its synchrotron light source has 17 experimental stations (beamlines), where research proposals can be conducted.

The scientific community will soon get reinforcement for researches that rely on synchrotron light. This is because LNLS is currently engaged in the development and construction of **Sirius**, a latest generation synchrotron light source that will open new experimental possibilities in several areas of research.

Planned to be one of the most advanced light sources in the world, it will open up new perspectives for research in many fields, such as material science, structural biology, nanoscience, physics, earth and environmental science, cultural heritage and many others.

Sirius is scheduled to start commissioning in 2018 and to be opened to users in 2019, with potential to elevate Brazil to a higher and more competitive level in scientific research.

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Ross Angel (Italy)
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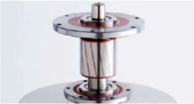

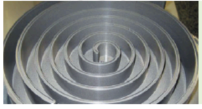

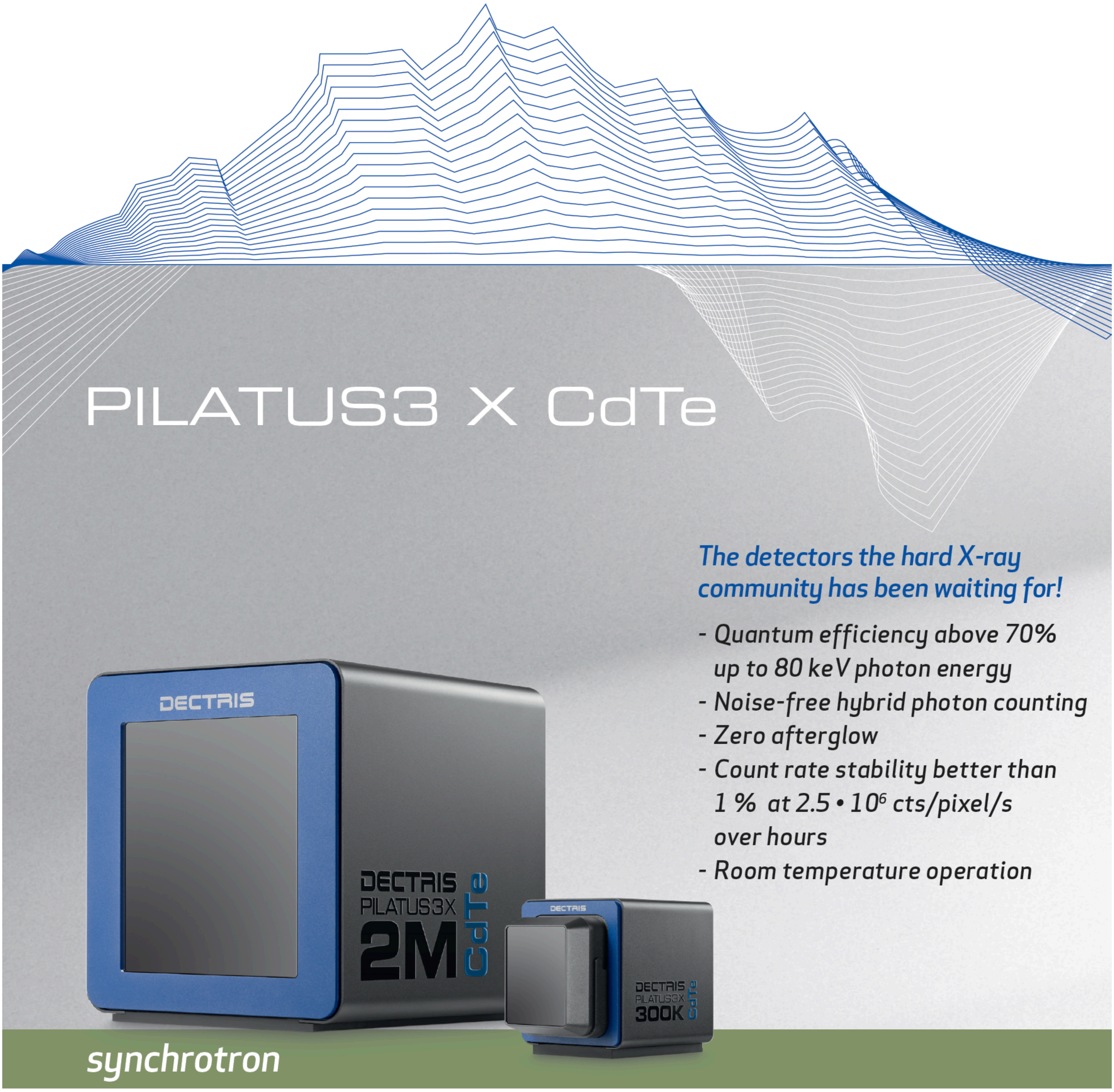
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Program

SATURDAY – 12 September 2015

16:00 **16:30**	Shuttle Buses from the Hotel to the LNLS Campus (please choose between the first or second bus time)
17:00	**Registration**
18:00	**Get together reception at the LNLS/CNPEM campus**
20:00 **20:30**	Shuttle bus back to the Hotel (please choose between the first or second bus time)

SUNDAY – 13 September 2015

7:40 **8:10**	Shuttle Buses from the Hotel to the LNLS Campus (please choose between the first or second bus time)		
8:40	**Opening remarks**		
	8:40 – 8:50	**Andrzej Katruziak** (IUCr HP Commission)	Welcome and info about the IUCr HP Commission
	8:50 – 9:10	**Narcizo Souza-Neto** (LNLS/SIRIUS)	Welcome and info about LNLS and SIRIUS
9:10	**New Frontiers in Extreme Conditions Crystallography (Haozhe Liu)**		
	9:10 – 9:50	**M. Zaworotko**	“High pressure applications of porous metal-organic materials”
	9:50 – 10:30	**J. Smith**	“Fast compression/decompression of materials in diamond anvil cells”
10:30	**Coffee Break**		
11:00	**Crystallographic controls on rheology and elasticity (Guoyin Shen & Lowell Miyagi)**		
	11:00 – 11:40	**L. Miyagi**	“Synchrotron radial diffraction studies at high pressures and temperatures in the diamond anvil cell”
	11:40 – 12:20	**S. Hunt**	“Deformation T-Cup: A 6-8 / Kawai-style deformation apparatus for controlled strain-rate deformation at pressures in excess of 20 GPa”
	12:20 – 13:00	**H. Marquardt**	“Internally consistent elasticity measurements of FIB-prepared single-crystals at high-pressure and high-temperature by Brillouin spectroscopy and X-ray diffraction”
13:00	**Lunch Break**		
14:30	**High-pressure chemistry, synthesis and biological systems (Boris Zakharov)**		
	14:30 – 15:10	**J. Haines**	“Use of Fourier Maps to Study High Pressure Guest Insertion and Polymerization in Zeolites”
	15:10 – 15:50	**N. Brooks**	“Probing membrane structure and dynamics at high pressure”
	15:50 – 16:30	**D. Paliwoda**	“A new high-pressure phase of ferrocene”
16:30	**Poster session** *(together with a Special Coffee Break)*		
19:00 **19:30**	Shuttle bus back to the Hotel (please choose between the first or second bus time)		

Monday – 14 September 2015

7:30 **8:00**	Shuttle Buses from the Hotel to the LNLS Campus (please choose between the first or second bus time)		
8:30	**Computational approaches (Renata M. M. Wentzcovitch)**		
	8:30 – 9:10	**R. Wentzcovitch**	"Spin crossover systems in the deep mantle"
	9:10 – 9:50	**K. Umemoto**	"Volume isotope effects in ice under high pressure by first principles"
	9:50 – 10:30	**K.-M. Ho**	"Crystal Structure Predictions Using Adaptive Genetic Algorithm and Motif Search methods"
10:30	**Coffee Break**		
11:00	**Materials Science (Julien Haines)**		
	11:00 – 11:40	**V. Solozhenko**	"Boron-phosphorus system at high pressure"
	11:40 – 12:20	**A. Cairns**	"Pushing the limits: designing next-generation negative compressibility materials"
	12:20 – 13:00	**S. Deemyard**	"Structures of lithium isotopes at low temperature"
13:00	**Lunch Break**		
14:30	**Polymorphism and crystal chemistry (Ania Olejniczak)**		
	14:30 – 15:10	**M. Pravica**	"Novel fluorine chemistry under extreme conditions using useful hard x-ray photochemistry"
	15:10 – 15:50	**M. Probert**	"Routes to More Polymorphs and Phase Changes"
	15:50 – 16:30	**R. Miletich**	"Decoding the mechanisms and pathways of pressure-driven structural transitions"
16:30	**Coffee Break**		
17:00	**High-pressure experiments and data deposition (Elena Boldyreva & Nicholas Brooks)**		
	17:00 – 17:40	**K. Dziubek**	"Deposition of high-pressure data and metadata"
	17:40 – 18:20	**J. A. Lima Jr**	"High pressure studies in crystalline amino acids"
	18:20 – 19:00		TBA
19:00	Shuttle transfer to the restaurant		
19:20	**Workshop Dinner** *(at a Brazilian Churrascaria)*		
21:30	Shuttle transfer to the hotel and guest house		

Tuesday – 15 September 2015

7:30 **8:00**	Shuttle Buses from the Hotel to the LNLS Campus (please choose between the first or second bus time)		
8:30	**High-pressure crystallography in earth and planetary science (Simon Redfern & Rommulo Conceicao)**		
	8:30 – 9:10	**Y. Le Godec**	"Next generation synchrotron portable Large Volume High-P/T/Stress/Tomography Cell for Extreme Chemistry and Earth Sciences"
	9:10 – 9:50	**S. Redfern**	"New challenges and opportunities for mineral physics of the deep Earth"
	9:50 – 10:30	**R. Conceicao**	"The role of clay minerals on the volatiles transport to the mantle and internal heating of the Earth"
10:30	**Coffee Break**		
11:00	**High-pressure spectroscopy (João A. H. da Jornada & Kamil Dziubek)**		
	11:00 – 11:40	**R. Bini**	"Pressure induced reactivity in molecular crystals: accessing the dynamics at molecular level by complementary structural and spectroscopic experiments"
	11:40 – 12:20	**C. Murli**	"Hydrogen Bonded Organic Molecular Solids under Pressure"
	12:20 – 13:00	**A. Gomes**	"Resonance high-pressure Raman spectroscopy in nanocarbon materials"
13:00	**Lunch Break**		
14:30	**Rising Stars (Andrzej Katrusiak & Simon Clark)**		
	14:30 – 15:10	**G. Finkelstein**	"Magnesiowüstite at high pressure using single-crystal synchrotron methods"
	15:10 – 15:50	**M. Marcondes**	"Hybrid experimental/theoretical thermodynamics and thermoelasticity of materials: the high T NaCl pressure scale"
	15:50 – 16:30	**O. Kurakevych**	"New silicon and carbon materials by in situ high pressure synthesis"
16:30	**Closing Remarks**		
18:00	Shuttle transfer to the hotel		

A tour around the synchrotron should be fitted in the slots during the workshop.

2015 IUCr High-Pressure Workshop

TALK ABSTRACTS

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High pressure applications of porous metal-organic materials

Zaworotko M.

University of Limerick

Fast compression/decompression of materials in diamond anvil cells

Smith J., Lin C., Bai L., Rod E., Sinogeikin S., and Shen G.

High Pressure Collaborative Access Team, Geophysical Laboratory, Carnegie Institution of Washington, Argonne, IL 60439, USA
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Complementary advances in high pressure research apparatus and techniques make it possible to carry out time-resolved high pressure research using what would customarily be considered static high pressure apparatus. Fast compression/decompression constitutes a fundamental approach to time-resolved high pressure research in the diamond anvil cell. Through careful choice of pressure generating apparatus and relevant time scale, a number of important scientific challenges can be address including, for example, non-equilibrium transformations and phase boundaries, unusual thermodynamic pathways to metastable phases, and compression-dependent nucleation rates and crystal growth. Here we present key technical aspects of the synchrotron beamline and ancillary equipment used for rapid (de)compression experiments. We also present the results of some recent experiments, each taking advantage of a particular apparatus and compression rate, including fast equation of state measurements, compression rate dependent synthesis of metastable states in silicon and germanium, and ultrahigh compression rates using a piezoelectric driven diamond anvil cell.

Synchrotron radial diffraction studies at high pressures and temperatures in the diamond anvil cell

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In-situ radial synchrotron diffraction in conjunction with the diamond anvil cell can be used to study the response of materials to non-hydrostatic stresses at extreme pressures and temperatures. In particular, radial diffraction can be used to measure lattice strain and texture (crystallographic preferred orientation) development during deformation at extreme conditions. Lattice strains can be used to calculate the stress supported by the sample and in turn to estimate the sample's flow strength. Texture development can be used to understand deformation mechanisms, phase transformation mechanisms, and anisotropy development in polycrystals. If a polycrystal is composed of anisotropic minerals, texturing can result in bulk anisotropy of physical properties such as magnetic properties, heat flow, electrical conductivity, elastic properties, and plastic properties. During deformation, texture development results from dislocation glide and twinning and can be modified by recrystallization and phase transformation. By using polycrystal plasticity codes to model experimental textures, slip system and twin activity can be determined for the conditions of the experiment. During phase transformations there is frequently an orientation relationship between parent and daughter phases. If the parent phase is textured, this can be inherited by the daughter phase. By observing texture changes during phase transformations, one can determine orientation relationships and constrain transformation mechanisms. This talk will focus on mineral phases relevant to the earth's deep interior and will discuss examples of deformation experiments and plasticity modeling as well as interpretation of transformation textures and implications for anisotropy development in the deep earth.

Deformation T-Cup: A 6-8 / Kawai-style deformation apparatus for controlled strain-rate deformation at pressures in excess of 20 GPa.

Hunt S. A.; Weidner D. J.; McCormack R. J.; Whitaker M. L.; Bailey E.; Li L.; Vaughan M. T. and Dobson D. P.

Department of Earth Sciences, University College London; Mineral Physics Institute, Stony Brook University; Department of Earth Sciences, University College London; Mineral Physics Institute, Stony Brook University; Department of Earth Sciences, University College London; Mineral Physics Institute, Stony Brook University; Mineral Physics Institute, Stony Brook University; Department of Earth Sciences, University College London;
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Controlled strain-rate deformation experiments, both offline and with synchrotron X-rays, form the basis of our understanding of the rheological properties of minerals and materials. In the Earth Sciences rheological studies at high-pressure are key to understanding the dynamic properties of the Earth's deep interior. This is because many of the minerals present in the Earth are not stable at atmospheric pressure and the effect of pressure on rheology may be significant. To date though, controlled strain-rate deformation experiments are generally limited to pressures below ~18 GPa, although one study has been performed at 24 GPa. Deformation experiments are limited to these pressures because at high pressures the failure rate increases dramatically as the ultimate strength of the carbide anvils is surpassed. The general limit of ~18 GPa means that deformation experiments are limited to phases stable in the Earth's upper-mantle and upper part of the transition-zone. The Kawai-type apparatus is capable of generating pressures in excess of 30 GPa and here we report the capabilities of a new deformation Kawai device, the DT-Cup. The DT-Cup is capable of deformation experiments at pressures in excess of 20 GPa, without the failure rate associated with previous apparatus. The apparatus consists of a 400 tonne Paris-Edinburgh load-frame with split-cylinder Kawai-type tooling. The set of eight, 16 mm, cubic anvils, is positioned with its axis aligned parallel to the action of the press. Controlled strain-rate deformation of the sample is undertaken by differential pistons advancing the 'top' and 'bottom' cubes of the cube set. The differences between the cubic DIA-type apparatus and the Deformation-DIA are analogous to the differences between standard Kawai-style split cylinder devices and the DT-Cup. At the time of writing, experiments have been performed on SiO2 and Mg2SiO4 polymorphs at high pressure and temperatures. The results of these high pressure deformation experiments will be presented, along with the technical specifications of the DT-Cup.

Hunt, S. A., Weidner, D. J., McCormack, R. J., Whitaker, M. L., Bailey, E., Li, L., Vaughan, M. T., Dobson, D. P. (2014) Deformation T-Cup: A new multi-anvil apparatus for controlled strain-rate deformation experiments at pressures above 18 GPa. Rev. Sci. Instrum. 85, 085103 Doi: 10.1063/1.4891338

Internally consistent elasticity measurements of FIB-prepared single-crystals at high-pressure and high-temperature by Brillouin spectroscopy and X-ray diffraction

Marquardt H., Kurnosov A., Ballaran T. B., Marquardt K., Frost D., Buchen J., Schulze K.

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Elasticity is a material property that reflects the atomic structure and interatomic forces in crystalline materials. As a result, elastic properties are strongly affected by changes in pressure and temperature. In Earth Sciences, knowledge of the elastic behavior of geomaterials at pressure and temperature conditions of the Earth's interior is key to constrain our planet's inner structure and dynamics through forward modelling of seismic observables. Here, we will discuss a new class of internally consistent single-crystal elasticity measurements that combine the opportunities emerging from the recent development of combined Brillouin scattering (to derive acoustic wave velocities) and x-ray diffraction (XRD) systems (for structure and unit-cell parameter determination) with the advantages of sophisticated sample preparation using the focused ion beam (FIB) technique (1). We will show results of experiments on single-crystals that were performed using the combined Brillouin scattering and rotating anode XRD system at the Bayerisches Geoinstitut BGI. Multiple single-crystals, FIB-tailored in size and shape, were loaded in the single sample chambers of resistively-heated diamond-anvil cells (DAC). Such a multi-sample approach allows for internally consistent determinations of all independent elastic constants from low-symmetry crystals by Brillouin spectroscopy and x-ray diffraction measurements. Furthermore, the multi-sample approach facilitates direct quantification of the effects of chemical substitution on the structure and elasticity of high-symmetry crystals at non-ambient conditions. Our experimental approach eliminates uncertainties arising from the combination of data collected under (potentially) different conditions in several DAC runs, in different laboratories and/or from using different pressure-temperature sensors. We will also discuss the possibility to derive pressure independent from a secondary pressure scale.

(1) H. Marquardt, K. Marquardt, Am. Mineral. 97, 299-304 (2012).

Use of Fourier Maps to Study High Pressure Guest Insertion and Polymerization in Zeolites

Haines J.; Thibaud J. M.; Alabarse F.; Rouquette J.; Hermet P.; Cambon O.; Coasne B.; Di Renzo F.; Van der Lee A.; Scelta D.; Ceppatelli M.,; Dziubek K.; Gorelli F.; Bini R.; Santoro M.,

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Zeolites represent an important family of porous materials based on corner sharing TO4 (T=Al, Si,…) tetrahedra. The microporous nature of these materials allows insertion of a great variety of guest atoms, ions or molecules giving rise to a large number of technological applications in catalysis, molecular sieves and ion-exchange materials. High pressure can be used to completely fill the subnanometric pores with guest molecules, thereby strongly modifying the mechanical, electrical and optical properties of the host zeolite. In the case of simple organic molecules, polymerization can be induced under high pressure eventually with the aid of UV irradiation to produce novel nanocomposite materials, which can be recovered at ambient pressure. Insertion of guest molecules (H2O, CO, CO2, C2H2, C2H4, Ar) in different hydrophilic and hydrophobic AlPO4 and SiO2 zeolite-type materials was studied by single crystal and powder x-ray diffraction using both synchrotron and laboratory sources [1-4]. The guest molecules present significant disorder and Fourier maps provide important information on the distribution of guests in the pores. In the case of zeolite/polymer nanocomposites, Fourier maps can be used to characterize the translational, orientational and occupational disorder of the isolated polymer chains, which have a strong influence on the properties of the nanocomposite.

1. J. Haines, O. Cambon, C. Levelut, M. Santoro, F. Gorelli, G. Garbarino, J. Am. Chem. Soc. 2010, 132, 8860. 2. M. Santoro, F. A. Gorelli, R. Bini, J. Haines, and A. van der Lee, Nature Commun ., 2013, 4, 1557. 3. D. Scelta, M. Ceppatelli, M. Santoro, R. Bini, F. A. Gorelli, A. Perucchi, M. Mezouar, A. van der Lee, J. Haines, Chem. Mater., 2014 , 26, 2249. 4. F. G. Alabarse, J. Rouquette, B. Coasne, A. Haidoux, C. Paulmann, O. Cambon, J. Haines, J. Am. Chem. Soc., 2015, 137, 584.

Probing membrane structure and dynamics at high pressure

Brooks N.

Imperial College London

A new high-pressure crystal phase of ferrocene

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Ferrocene is a prototypic metallocene built of parallel cyclopentadienyl rings and the metal ion sandwiched in-between. Today, the family of such sandwich complexes includes tens of thousands of others compounds. The simplest of them with different metal ions in the solid state are isostructural with ferrocene. For over 60 years after the serendipitous discovery of ferrocene its molecular structure still raised some doubts because of the possible rotation of cyclopentadienyl (Cp) rings. In general, it can be assumed that Cp-rings are in eclipsed or staggered conformation, and that the energy barrier between these two conformations is low [1]. Ferrocene forms several polymorphs. At ambient conditions it forms monoclinic crystals with average staggered Cp-rings conformation [2]. Below 164 K it transforms to slightly different triclinic form, with almost doubled unit cell dimensions [3]. The recrystallization of ferrocene below 98 K yields in orthorhombic form with eclipsed conformation of Cp-rings [4]. The staggered conformation of the ambient-pressure monoclinic polymorph is energetically unfavoured and high-resolution neutron-diffraction measurements revealed structural models with Cp-rings disordered in two or three sites [5]. In our recent high-pressure study of ferrocene up to 12 GPa we have plotted the pressure dependence of unit-cell dimensions and atomic displacement parameters (ADPs) of carbon atoms in Cp-rings. We have observed a negative linear compression of parameter b and significant discontinuities in the pressure evolution of parameter c, β-angle and atomic displacement parameters. It is noteworthy that high pressure reduces significantly ADPs of the C-atoms, which in turn results in exactly staggered conformation of the Cp-rings. Moreover, the $\beta = 90^{\circ}$ coincides with the point of structural transformations when the first and second shortest intermolecular contacts between the centres of molecules in monoclinic ferrocene become equal and then reversed at higher pressure. In these respects, the structure of both monoclinic phases of ferrocene resembles a mechanical box with meshing gears regulated by their positions and distances. Hence, we proposed an isostructural phase transition of ferrocene at 3.24 GPa [6].

[1] A. Haaland, J. E. Nilsson, Acta Chem. Scand., 22, 2653−2670 (1968). [2] J. D. Dunitz, L. E. Orgel, A. Rich, Acta Crystallogr. 9, 373–375 (1956). [3] P. Seiler, J. D. Dunitz, Acta Crystallogr. Sect. B 35, 2020–2032 (1979). [4] P. Seiler, J. D. Dunitz, Acta Crystallogr. Sect. B 38, 1741–1745 (1982). [5] F. Takusagawa, T. F. Koetzle, Acta Crystallogr. Sect. B 35, 1074–1081 (1979). [6] D. Paliwoda, K. Kowalska, M. Hanfland, A. Katrusiak, J. Phys. Chem. Lett. 4, 4032–4037 (2013).

Spin crossover systems in the deep mantle

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There has been much interest in spin crossovers found experimentally in the most abundant minerals of Earth's lower mantle ((MgFe)O and (MgFe)(Si,Fe)O3-perovskite) under pressure. Spin crossovers depend strongly on thermodynamic conditions and a full understanding of this problem requires its investigation as function of pressure and temperature. There are several controversies, especially in the perovskite systems, and surprises are revealed by electronic structure calculations. The geophysical consequences of these crossovers are yet to be fully understood. I will review progress we have made in understanding spin crossovers and give an overview of this phenomenon and its potential implications for the Earth. Research carried out in collaboration with Z. Wu, H. Hsu, K. Umemoto, P. Blaha, J. F. Justo, and S. de Gironcoli.

T. Tsuchiya, R.M. Wentzcovitch, S. de Gironcoli, Spin transition in Magnesiowüstite in Earth's lower mantle, Phys, Rev, Lett. 96, 198501 (2006). R. M. Wentzcovitch, J. F. Justo, Z. Wu, C. R. S. da Silva, D. Yuen, and D. Kohlstedt, Anomalous compressibility of ferropericlase throughout the iron spin crossover, Proc. Natl. Acad. Sc. USA, 106, 8447 (2009). H. Hsu, P. Blaha, M. Cococcioni, and R. M. Wentzcovitch, Spin-state crossover and hyperfine interactions of ferric iron in MgSiO3 perovski

Volume isotope effects in ice under high pressure by first principles

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The volume isotope effect (VIE) in ice is very complex. In ice Ih and XI, prototypical forms of low-pressure ice, the VIE is anomolous, i.e., volume of D2O is larger than that of H2O [1]. However, in ice VIII and VII at 0 GPa, the VIE was reported to be normal, i.e., volume of D2O is smaller than that of H2O [2,3]. Here we investigate the VIE in ice XI and in ice VIII by first principles within the quasi harmonic approximation. We reveal that both normal and anomalous VIEs can be induced in ice XI and VIII in sequence by applying pressure. Furthermore, we find the third type of VIE, anomalous VIE with zero-point volume contraction, which should contribute to the isotope effect in the ice VII-X transition. Very recently our theoretical prediction has been confirmed by an x-ray diffraction experiment. The discussion of VIE we present here is general and should be applicable to other solid phase of H2O, possibly to other hydrogen-bonded materials.

[1] B. Pamuk et al., Phys. Rev. Lett. 108, 193003 (2012). [2] É. D. Murray and G. Galli, Phys. Rev. Lett. 108, 105502 (2012). [3] K. Umemoto, R. M. Wentzcovitch, S. de Gironcoli, and S. Baroni, Chem. Phys. Lett. 499, 236 (2010).

Crystal Structure Predictions Using Adaptive Genetic Algorithm and Motif Search methods

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The urgent demand for new energy technologies has put great pressure on the capabilities of today's materials and chemical research. Accurate and fast computational structure/property determinations can complement the traditional experimental try and error efforts in material design and accelerate the pace of technological advances. I will describe some of our recent work in this area. Work done in collaboration with X. Zhao, M. C. Nguyen, S. Q. Wu, M. Ji, Z. Ye, F. Zhang, X. G. Gong, M. J. Kramer, and C. Z. Wang. Work at Ames Laboratory was supported by the US Department of Energy, Basic Energy Sciences, Division of Materials Science and Engineering, under Contract No. DE-AC02-07CH11358, including a grant of computer time at the National Energy Research Supercomputing Centre (NERSC) in Berkeley, CA.

Boron-phosphorus system at high pressure

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Chemical interaction and phase relations in the B-P system have been systematically studied up to 8 GPa and 2800 K using multianvil press and synchrotron X-ray diffraction (F2.1, HASYLAB), and a reaction p-T diagram of the B-P system has been constructed. It was found that solid phosphorus does not react with boron in the whole studied pressure range. At 5.5 GPa, phosphorus melts at 1300 K that is accompanied by appearance of reflections of cubic BP. However, unreacted solid boron and liquid phosphorus are still present, even at 2000 K. For the mixture with BP stoichiometry, the reaction is completed only above 2100 K, and quenched samples are single-phase boron phosphide. For reaction mixture of B6P stoichiometry, BP formation is observed immediately after phosphorus melting (~1300 K), while formation of rhombohedral boron subphosphide B12P2 starts only above 1750 K, and both boron phosphides coexist in a rather wide (1750-2000 K) temperature range. Above 2000 K, only reflections of B12P2 are present in the diffraction patterns, and quenched samples are single-phase boron subphosphide. Similar behavior in the B-P system is observed at lower pressures. All this is indicative of the substantial kinetic barrier of reaction between elemental boron and liquid phosphorus at temperatures below 2000 K, perhaps due to a high viscosity of the phosphorus melt under pressure. The changes in lattice parameters and Raman active modes (TO and LO) of cubic boron phosphide have been measured up to 50 GPa at 300 K in a diamond anvil cell using synchrotron X-ray diffraction (ID27, ESRF) and Raman scattering. A least-squares fit using the Murnaghan equation of state to the volume-pressure data yields the bulk modulus 174(2) GPa and its pressure derivative 3.2(2) that is in excellent agreement with our ab initio calculations. Melting of boron phosphides has been in-situ studied up to 26 GPa and 3100 K using laser-heated diamond anvil cells and synchrotron X-ray diffraction (P02.2, HASYLAB), and a melting p-T diagram of the B-P system has been constructed. Bulk polycrystalline BP and B12P2 synthesized at 7.7 GPa and 2600 K exhibit Vickers hardness of 28(2) and 35(3) GPa, respectively, which coincides with theoretical values calculated in the framework of the thermodynamic model of hardness [1]. This work was supported by the Agence Nationale de la Recherche (grant ANR-2011-BS08-018).

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Pushing the limits: designing next-generation negative compressibility materials

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Negative linear compressibility (NLC) is a rare but desirable property whereby a material's crystal structure actually expands in one direction against increasing hydrostatic pressure [1]. The performance of NLC materials—for use in areas such as sensitive pressure sensing, actuators, and development of artificial muscle—critically depends on the intrinsic NLC response. Until recently very few NLC materials were known, and of those the expansion was small in comparison to the normal contraction of common engineering materials. This situation is rapidly changing since the discovery of sustained large NLC and NAC in a range of molecular framework materials. In this talk I will explore how understanding the mechanistic origins of these phenomena can inform material design, drawing on both our own work [3–5] as well as that of others [1,2]. What becomes clear is that the emerging class of molecular framework materials allows us to target, enhance and couple advanced functionalities. I will discuss our first report of "giant" NLC in zinc (II) dicyanoaurate—where the crystal structure expands ~10% over 1.8 GPa [2]— NLC in the established negative thermal expansion material Zn(CN)2, as well as the unprecedented prolonged NAC in silver (I) tricyanomethanide [3]. I will conclude with a personal perspective for the challenges and opportunities in this field and the quest for even more extreme responses.

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Structures of lithium isotopes at low temperature

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At low temperature, large lattice zero point energy of light materials dominates the lattice kinetics leading to unusual effects such as superfluidity in helium isotopes. The physics of ultra light systems, especially at low temperatures, is not sufficiently explained by the static lattice models. It has been argued that lattice quantum contributions become enhanced under compression in systems with long-range interactions such as Coulomb interactions. Lithium is the lightest metal. At ambient pressure, lithium is the prototype of a simple metal, with a nearly spherical Fermi surface. The structural and electronic properties of lithium at high densities, however, are highly counterintuitive and lithium undergoes series of symmetry breaking structural phase transition during which, its electronic properties drastically deviate from a free electron system. In addition, because of its low atomic mass, lithium may behave as a quantum solid. Studies on properties of lithium under high pressure has been challenging due to its strong reactivity. In this work I will present the structural phase boundaries of lithium isotope at low temperature in relation to its superconducting phase diagram.

Novel fluorine chemistry under extreme conditions using useful hard x-ray photochemistry.

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Utilizing our newly developed methods to release highly reactive molecular fluorine inside a pressurized diamond anvil cell in situ via irradiation with hard x-rays[1], we have been performing experiments examining novel fluorine chemistry/bonding under extreme conditions. We report on two experiments. In the first, a mixture of CsF and KBF4 was pressurized and irradiated in the hope of forming CsF2, CsF3, and higher oxidation states of Cs at pressures up to 70 GPa. The post-irradiated sample was interrogated via XANES, IR, Raman and XRD techniques. In the second experiment, a segregated mixture of KClO4 and KBF4 was pressurized to near 3 GPa irradiated to release molecular oxygen and molecular fluorine, respectively. Oxygen was observed to diffuse throughout the sample regions whereas fluorine was more localized to the irradiation area. The is some evidence for the production of OF2.

[1]"Novel method for producing molecular fluorine," M. Pravica, D. Sneed, M. White and Y. Wang, Review of Scientific Instruments, 85, 086110 (2014); http://dx.doi.org/10.1063/1.4893384 (2014).

Routes to More Polymorphs and Phase Changes

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It has been known for some time that the application of pressure, as an external stimulus, can change the properties of materials. This is sometimes coupled with spectacular results; such as the highly desirable transformation of carbon from one allotrope to another. In single crystal X-ray diffraction studies the diamond anvil cell (DAC) has become the modus operandi to generate high pressures. The technique, although rapidly becoming more widely used, is still being explored and developed to enhance the accessible science. We have found that minor modifications to operational protocols may enhance the frequency with which new polymorphs and/or phase changes may be observed. Two such modifications will be discussed with examples from recent studies. These will span the use of DAC's in their conventional sense, of pressurizing a known crystalline sample, and in their use for in situ crystallization of compounds that are in the liquids under standard conditions. Often in situ crystallisation generates morphologies that are significantly different to those obtained through other methods such as cryo cooling. Further still, we will demonstrate, that even the manner in which the pressure is applied may afford different polymorphs of a compound[1]. The modification to the standard use of the DAC's provides a tantilising route to new phase changes that require careful analysis to determine the driving forces that are involved, details will be discussed of this currently unpublished work.

Ridout J., Price L.S., Howard J.A.K., and Probert M.R., Cryst.GrowthDes., 2014, 14, 3384−3391

Decoding the mechanisms and pathways of pressure-driven structural transitions

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Using the existing toolbox of modern high-pressure crystallography applied to single-crystal diffraction methods, it is possible to record structural states in crystals. In particular on approaching structural instability conditions, which include the states of metastability, careful interpretation of crystal structures shed light onto the mechanistic pathways of critical atoms triggering the changes as manifested by the cooperative interaction of the transition mechanism. Nowadays this starts including the understanding of pathways not only in space but also in time with respect to both displacive and diffusion-oriented mechanisms. In this contribution results of high-pressure single-crstal XRD investigations will demonstrate in a few selected examples the possibilities to extract information on mechanisms and pathways. Examples include the displacive transition of pyroxene-type ABT_2X_6 germanates, subtle changes of second-order transitions such as in $BaTiSi_3O_9$, the structural changes in simple carbonate phase ($CaCO_3$, $BaMg(CO_3)_2$) or complicated open framework structures (e.g. $Mg_2Al_4Si_5O_{18}$).

Deposition of high-pressure data and metadata

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High pressure studies in crystalline amino acids

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Amino acids are the small molecules that form proteins and peptides that constitute all living beings. This condition is essential, but amino acids are so intriguing that have attracted attention not only in biology, but also in physics, chemistry, pharmaceutic industry and material science. Some amino acids present ferroelectricity, piezoelectricity and non-linear optical properties. Amino acids have the general formula $H\text{-}C\text{-}CO_2^{-}\text{-}NH_3^{+}\text{-}R$, where R is a lateral chain characteristic of each molecule. In crystalline state their structure is stabilized mainly by hydrogen bonds between the carboxylic group of a molecule and the amino group of the adjacent. The versatile of this three-dimensional structure allows they have polymorphs. Glycine, the simplest non-chiral amino acid (its lateral chain is formed only by an hydrogen atom) presents at ambient conditions three polymorphs (α, β, and γ) and except for α-Glycine that is stable for pressures up to 23 GPa, β and γ polymorphs exhibit phase transitions under pressure. Amino acids also present enantiomers L, and D as well as a racemate DL. Some studies comparing chiral and racemic counterparts have been reported. L-leucine undergoes three phase transitions up to 5.0 GPa. Results for DL-leucine crystal indicate that the racemic form is more stable than the chiral L-leucine crystal because it presents only one phase transition in the same range of pressure. Alanine, the simplest chiral amino acid, is one of the most studied amino acids. For a long time it was thought that the L form undergone a phase transition at around 2.3 GPa, but recently studies reported that its structure is stable up to 8.0 GPa as well as the DL-Alanine. It was observed that for pressures up to 12.0 GPa the L-Alanine presents amorphization. This is very interesting because so far it was the only crystal→amorphous phase transition in amino acids even more interesting when comparing this result with that obtained in L-Asparagine monohydrated that was investigated under pressure and many phase transitions were observed for pressure up to 29.0 GPa and no amorphization process took place. Some more examples will be given to show the complexity of this system.

Next generation synchrotron portable Large Volume High-P/T/Stress/Tomography Cell for Extreme Chemistry and Earth Sciences

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We describe a recently developed portable large volume high-P/T/stress/tomography device installed at ESRF and SOLEIL for extreme chemistry, materials and Earth sciences. The system uses the V7 type Paris-Edinburgh (PE) press. The V7 has a capacity of 450 tonnes but only a weight of less than 90 kg. The ~ 20% larger overall dimensions permit accommodation of various modules whose volume is too large to be incorporated in the “traditional” PE press. We present mainly two interesting modules: T-cup module and rotoPEc module.

The Stony Brook “T-cup system” is a miniaturised KAWAI-type apparatus which operates routinely to 25 GPa and 2500 K. The novel feature of this apparatus is its extreme compactness, which provides important advantages compared to conventional multi-anvil cells. We outline some recent results obtained with this new device.

Also, synchrotron X-ray microtomography is a non-destructive 3D imaging/microanalysis method selective to a wide range of properties such as morphology, density, chemical composition, chemical states, structure, and crystallographic perfection with extremely high sensitivity and spatial resolution. To extend this technique to extreme conditions (high-pressure/high-temperature/high stress), we developed at ESRF on beamline ID27 a new portable device, the RoToPEc [1]. In our new system, both anvils can rotate independently under load, with no limitation in angle, through two sets of gear reducers and thrust bearings. Hence, our portable device can operate in four different modes: (i) tomography, (ii) shearing, (iii) deformation or (iv) combination of (iii) or (ii) and (i). Our portable device has been easily and successfully adapted to various multi-modal synchrotron experimental set-up at beamlines ID27 (ESRF), PSICHE (SOLEIL), and I12 (DIAMOND). The potential of our new equipment for in situ synchrotron experiments will be illustrated by preliminary results recently obtained from these facilities on many scientific cases: direct visualisation and quantification of melt migration at extreme P-T-Stress conditions [2], XRD-CT of C_{60} sample [3], determination of the density of amorphous materials at extreme conditions [4], anelasticity and attenuation in olivine at upper mantle conditions and seismic frequencies [5], etc.

To conclude, we will present the new scientific opportunities our portable device allows for studies of phase transition, density, crystallization and deformation under extreme PT conditions.

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high-pressure; shear; tomography

New challenges and opportunities for mineral physics of the deep Earth

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The role of clay minerals on the volatiles transport to the mantle and internal heating of the Earth

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Pressure induced reactivity in molecular crystals: accessing the dynamics at molecular level by complementary structural and spectroscopic experiments

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The pressure induced reactivity of simple molecules has captured in the last years the attention of several research groups for the implications in different research fields spanning from geophysics, geochemistry, materials science to fundamental physics and chemistry. Reactivity in these systems derives from a complex interplay of structural properties, lattice dynamical processes and electronic arrangement, all of them ruled both by pressure and temperature1. This scenario is further perturbed by the probing techniques that, through the employment of energetic photons (from visible to x-ray), can modify the charge distribution thus triggering the chemical transformation. In order to understand the reactivity at the molecular level it is therefore mandatory to disentangle the effects of pressure, temperature and laser (or x-ray) radiation on the reaction activation. Here, I will show as the combined investigation of these processes by different linear and non-linear spectroscopic techniques and synchrotron based x-ray diffraction experiments is able to provide a quantitative insight about the reaction trigger and dynamics. The reactivity of two model systems, benzene2 and s-triazine3, will serve as textbook examples of the procedures adopted to unveil the reaction dynamics.

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Hydrogen Bonded Organic Molecular Solids under Pressure

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High pressure research explores structural, physical and chemical properties of materials by tuning their inter-molecular interactions under pressure. Organic hydrogen bonded molecular solids undergo a wide range of pressure induced structural transitions, which involve changes in the ionic and conformational states, hydrogen-bond-assisted polymerization, etc., through reorientations of hydrogen bonds, proton tunnelling/transfer, hydrogen bond symmetrization etc. In this talk, pressure induced structural changes in a wide range of hydrogen bonded materials of importance to basic and advanced materials research will be discussed. For example, the study of intra-molecular hydrogen bonds in ethylene glycol, which has proximal hydroxyl groups, can be used as a model system for studying complex hydrogen bonding networks in sugars and polysaccharides. Organic and semi-organic complexes of glycine display novel structural modifications mediated through hydrogen bonds under pressure and have promising materials research applications. Hydrogen bonds are found to play an important role in the pressure induced polymerization in materials such as acrylic acid, acrylamide, monomers of industrial polymers and biomaterials such as carnosine, imidazole, etc. We have used primarily spectroscopic methods, as they provide first hand information on the changes pertaining to hydrogen bonds in these systems. The diverse spectroscopic signatures of pressure induced structural variations noted in the strong and weak hydrogen bonded systems indicate that a lot more remains to be explored in the high pressure spectroscopy of hydrogen bonds.

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Resonance high-pressure Raman spectroscopy in nanocarbon materials

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Low dimensional (2D and 1D) carbon materials exhibit interesting physical properties which make them very attractive for advancing science and open possibilities for designing novel devices. Strain plays an important role on shaping the physical properties of nanocarbons. Raman spectroscopy is a quite powerful technique for probing both electrons and atomic arrangements in this materials by means of phonon spectrum and in this talk we discuss recent results obtained in nanotubes, graphene and linear carbon chains under high pressure conditions using inelastic light scattering.

Magnesiowüstite at high pressure using single-crystal synchrotron methods

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In recent years, seismic observations have provided increasing evidence for significant heterogeneity in Earth's lower mantle at both large (i.e. large low shear velocity provinces, or LLSVPs) and comparatively small (ultra-low velocity zones, or ULVZs) scales. One possible source of heterogeneity is variation in the Fe-content of the (Mg,Fe)O component of the lower mantle due to melting events and/or reactions with Earth's outer core. Most previous studies to megabar pressures have focused on compositions containing ~10-20 mol% Fe, but small amounts of compositions with an enhanced Fe concentration may strongly impact the elastic properties of the bulk phase assemblage. Here, we present results from high-precision single-crystal x-ray diffraction studies on (Fe0.78Mg0.22)O magnesiowüstite to pressures of about 55 GPa at 300 K using neon and helium as pressure-transmitting media. We observe a noticeably different compression behavior in the two pressure media at pressures greater than about 20 GPa, and compare to previous work on similar compositions. In addition, we are currently complementing the results of this work with synchrotron Mössbauer spectroscopy and inelastic x-ray scattering measurements to gain insight into the atomic and lattice dynamical properties of magnesiowüstite, and will present preliminary results from these studies.

Hybrid experimental/theoretical thermodynamics and thermoelasticity of materials: the high T NaCl pressure scale

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Despite the importance of thermodynamic and elastic properties of minerals, their measurements at high pressures and temperatures (PT) are limited. Thereby, ab initio calculations are an essential tool for predicting these properties at extreme conditions. Density functional theory (DFT) and quasiharmonic approximation (QHA) are the essential methods involved in these calculations. This approach has two main problems, first, a poor description of the exchange correlation energy, and second, intrinsic anharmonicity at high temperatures. These lead to well-known systematic deviations from experimental measurements. In this study, we have improved, developed, and tested hybrid schemes to combine experimental data and ab initio results to remove DFT/QHA errors and produce predictive equations of state at high pressures and temperatures, and applied them to NaCl. These correction schemes were further extended to calculate corrected thermoelastic properties. These schemes make accurate predictions when tested against experimental data.

New silicon and carbon materials by in situ high pressure synthesis.

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SILICON. Silicon is the second abundant element, after oxygen, in the earth crust. It is essential for today's electronics because of its ability to show various electronic behaviors that allow covering the numerous fields of cutting-edge applications. Our recent high-pressure studies of the chemical interaction and phase transformations in the Na-Si system [1], revealed a number of interesting routes to new and known silicon compounds [1] and allotropes [2]. The pressure-temperature range of their formation is suitable for large-volume synthesis and future industrial scaling. The variety of properties observed (e.g. quasi-direct bandgap of open-framework allotrope Si24)2 allow us to suggest future industrial applications. CARBON. After exploring pressure as an additional dimension for the chemistry of the Mg−C system, four magnesium carbides are now known: (1) tetragonal MgC2, (2) orthorhombic α-Mg2C3, (3) monoclinic β-Mg2C3 [3], and (4) cubic Mg2C [4]. Taking into account that at ambient pressure and at pressures up to ~5 GPa the elements do not interact at any temperature, it is quite astonishing to observe such rich chemistry. Finally, these results indicate that the Mg-C system should be completely revised under high pressure [5]. The phase behavior in this system is important for the production of structurally-perfect diamonds with high growth rates as compared to other known metal-carbon systems, and also for the synthesis of unique nitrogen-free and boron-doped semiconductive diamonds. With these new results, we now have a much deeper understanding of Mg-C thermodynamics under extreme conditions.

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High Pressure Raman spectra of Pb8O5(VO4)2

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The application of Raman spectroscopy under high pressures has provided new and different information to different fields of science. In this context the Raman spectroscopy under increased pressure was critical to analyze new structural features shown by the ferroelastic Pb8O5(VO4)2. The crystalline structure of this compound can be generally represented by a plane of tetrahedral VO43- anions interspaced with layers of PbO. It was previously reported that this ferroelastic shows two structural transition phase as a function of temperature. It was also verified that the high temperature phases can be stabilized at room temperature by the crystal size. In this study, the Raman spectra of Pb8O5(VO4)2 crystals were recorded from atmospheric pressures up to 17 GPa in order to monitor possible structural changes. Under increasing pressure, the Raman spectra of Pb8O5(VO4)2 exhibit well- defined modifications that can be ascribed to structural phase transitions at approximately 1, 3.5 and 6 GPa, as well as a reversible amorphization process around 11 GPa. These results will be discussed in terms of the previously reported Raman spectra.

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Structural Transitions Induced by Gas Pressure and Temperature in Flexible Framework Nanoporous Materials

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The most of nanoporous materials reported to date have been found to exhibit little structural changes during guest exchange. In recent years, however, a number of interesting compounds known as flexible framework nanoporous materials have been discovered, which show reversible structural transitions between low porosity and high porosity phases during the adsorption and desorption of guests. The functional properties of these materials are closely related to their crystal structure and, particularly, to the structural transitions induced by thermal energy and pressure. Nevertheless, until now there are very few published investigations dedicated to determining this behavior. So, in this project, the possible structural transitions for a series of flexible framework nanoporous materials as consequence of gas pressure in the porous framework and changes in the temperature will be studied. The structural study will be carried out using Calorimetric and Raman data to identify the possible temperature induced structural transitions. For those samples that present thermal structural transitions, high resolution XRD data will be collected in order to resolve and refine their crystal structures. The pressure effect on the porous framework will be explored using N2 and H2 adsorption isotherms. For those solids with step-like adsorption curves, high resolution XRD data with adsorbed species using a capillary cell at gas pressure will be recorded and then used to solve the crystal structure of the new phases. The structural study will be complemented with the information of techniques such as IR Spectroscopy and Elemental Chemical Analyses. The structural information to be obtained and its correlation with the materials adsorption, thermal and spectroscopic properties for the considered series of materials have no precedent in the available scientific literature. Such information is relevant for the potential applications of these porous solids, such as gases storage, smart membranes and others.

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Pressure induced green-to-dark piezochromism in a polycyclic aromatic hydrocarbon

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The new discovery of alkali-metal doped organic superconductors in herringbone-like polycyclic aromatic hydrocarbons (PAHs) has led to re-vitalization of the area of superconducting π-electron materials.[1] The electronic structure of PAHs can be finely tuned by the external pressure (e.g. picene).[2] In the work, we studied the structural and electronic changes of solid hydrocarbon C18H12 up to ~30 GPa using diamond anvil cells (DACs) through powder synchrotron X-ray diffraction, absorption spectra, four-probe resistivity measurements. We observed pressure induced drastic colour change of the sample from light green to opaque black. These interesting physical properties under high pressure will be presented.

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X-ray crystallography analysis of compound lassbio-1606 at room pressure and at high pressure

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The techniques used in the search for new polymorphs are based, generally, on crystallization in different solvents and under various temperatures. In this work, we explore the variations of pressure as an additional tool in that quest. The compound LASSBio-1606, C17O4N3H15S, belongs to a series of benzothiazine N-acylhydrazones derivatives with antinociceptive and anti-inflammatory activities [1]. The single crystals were obtained by slow evaporation method in dimethyl sulfoxide solution at room temperature. Data collection was performed in the APEX II DUO diffractometer of Bruker (Mo-Ka = 0.71073 Å). The unit cell (a = 15.69798(7) Å, b = 11.6145(5) Å, c = 19.7205(8) Å, beta = 113.152(2)°, volume = 3305.94(31) A^3), was obtained based on the refinement of 3029 reflections. The compound crystallized in the C2/c space group. In the following, a single crystal of the compound was subjected to X-ray diffraction data collection at high pressure using a Merrill-Bassett diamond anvil cell. Data collection was performed in the APEX II DUO diffractometer (Mo-Ka = 0.71073 Å). Based on the refinement of 438 reflections, the following unit cell was obtained: a = 14.65(3) Å, b = 10.65(3) Å, c = 17.97(4) Å, beta = 112.20(3)°, volume = 2596(11) A^3. The space group was the same as in ambient pressure. Due to the space group being the same, it is inferred that there were no changes in the symmetry of the structure, and the main changes occurred in the intermolecular interactions. Considering an invariant crystal packing, we notice that this structure behaves in a elastic way in the pressure range that has been analysed. In this way, an attempt was made to perform the refinement of the high pressure diffraction data using the unit cell coordinates from ambient pressure data, keeping constants the bond distances, in order to visualize the effects of the pressure in the intermolecular contacts

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Crystalographic changes of NH4-smectite in high pressure and high temperature (HPHT) conditions: An experimental insight applied for nitrogen cycle on Earth

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Our planet atmosphere is anomalously rich in nitrogen (in its N2 form) compared with the atmospheres of Mars and Venus (Mikhail & Sverjensky, 2014), but the mechanisms that acted to transform Earth's atmosphere are still in debate. NH4-bearing smectites could play an important role in the planetary nitrogen cycle (Cedeño et al., 2014) as a transport agent of nitrogen from the surface to deeper levels of the planet. High pressure and high temperature experiments performed in this mineral on 1000 tonf hydraulic press coupled with toroidal chambers suggest that nitrogen, speciated as ammonium, could occupy the 12-fold crystallographic site (interlayer site) in smectite and remain in the mineral structure during the phase transformation of this mineral for higher pressure more stable phases. The smectite used in these experiments is a product of Ca+2/ NH4+ cation substitution in a natural Ca-smectite (montmorillonite). The introduction of a different ion with a different ionic radius does not change the smectite crystal structure, although there is a significant variation in the interlayer distance, represented by the 001 crystallographic plane: from 15.35 Å in natural Ca-smectite to 12.32 Å in exchanged NH4-smectite, as evidenced by XRD analyzes. This change is believed to be an influence of both the exchanged ion and the water spheres that follow such ion (Sposito et al., 1999), fact that could explain the drastic differences between Ca- and NH4-smectites. These H2O molecules are connected to the interlayer ion and to the main sheet-like structure of the mineral by electrostatic forces. The nature of the bond could make possible for water molecules to organize themselves as a high-pressure ice polymorph insite the smectite structure. When exposed to HPHT conditions, NH4+-smectite exhibits some interesting structural changes that recondition its internal order. At 2.5 GPa and 250oC, the mineral evolves to a illite-smectite mixed-layer crystal structure and to tobelite phase at 350°C. Tobelite is a NH4+-mica structure with a 001 plane distances of 10.8 Å, identified both in XRD and FTIR analyzes. At 4.0 GPa, the first change occurs at 350oC, while the second one occurs to more extreme conditions (450oC at 4.0 GPa), in which the mixed-layer structure is reorganized in a tobelite phase. Next step of our study is performing HPHT experiment and process XRD analysis in situ in order to observe the possible crystallization of the high pressure ice phase.

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Raman spectroscopic study of DL Valine under pressure

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Amino acids in L-form are the constituents of all living beings. In crystalline state their structure is stabilized mainly by hydrogen bonds and they can present two enantiomers (L and D) and a racemic (DL) form. The amount of papers dealing on DL form of amino acid has increased in the last years, but it is still fewer than that on L-form. Although L and DL for being formed essentially by the same molecule the way they are linked can provide very different properties. In this way high pressure Raman spectroscopy is an useful tool that can be used to study the role of hydrogen bonds in the structure that compose amino acids as well as compare the behavior of its counterparts. In this report we present a detailed analysis of the vibrational properties of DL-Valine for pressure up to 19.4 GPa. At ambient conditions the crystallographic structure of our sample was confirmed by X-ray diffraction experiments as been triclinic (P-1 space group) with cell parameters: a=5.222(1)Å, b=5.406(1) Å, c=10.838 Å, α=90.89(1)o, β=92.34(1)o, and γ=110.02(1)o [1]. Under pressure it was observed modifications in the bands associated with external and internal modes indicate that the crystal undergoes structural phase transitions: (i) between 1.4 and 1.8 GPa; and (ii) between 8.8 and 10.0 GPa. All the phase transitions are reversible.

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Towards time-resolved studies using x-ray diffraction at synchrotrons

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The advent of new 3rd generation light sources with unprecedented brilliance such as PETRA III in Hamburg, Germany as well as introductions of fast area detectors optimized for high energies such as PerkinElmer XRD1621 have made it possible to conduct time-resolved angle-dispersive XRD experiments on continuously compressed materials in DAC with time resolution of tens of milliseconds. Both membrane driven DAC (mDAC) and dynamically driven DAC (dDAC) techniques have been advanced to bridge the gap between quasi-static conditions and dynamic shock loading by reaching strain rates in the range of 10^{-2} - 10^2 s^{-1}. Fast compression experiments have been carried out on number of samples, including geophysically relevant materials such as carbonates and silicates and simple metals such as iron, tungsten and platinum to gain insights into stress and strain distributions during compression cycles in the DACs. Several experiments will be reviewed with focus on the analysis of strains and stress distribution under non-hydrostatic pressure from fast compression experiments on iron [Konopkova2015]. Our results emphasize the importance of a controlled pressurization in DACs because of the effect of the loading rate on the stress state of the sample, particularly on decompression.

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Theoretical calculations of high-pressure phases of CoF2: An ab initio constant-pressure study

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In this study, we have studied the structural properties of the antiferromagnetic CoF2 in tetragonal structure with symmetry P42/mnm using density functional theory (DFT) under rapid hydrostatic pressure up to 168 GPa. For the exchange correlation energy we used the local density approximation (LDA) of Ceperley and Adler (CA). A phase transformation is successfully observed through the simulation. The structure of XF2-type compounds crystallizes in rutile-type structure. CoF2 undergoes phase transformations from the tetragonal structure to orthorhombic structure with space group Pnnm at 96 GPa. These structures have 6, 6 atoms per unit cell. These phase changes are also studied by enthalpy calculations and total energy. According to the calculations of enthalpy, we obtained phase transformations at about 15 GPa.

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X-ray absorption studies and f-level occupancy in Ce2Rh(1-x)IrxIn8.

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Within the series of heavy fermions Ce2Rh(1-x)IrxIn8 intermetallic compounds it has been recently observed the occurrence of two low-temperature superconducting (SC) phases as a function of temperature both at ambient pressure and under applied pressure for intermediate Ir-content (x~0.25 - 0.70) with remarkable different behaviour of both states as a function of pressure and Iridium content (x) [1]. The observed results seem to be reminiscent of the two SC phases found in the CeRh(1-x)IrxIn5 system [2] but the SC phases in the title compounds appear for smaller x ranges which has been associated to its higher dimensionality and structural disorder. In this work, we have performed EXAFS (X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge Structure) measurements in the series Ce2Rh(1-x)IrxIn8 (x = 0.00, 0.25, 0.50, 0.75) in order to shed light into the complex phase diagram obtained [1] as well as into the relationship between the local atomic order and the interesting ground states observed as a function of temperature and Ir concentration. The experimental data were obtained at the Brazilian Synchrotron Light Source (LNLS) in the Ir (L3), Rh (K) and Ce (L3) absorption edges. Our results have been analysed by using FEFF and IFEFFIT codes and they suggest that there is no evidence for the presence of local structural disorder until de lowest temperature measured (10K), contrary to what has been suggested, however sample inhomogeneities (Rh clustering) and changes in the Rh/Ir stoichiometry could be responsible for the smaller doping range where SC were observed. XANES data reveals that Ce valence is 3+ over the entire studied T interval. Preliminary results of EXAFS data under pressure of up to 20 kbar will be presented and compared to the ambient pressure EXAFS data.

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Glycine co-crystals at low temperature and high pressure: X-ray diffraction and spectroscopic study

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There are three “true” co-crystals of glycine with carboxylic acids (with no proton transfer from acidic component to basic one) reported up to now: those with glutaric (**GG**), DL-tartaric (**GT**) and phthalic (**GP**) acids. The co-crystal of glycine with glutaric acid was obtained in two research groups independently in 2011. The behaviour of this co-crystal at low temperature and high pressure was investigated in our laboratory previously and first order phase transition was discovered. The present study was focused on the effect of variations in temperature and pressure on two other co-crystals of glycine - with DL-tartaric and phthalic acids. Both co-crystals were stable on cooling down up to 100 K. The changes of unit cell parameters and in the geometry of the hydrogen bonds were followed. No phase transitions were detected, in contrast to **GG** co-crystal. The effect of pressure on selected co-crystals was much more significant. The two molecular co-crystals underwent reversible phase transformations at quite low pressures. The phase transitions were accompanied by fracture. Despite this, the crystal structure of the high-pressure phase of **GT** co-crystal could be solved by single crystal X-ray diffraction. The changes in the structure as compared with the low-pressure phase were analysed in terms of molecular conformations and hydrogen bonded motifs. However, it was impossible to solve the structure of **GP** co-crystal after the high-pressure phase transition, due to a complete fracture of the single crystal, although Raman spectra could be measured for the new phase. The crystal structures of high-pressure phases of glycine co-crystals were compared with each other. The features of structural rearrangement and changes in hydrogen bond network were analysed using X-ray diffraction and spectroscopic data.

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High-pressure dependent X-ray absorption of SmNiO3 at the Ni K- and Sm-L3 edges

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SmNiO3 is a member of the family of undoped compounds RNiO3 (R=Rare Earth) in which a sharp temperature driven insulator to metal phase transition takes place. The transition from high temperature orthorhombic metallic to an insulating charge disproportionate (2Ni3+ → Ni3+δ+Ni3−δ) monoclinic distorted phase is consequence of the Ni-O bond length increase and a simultaneous decrease of the Ni-O-Ni angle. SmNiO3, TIM = 400 K, also has an intermediate paramagnetic insulating phase, and orders magnetically below TN~205 K The magnetic ground state consist of an unusual antiferromagnetic structure, with k=(1/2,0,1/2). Pressure P causes increments in the Ni-O-Ni angle and simultaneous diminution of the Ni-O distances inducing the interplay of bandwidth W, charge energy transfer Δ, and Coulomb repulsion energy U. An increment in W and thus W/U, eventually closes the insulating gap yielding a reduction of TIM. This negative slope, -TMI/dP, is shared by all RNiO3 (R=Rare Earth≠ La.). Here we report XANES and EXAFS measurements of SmNiO3 from 20 K to 600 K and up to 38 GPa at the Ni K- and Sm L3- edges. They were performed at Laboratorio Nacional de Luz Sincrotron, Campinas, Brazil, in the DXAS energy dispersive beamline. Increasing pressure induces Ni-O-Ni angle increments toward more symmetric Ni3+ octahedra of the rhombohedral $R\bar{3}c$ space group (metallic LaNiO3). A multiple component pre-edge tail accounts for 1s transitions to 3d-4p states while a post-edge shoulder raises distinctively smoother due to the reduction of electron-phonon interactions as Ni 3d and O 2p orbitals overlap. Pressure dependent room temperature Ni white line peak energies show an abrupt 2.4 GPa valence discontinuity understood as due to non-equivalent Ni sites with Ni3+δ + Ni3-δ charge disproportionate in the monoclinic distortion turning at TMI into Ni3+ of the perovskite distorted orthorhombic Pbnm metal oxide phase. At 20 K, still distinctive, this turns smoother due to localization. Octahedral bond contraction at 300 K and 20 K show breaks in its monotonic increase at the different structural changes up to 38 GPa. We also found that Sm L3-edge does not show distinctive behaviors either at 300 K or 20 K up about 35 GPa but bonds contraction undergoes a critical distortion at intermediate pressures. Our findings suggest that the white line pressure dependent anomaly may be used as a reliable alternative for delineating pressure phase diagrams in RNiO3 (R=Rare Earth).

Non-ambient Crystallography of Technetium Metal

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Technetium metal is one of the last elements to be subjected to a systematic study of its structural properties at non-ambient conditions. Due to the challenges involved with radioactive materials, high precision structural measurements have been forgone on this elemental at all but the most accessible environments. A precise description of the structural behavior of technetium metal is important for the design of nuclear fuel, nuclear waste storage and the analysis of nuclear material. In this work we will present a structural investigation of technetium metal at high pressure, variable temperature and a redetermination of the ambient structure using high resolution synchrotron powder X-ray diffraction. The isothermal equation-of-state has been determined up to 151 GPa using diamond-anvil cells. DFT-base simulations performed over a range up to 275 GPa agree within 1% over the experimental range. Thermal expansion measurements have been made using synchrotron radiation over a range of 100-900K. The advances in non-ambient sample environment for powder and single crystal diffraction of radioactive samples for use at synchrotron facilities will be discussed.

High Pressure study and oligomerization of 2-aminoterephthalate/Ni-Al Layered Double Hydroxide composites

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Layered double hydroxides (LDHs) are a class of ionic layered materials built up of positive charged brucite-like layers and an interlayer region containing charge compensating anions/molecules.1 Terephthalic acid (TPA) and its derivatives such as 2-aminoterephthalic (2-ATA) acid are useful molecules in making condensation polymers and 2-ATA derivatives are of great interest because of an intense blue-violet fluorescence. 2,3 High pressures in the GPa range (0.1 up to dozens of GPa) are capable of tuning the intermolecular/atomic distances severely changing the atomic scale chemical framework, inducing a great number of phenomena.4,5 It is reported the high pressure behavior of composites comprising LDH containing Ni(II) and Al(III) in the brucite-like layer and 2-ATA anion between the layers (LDH/2-ATA) and its reactivity monitored through Raman and infrared spectroscopies and supported by quantum calculations. Raman spectroscopy was used to characterize and follow the stability of the LDH-ATA composite as a function of pressure up to 8.2 GPa. The spectrum at 0.1 MPa (1 atm) presents Raman bands at 580, 800, 1244, 1401 and 1618 cm-1, assigned to v6b, ring breathing, vC-C+vC-NH2, vC-C+vC-CO-2 and vC=C,2 respectively. Increasing pressure a broadening and a blueshift of the bands is observed. Under the decompression, the changes are clearly reversible and apparently no major structural change is occurring. The frequency shifts as a function of pressure of the Raman bands did not exhibit any discontinuity that could suggest changes in the chain packing of 2-ATA inside the Ni-Al LDH and the pressure shifts of all vibrational modes during the compression were nearly linear with slopes ranging between 0.6 to 1.7 cm-1/GPa. It is also observed that during the decompression step the frequency values of the composite are almost completely recovered. However, a deeper analysis of the 1600 cm-1 region of the Raman spectrum of the loaded sample, at 8.2 GPa and the recovered sample, indicates that during the compression of the composite the disappearance of the component characteristic of the vNH2 is observed, which is not recovered after the decompression, suggesting the occurrence in the sample of a small extension of 2-ATA oligomerization through the condensation of two molecules leading to an extended chemical framework. DFT calculation supports these results, indicating that the condensation reaction is feasible.

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High-pressure solvates

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High pressure can efficiently induce polymorphic transformations and it can promote the formation of solvates. [1,2] Various solvates of 1,4-diazabicyclo[2.2.2]octane salts, dabcoHX (X=I, Br, ClO4) have been obtained at high pressure. At ambient conditions they crystallizes exclusively in the unsolvated forms and are well known for their relaxor and ferroelectric properties. [3] However at high pressure they easily cocrystallize with the applied solvent (water, methanol, ethanol or their mixture). [4-6] A single crystals of dabco solvates have been in situ grown in a diamond-anvil cell and their structures determined by X-ray diffraction. Structures of unsolvated dabco salts are governed by the NH+•••N hydrogen bonds, linking the dabco cations into chains. High-pressure transforms the H-bonding pattern and the hierarchy of different cohesion forces. The NH+•••N hydrogen bonds are replaced by hydrogen bonds between cations and solvent molecules. The solvate formation is additionally favored by the molecular volume, this of the solvated compound being lower than the sum of equimolar unsolvated components. Phase transition or cocrystals formation can change the physical or chemical properties of the compounds. Therefore, it is important to understand the mechanism of solvates formation and their production in a controlled way. The systematic high-pressure effect destabilizing the NH+•••N bonds has been demonstrated for the series of dabco salts and solvates.

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Raman spectroscopy and molecular dynamics simulations of ionic liquids under high pressure

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Ionic liquids are salts with low melting point (below 100°C by definition). We have been using Raman spectroscopy to explore the rich phenomenology of phase transitions exhibited by ionic liquids at low temperature or high pressure. Raman spectroscopy of ionic liquids up to ca. 4.0 GPa unravel intermolecular vibrations within the low-frequency range (10 < w < 200 cm-1).[1] In case of [C3H7NH3][NO3], which crystallizes at 1.0 GPa, we found that the sample became microscopically heterogeneous allowing for micro-Raman imaging of different ordered phases within the diamond anvil cell.[2] Spectral modifications in Raman bands belonging to anion and cation normal modes indicate structural changes occurring in both the polar and the non-polar nanoscale domains of ionic liquids. For those ionic liquids which do not crystallize, the glass transition pressure, pg, was obtained from the pressure dependence of the bandwidth of the ruby fluorescence line.[3] We also found that ionic liquids based on the [(CF3SO2)2N]- anion could be used for pressure calibration as the characteristic Raman band at 740 cm-1 exhibits linear frequency shift (4.2 cm-1/GPa) for pressures up to 2.5 GPa.[4] The pressure induced shift of the vibrational frequency of the totally symmetric stretching mode of the [PF6]- anion has been calculated by a hard-sphere model of a pseudo-diatomic solute under short-range repulsive interactions.5 Equations of states needed for applying this theory were based on a modified Tait equation, and the resulting density was compared with data obtained by molecular dynamics (MD) simulations.[6] MD simulations of the well-known glass-former molten salt mixture 2Ca(NO3)2.3KNO3, CKN, were performed as a function of temperature and pressure in order to obtain Tg(p) and to show that dynamical properties scale as 1/(V^gT). The density scaling parameter g = 1.8 is related to the exponent of the repulsive part of an effective intermolecular potential for the atoms at shortest distance in CKN.[7]

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Isostructural Second-Order Phase Transition of Beta-Bi2O3 at High Pressure: An Experimental and Theoretical Study

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We report a joint experimental and theoretical study of the structural and vibrational properties of synthetic sphaerobismoite (Beta-Bi2O3) at high pressures where room-temperature angle-dispersive x-ray diffraction and Raman scattering measurements have been complemented with ab initio total-energy and lattice dynamics calculations. Striking changes in Raman spectra were observed around 2 GPa while x-ray diffraction measurements evidence no change in the unit cell volume and the tetragonal symmetry of the compound up to 20 GPa; however, a significant change exists in the compressibility when increasing pressure above 2 GPa. These features have been understood thanks to theoretical calculations, which show that Beta-Bi2O3 undergoes a pressure-induced isostructural phase transition from the Beta to the Beta' phase near 2 GPa. The study of the Bi eccentricity indicates that in the Beta' phase the Bi3+ environment becomes more regular than in the Beta phase likely due to the decrease of the lone electron pair activity of Bi3+ with increasing pressure. Interestingly, our results indicate that the isostructural phase transition is not consequence of the vanishing of the lone electron pair activity since the eccentricity does not disappear completely even up to 20 GPa. Raman measurements and theoretical calculations indicate the presence of a soft mode related to the second-order nature of the pressure-induced isostructural transition. Above 20 GPa, XRD measurements suggest a partial amorphisation of the sample despite Raman measurements still show weak peaks, probably related to a new unknown phase, which still remain up to 27 GPa. On pressure release, XRD patterns and Raman spectra below 2 GPa correspond to elemental Bi-I; thus evidencing a pressure-induced decomposition of the sample during downstroke.

Advanced Processing of High-Pressure Data from CMOS APS Detector Systems

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A major challenge in the field of High Pressure crystallography is the acquisition of sufficient quality data for a successful structure determination especially for low symmetry samples. The volume of reciprocal space accessible for X-ray examination is constrained by the shape and size of the Diamond Anvil cell used and mostly determined by its opening angle. In addition the acquired data suffer from absorption effects from the Diamond Anvils, high background Tungsten gasket and Beryllium powder diffraction as well as overlapping of sample reflections with those from the diamonds used in the experiment. The advantages of using CMOS APS detectors in the field of high-pressure single-crystal structure determination have been well recognized in recent years. Modern 3- and 4-axes goniometers equipped with a CMOS detector allow the acquisition of virtually all accessible data. These diffraction systems are very sensitive and fast with highly automated software for strategy planning, data acquisition and data processing. This presentation will focus on recent advances in software development which help tackling the problems with data acquired in high-pressure experiments as outlined above. We will present new algorithms for data integration for simultaneous processing and deconvolution of reflections from the sample and the diamond reflections.

Synthesis and characterization of RNiO3 nanowires produced by template assisted method

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The rare-earth nickelate series RNiO3 have been extensively studied due to their interesting physical properties. In fact, these compounds display a rich phase diagram with striking structural, magnetic and metal-insulator transitions. This work reports the preparation and characterization of nanowires of RNiO3 (R= La, Nd) compounds by template-assisted method. The nanowires arrays were prepared using commercial porous polycarbonate membranes, which were used as template with the porous filled with polymeric solutions. Such precursor solutions were prepared through the modified-polymeric precursor method. In such route, stoichiometric amounts of [La(NO3)3.6H2O] or [Nd(NO3)3.6H2O], and Ni(OCOCH3)2.4H2O are dissolved in a citric acid and ethanol, then the solution is heated-treated at 70 °C. Then the solutions were deposited on the template in vacuum. We used polymeric precursor solution with different viscosities and heat-treated at 900 °C and under 1 to 60 bar of oxygen pressure. The morphology, microstructure and crystal structure were investigated by scanning electron microscopy (SEM), of X-ray diffraction (XRD), the transport properties were characterized by measurements of electrical resistance as a function of temperature. The XRD results revealed that these samples crystallize in a perovskite structure. SEM images showed that this synthesis procedure produced polycrystalline RNiO3 nanowires with diameters ranging from 50 to 70 nm and lengths of 0.7 to 5 micrometers. We have observed that the resistance has a different behavior than those reported in the literature for bulk materials. In fact, sintered pellets of these samples present a smooth metal-insulator transition.

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High Pressure Investigation of Neodymium Monopnictides Using Density Functional Theory

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In the present manuscrip structural and phase transition properties of NdX (X = P, As) under high pressure have been investigated using an ab-initio FP-LAPW+lo approach within the framework of density functional theory as implanted in the WIEN2k package. In this approach the generalized gradient approximation is chosen for the exchange-correlation functional energy optimization for calculating the total energy. At ambient conditions NdX stabilize in NaCl (B1 phase) structure. Under compression, it undergoes first-order structural transition from Fm-3m to P4/mmm (body centre tetragonal) phase at 29.53 and 24.06 GPa which is found to be in good agreement with the available experimental data 30.0 [1] and 24.2 GPa [2] respectively. The structural properties viz., equilibrium lattice constants, bulk modulus and its pressure derivative and volume collapse are also calculated and compared with previous calculations and available experimental data. The variations of enthalpy with pressure for Neodymium phosphide in B1 and BCT phases have been shown. It is obvious from this curves that the enthalpies in both the phases become equal at 29.53 showing that both the phases are in equilibrium at this pressure, hence structural phase transformation occurs at this point .

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High Pressure Phase Transition Properties of Lutetium Monopnictide: A Density Functional Theory Study

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We have systematically investigated the structural and phase transition properties of the heaviest lanthanides i.e lutetium monopnictides LuX (X= N, P, As) compound using an ab initio calculations based on the density functional theory with Perdrew, Burke and Ernzerhof generalized gradient approximation (PBE-GGA) as implemented in WIEN2k code. The basic ground state properties viz., lattice constants (a), bulk modulus (B0) and its pressure derivative (B0') and total energy (E0) are calculated. The calculated equilibrium lattice constant are a= 4.765, 5.533 and 5.694 Å which are very close to the experimentally observed lattice constant a=4.766 [1], 5.533 [2] and a=5.680 Å [3] for LuN, LuP and LuAs respectively. The relative stabilities of LuX at high pressure in the NaCl (B1), CsCl (B2), zinc blende (B3) and body centred tetragonal (BCT) structures are also analysed. Reduced volume versus pressure for B1 to B2 phase are persented in Figure 1. The calculated value of volume collapse is 3.53% for LuP.

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Novel Radionuclide Wasteforms Prepared Under Pressure

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As of 2012, nuclear power makes up 5.7% of the world's energy [1] and is growing every year. The United States has an open-cycle approach which produces ~27 tons of waste/year/reactor. Currently, the most widely used waste form for nuclear waste is borosilicate glass. Although glass and ceramic waste forms have proven to be durable and sufficient at immobilizing many radionuclides; they are not ideal for certain radionuclides including I2, Kr, Tc and actinides. These nuclear waste products have long half-lives and have particularly harmful health and environmental effects. There is a need to design new waste forms that can immobilize these problematic radionuclides and reliably store them for thousands – and in some cases millions of years. Zeolites are a family of either naturally occurring or synthetic aluminosilicate minerals composed of Earth-abundant, inexpensive, low toxicity elements. Although the diameter of the windows to these cages is smaller than the diameters of the intended guests; under certain conditions the windows can accommodate diffusion of larger guest atoms/molecules. Lattice distortions and vibrations brought on by pressure and temperature can make the structure flexible enough to allow for the diffusion of small molecules/ions. Transition state theory calculations have also estimated the diffusion rates of Ar and Kr into sodalite cages [3]. Compression of the rhombohedral form of silica-sodalite was performed in hopes of learning the behavior and capabilities of the structure and how to possibly improve it for waste immobilization. Also, using General Utility Lattice Program (GULP) we predict pressure dependent changes to the structures.

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In Situ Impedance, Resistivity, and Raman Spectroscopy Measurements of Perchlorates Under Extreme Conditions

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We report an in situ Impedance, resistivity, and Raman spectroscopic study of $KClO_4$ and $LiClO_4$ under high pressure inside a diamond anvil cell. The perchlorates were examined before and after being decomposed by x-ray irradiation at the B-MB beamline at the Advanced Photon Source at Argonne National Laboratory. The x-rays cause the potassium perchlorate to decompose into KCl and O_2. This has been confirmed by Raman spectroscopy[1] and XRD[2]. The oxygen produced, has also been proven to diffuse through the damaged lattice quite readily[3]. The impedance of the samples were measured with a Solatron Analytical® Impedance/Phase Gain Analyzer. The resistivity of the samples were determined using a 4-probe Van der Pauw technique. The maximum pressure attained was 15GPa. The outcomes of this research can pave the way for novel materials for rugged electronics designed to survive the most inhospitable environments in the world.

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β-Alanine: different phases at different protocols of increasing pressure

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Crystalline amino acids attract attention of researches due to their interesting physical properties (non-linear optical, piezoelectric, ferroelectric) and ability to mimic behavior of larger biologically active molecules (peptides, proteins) [1]. Phase transitions in these systems are also of great interest during the last decades due to this fact [2]. For β-Alanine a series of phase transitions has been reported, which are poorly reproducible and strongly dependent on the protocol of varying pressure that makes this object unique in this respect [3]. New high-pressure phase of the title compound has been found previously and characterized by powder X-ray diffraction at a laboratory source and by Raman spectroscopy. The aim of the title study was to find conditions at which new high-pressure phase of β-alanine can be obtained and to solve crystal structure of this phase. For this purpose we used single-crystal X-ray diffraction at synchrotron source (ESRF). At ambient conditions β-alanine crystallizes as orthorhombic phase I with space group Pbca. We have refined the crystal structure of β-alanine at ambient conditions in the DAC without a pressure-transmitting medium, after which the pressure was increased to 4.7 GPa, 5.5 GPa, and 6.3 GPa. The cell parameters corresponded to compressed phase I. At 6.3 GPa the crystal structure was refined and was found to be equal to phase II according to powder diffraction data for phase II given in [3]. Then the sample was held at this pressure for ~ 15 hours. A new domain appeared as a fragment of the initial crystal after 15 hours. X-ray diffraction showed the domain to be a single-crystal. Its structure was solved (phase V) and refined in a monoclinic space group P21/c. After 30 hours from starting the experiment another transition into a finely disperse form, presumably form IV [3], is observed. At the same time, if form I was compressed immediately to 8 GPa then the transformation into monoclinic phase V was avoided and form II was preserved. The work was supported by grant from RSF 14-13-00834.

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