Book of Abstracts

“Advances in Static and Dynamic High-Pressure Crystallography”

2013 Workshop of the IUCr Commission on High Pressure

September 8th – 11th
DESY, Hamburg

Final Schedule

Sunday September 8th		
18:00 – 20:00	Registration and Reception	Lobby of Auditorium
Monday September 9th		
7:45 – 8:15	Registration and Breakfast	Lobby of Auditorium
8:15 – 8:20	Welcome IUCr Commission on High-Pressure	I. Loa (Secretary of Commission on High Pressure)
8:20 – 8:25	Welcome from DESY	E. Weckert (DESY)
8:25 – 8:30	Greetings from the DKG	U. Schwarz (DGK)
Session A ***Rising Stars*** ***Chairs: Yoshinori Katayama and Francesca Fabbiani***		
8:30 – 9:05 (invited talk)	Experimental constraints on thermal conductivity of the core-mantle boundary region	K. Ohta (Osaka U.)
9:05 – 9:40 (invited talk)	Gas Hydrates – when water meets gas under pressure	A. Falenty (U. Göttingen)
9:40 – 10:10	Coffee Break	Lobby of Auditorium

Session B ***Electronic and magnetic phenomena*** ***Chairs: Björn Winkler and Konstantin Kamenev***		
10:10 – 10:45 (invited talk)	Pressure-induced interrelated structural and electronic transitions in α-FeOOH and Fe_2O_3	E. Greenberg (Tel Aviv U.)
10:45 – 11:20 (invited talk)	Pressure-induced magnetic phase transition in Cr_2O_3 determined by second harmonic generation measurements	L. Bayarjargal (U. Frankfurt)
11:20 – 11:40	High pressure studies of structural and electronic properties of lead selenide	P. Bhambhani (Banasthali U.)
11:40 – 12:00	High Pressure and Low Temperature Studies on Raman Spectra and Resistivity on Bi_2Se_3 Single Crystals	V. Bhatt Sandip (Sardar Patel U.)
12:00 – 13:30	Lunch Break	Lobby of Auditorium
Session C ***Polymorphism and crystal chemistry*** ***Chairs: Kamil Dziubek and Przemyslaw Dera***		
13:30 – 14:05 (invited talk)	Zeolite host-guest systems under pressure: towards the high pressure synthesis of zeolite/polymer nanocomposites	J. Haines (CNRS-Université Montpellier)
14:05 – 14:40 (invited talk)	Copious in Polymorphs Dabco Monosalts	A. Olejniczak (Adam Mickiewicz U.)
14:40 – 15:00	Advancing from static to dynamic diffraction studies on the high pressure melting of materials	R. Briggs (Edinburgh U.)
15:00 – 15:20	High-Pressure Mixing in the Water-Ammonia System	J. S. Loveday (Edinburgh U.)
15:20 – 15:40	Order-Disorder and Intra-phase Transitions in Incommensurate Host-Guest Potassium	E. E. McBride (Edinburgh U.)
15:40 – 16:10	Coffee Break	Lobby of Auditorium

<table>
<tr><th colspan="3"><i>Session D</i>
<i>Amorphous, liquid, non-crystalline and crypto-crystalline solids</i>
<i>Chairs: Andrew Goodwin and Vadim Brazhkin</i></th></tr>
<tr><td>16:10 – 16:45
(invited talk)</td><td>Networks under Pressure</td><td>P. Salmon (U. Bath)</td></tr>
<tr><td>16:45 – 17:00</td><td>Structural Behaviour of Metallic Glasses under High Pressure</td><td>N. Mattern (IFW Dresden)</td></tr>
<tr><td>17:00 – 17:15</td><td>In-situ high-pressure XRD studies of Co-Zr metallic glass</td><td>J. Bednarcik (DESY)</td></tr>
<tr><td>17:15 – 17:30</td><td>Pressure-induced structural change in molten basalt</td><td>P. Dalladay-Simpson (U. Edinburgh)</td></tr>
<tr><td>17:30 – 18:30</td><td>Tour of FLASH and PETRA III
Meeting of the IUCr Commission on High-Pressure</td><td></td></tr>
<tr><td>18:30 – 21:00</td><td>Poster Session and BBQ</td><td>DESY Cantina</td></tr>
</table>

Tuesday September 10th		
Session E ***Crystallographic controls on rheology and elasticity*** ***Chairs: Simon Redfern and Nori Nishiyama***		
8:00 – 8:30	Registration and Breakfast	Lobby of Auditorium
8:30 – 9:05 (invited talk)	Defect chemistry and Si-diffusion in forsterite	T. Katsura (BGI)
9:05 – 9:40 (invited talk)	Advances in high-pressure materials rheology: from single-crystal to aggregate plasticity	P. Raterron (CNRS / Université Lille 1)
9:40 – 10:10	Coffee Break	Lobby of Auditorium
10:10 – 10:30	In-situ observation of crystallographic preferred orientation of olivine deformed in simple shear	T. Ohuchi (GRC, Ehime U.)
10:30 – 10:50	In Situ Stress-Strain Measurements on Ringwoodite at 18 GPa and 1700 K Using a Deformation-DIA Apparatus Combined with Synchrotron Radiation	T. Kawazoe (BGI & GRC, Ehime U.)
10:50 – 11:10	Brillouin Scattering and X-ray Diffraction of Solid Argon to 65 GPa and 700 K: Shear Strength of Argon	H. Marquardt (GFZ)
Session F ***New Frontiers in Extreme Conditions Crystallography*** ***Chairs: Hanns-Peter Liermann and Ingo Loa***		
11:10 – 11:45 (invited talk)	Equations of state of metals from X-ray diffraction data at static pressures above 5 Mbar	L. Dubrovinsky (BGI)
11:45 – 12:20 (invited talk)	Time-resolved studies of phase transition dynamics in Bismuth and Krypton	W. Evans (LLNL)
12:20 – 13:30	Lunch Break	Lobby of Auditorium
13:30 – 13:50	Melting Studies of iron from in-situ XRD at megabar pressures with short laser pulses	Z. Konôpková (DESY)
13:50 – 14:10	Novel high-pressure Fe_2O_3 polymorph	E. Bykova (BGI)

14:10 – 14:30	Newly Developed Micro X-ray Focusing Optics for High-pressure X-ray Diffraction at SPring-8	Y. Ohishi (SPring-8)
14:30 – 14:50	New perspectives for dynamic high-pressure research: the high-energy density instrument at the European XFEL	K. Appel (European XFEL GmbH)
14:50 – 15:20	Coffee Break	Lobby of Auditorium
Session G ***Studies of Organic and Biological Systems*** ***Chairs: Andrzej Katrusiak and Elena Boldyreva***		
15:20 – 15:55 (invited talk)	Proton dynamics in Shewanella oneidensis at high pressure	P. McMillan (UCL)
15:55 – 16:30 (invited talk)	Crystallographic structure of neuroglobin under high hydrostatic pressure. A tribute to Roger Fourme	N. Colloc'h (U. Caen)
16:30 – 16:50	The Effect of Water on an Imidazolium Based Ionic Liquid	S. Saouane (U. Göttingen)
16:50 – 17:10	Pressure effect on D,L-mandelic acid racemate crystallization	M. Andrzejewski (Adam Mickiewicz U.)
17:10 – 17:30	Conformationally Assisted Compression in Methyl Benzoate	W. Cai (Adam Mickiewicz U.)
18:00	Leave for Banquet with Bus	
19:00 – 22:00	Banquet on the Alster River	
ca. 22:30	Return to DESY	

Wednesday September 11th		
Session H ***Computational approaches*** ***Chairs: Nandini Garg and Rajeev Ahuja***		
8:00 – 8:50	Registration and Breakfast	Lobby of Auditorium
8:50 – 9:25 (invited talk)	Density Functional Theory: Applications to High-Pressure Crystallography	M. Mattesini (U. Complutense Madrid)
9:25 – 10:00 (invited talk)	Melting Curve and Atomic Diffusion in Solid Molecular Hydrogen at Extreme Pressures	M. Ramzan (Uppsala U.)
10:00 – 10:30	Coffee Break	Lobby of Auditorium
Session I ***Materials Science*** ***Chairs: Wilson Crichton and Vladimir Turkevich***		
10:30 – 11:05 (invited talk)	Creation of bulk nanostructured ultra-hard materials by extreme conditions	Y. Le Godec (U. P&M Curie, Paris)
11:05 – 11:40 (invited talk)	The local view of materials under pressure @ ISIS and Diamond	M. Tucker (ISIS/RAL)
11:40 – 12:00	High-pressure behavior of unconventional spin-Peierls compounds TiOCl and $TiPO_4$	M. Bykov (U. Bayreuth)
12:00 – 13:30	Lunch Break	Lobby of Auditorium
13:30 – 13:50	Pressure-Temperature Phase Diagram of $LuFe_2O_4$	J. Rouquette (U. Montpellier)
13:50 – 14:10	Pressure induced water insertion in synthetic clays	A. V. Talyzin (Umeå U.)

Session J ***Chemistry*** ***Chairs: Vladimir Solozhenko and Alexandr Talyzin***		
14:10 – 14:45 (invited talk)	High-Pressure Chemistry of Light Elements: New Compounds and Crystal Structures	O. O. Kurakevych (U. P&M Curie, Paris)
14:45 – 15:20 (invited talk)	Recent Advances in the High-Pressure Chemistry of Alkali Metal Borates	H. Huppertz (U. Innsbruck)
15:20 – 15:50	Coffee Break	Lobby of Auditorium
15:50 – 16:25 (invited talk)	Metal Hydrides at Extreme Conditions	E. Gregoryanz (U. Edinburgh)
16:25– 16:45	Chemical reactions at extreme conditions – polymerization of CO and decomposition of SF_6 in the diamond anvil cell	N. Rademacher (U. Frankfurt)
16:45 – 17:05	High-(p,T) synthesis and stability of tantalum and rhenium nitrides and their characterization	A. Friedrich (U. Frankfurt)
17:05 – 17:25	Calcium – Hydrogen System under High Pressures	S. Besedin (MPI Mainz)
17:25 – 17:45	The high-pressure behavior of the H_2O-CO_2 system	D. M. Amos (U. Edinburgh)
17:45 – 18:00	Concluding Remarks	I. Loa (Secretary of Commission on High Pressure)

Talk Abstracts
by Sessions

Experimental constraints on thermal conductivity of the core-mantle boundary region

*K. Ohta**[1]

[1]*Center for Quantum Science and Technology under Extreme Conditions, Osaka University*

Heat in the Earth's interior is transported by convection in the mantle and core, and by conduction at thermal boundary layers. The thermal conductivity at the core-mantle boundary region determines the magnitude of heat flux from the core, and is intimately related to the formation of mantle plumes, the long-term thermal evolution of both mantle and core, and the driving force for generations of the geomagnetic field [1]. The thermal conductivity in this region has been predicted to be 10 W/m/K for the lowermost mantle and 30 W/m/K for the outermost core based on large pressure and temperature extrapolations of laboratory data [2]. These values have been widely used for simulation of the mantle and core dynamics, and estimation of core heat flux. Recent technical progress both in the high-pressure experiment and the theoretical calculation enables us to reveal high pressure and high temperature behavior of thermal conductivities of lower mantle minerals and core materials.

We have measured the lattice thermal diffusivity of $MgSiO_3$ perovskite and post-perovskite, the primary minerals in the Earth's lower mantle, up to 144 GPa and 300 K in a diamond anvil cell [3]. Our results show that the thermal diffusivity of perovskite at 300 K increased with applying pressure; it increased from 2.5 ± 0.2 mm^2/s at 11 GPa to 11.7 ± 2.4 mm^2/s at 144 GPa. In addition, the lattice thermal diffusivity of post-perovskite at 135 GPa was 19.2 ± 4.4 mm^2/s, 70 % greater than that of perovskite at equivalent pressure. Obtained lattice thermal conductivity of perovskite-dominant lowermost mantle assemblage is about 11 W/m/K, while post-perovskite-bearing rocks may exhibit ~70 % higher conductivity. Our new measurements of the electrical resistivity of iron to 2 Mbar pressure show that the thermal conductivity of the uppermost core is greater than 90 W/m/K. These values are significantly higher than conventional estimates [2], but in good agreement with recent theoretical calculations [4,5]. Our results of the thermal conductivities of the lowermost mantle and the outermost core support the recent notion of high core–mantle boundary heat flow, implying rapid secular cooling, an inner core younger than 1 Giga years, and ubiquitous melting during early Earth.

References

[1] T. Lay, J. Hernlund, and B.A. Buffett, *Nature Geoscience* **1**, 25 (2008).
[2] F.D. Stacey, in *Physics of the Earth* (1992).
[3] K. Ohta *et al., Earth Planet. Sci. Lett.* **349-350**, 109 (2012).
[4] N. de Koker, G. Steinle-Neumann, and V. Vlček, *Proc. Natl. Acad. Sci. USA* **109**, 4070 (2012).
[5] M. Pozzo, C. Davies, D. Gubbins, and D. Alfè, *Nature* **485**, 355 (2012).

* ohta@hpr.cqst.osaka-u.ac.jp

Gas Hydrates – when water meets gas under pressure

A. Falenty[1] and W.F. Kuhs[1]*

[1]*GZG Abt.Kristallographie, Universität Göttingen, Goldschmidtstr.1, 37077 Göttingen, Germany*

Under suitable p-T conditions, gas and water crystallize into ice-like solids known as gas hydrates or clathrate hydrates. The host structure of these compounds formed by H-bonded water molecules creates a three-dimensional network of cages occupied by guest molecules. Through this cellular structure, clathrates are capable of reaching high gas densities thus becoming a potential storage medium for hydrocarbons, hydrogen or noble gases.

These seemingly exotic compounds are found frequently on Earth within sediments of continental shelves and permafrost where clathrates of such common gases like CO_2, H_2S, CH_4 or other lighter hydrocarbons can be formed already under moderate pressures. Such accumulations are considered to be an attractive and jet still not exploited source of gas. Gas hydrates also frequently addressed in the context of processes in extra-terrestrial environments of icy planets, their moons and in comets where cage-like structure might be exposed to a wide range of temperatures and pressures ranging from deep vacuum to a few GPa. Clathrates of various gases have been invoked to explain numerous morphological features on the surface, out-gassing events or the atmospheric composition of celestial bodies; they nourished a rich variety of hypotheses in planetary sciences challenged only by theoretical and laboratory studies [1,2].

We will present our experimental work on the thermodynamics and formation/dissociation kinetics of various gas hydrates at conditions relevant to terrestrial [3,4] and extra-terrestrial environments [1-3] together with other recent results. Special attention is given to the diffusion of gas molecules in the crystalline hydrate lattice (which is important for the gas hydrate formation process) and to the noble gas systems that might hold a key to a deeper understanding of the fundamental properties of the host structure and gas-water interactions.

References

[1] A. Falenty and W.F. Kuhs, J.Phys.Chem. B **113**, 15975-88, (2009).
[2] A. Falenty, G. Genov, T.C. Hansen, W.F. Kuhs, A.N. Salamatin, J.Phys. Chem. C **115**, 4022-32, (2011).
[3] A. Falenty, A.N. Salamatin, W.F. Kuhs, J.Phys.Chem.C **177**, 8443-57, (2013).
[4] W.F. Kuhs, D. Staykova, A.N. Salamatin, J.Phys.Chem. B **110**, 13283-95, (2006).

* afalent@gwdg.de

Pressure-induced interrelated structural and electronic transitions in α-FeOOH and Fe_2O_3

E. Greenberg[1], E. Bykova,[2] W. M. Xu [1], G. Kh. Rozenberg,[1] M. P. Pasternak,[1] L. Dubrovinsky,[2] T. Boffa Ballaran,[2] V. Prakapenka,[3] M. Hanfland [4] and Z. Konopkova[5]*

[1] *School of Physics and Astronomy, Tel Aviv University, 69978, Tel Aviv, Israel*
[2] *Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany*
[3] *Consortium for Advanced Radiation Sources, University of Chicago, Argonne, IL 60439*
[4] *European Synchrotron Radiation Facility, F-38043 Grenoble Cedex, France*
[5]*DESY, HASYLAB, PETRA-III, P02, Notkestr. 85, Bldg. 47c, Hamburg, Germany*

The hydrogen bond plays a crucial role in a wide variety of chemical and physical processes. Under high pressures the hydrogen bonds were predicted [1] to transform from a highly asymmetric soft O–H···O to a symmetric rigid configuration in which the proton lies midway between the two oxygen atoms. Despite four decades of research on water- and hydroxyl containing compounds, pressure induced hydrogen bond symmetrization has been unambiguously established [2] only in H_2O (Ice X) at $P > 60$ GPa. Following single crystal X-ray diffraction, Mössbauer (MS) and Raman spectroscopy measurements, we report the discovery of the H-bonds symmetrization in goethite, α-FeOOH, resulting from the Fe^{3+} high-to-low spin crossover at $P > 45$ GPa. The isosymmetric phase transition, induced by the spin crossover, results in a discontinuous volume reduction of ~11%, a symmetrization of the FeO_6 octahedra and an unexpected shortening of the O–H···O distances to ~2.2 Å at 50 GPa, which are characteristic of the *hydrogen-bond symmetrization*. Our findings suggest that hydrogen bond symmetrization may occur in crystalline materials at relatively low pressures if electronic transformations result in significant volume reduction.

In the case of an archetypal 3d transition metal oxide, Fe_2O_3 hematite, in spite of significant progress in studies of a series of pressure-induced structural, electronic and magnetic transformations the nature of these intertwined transitions still remains controversial. MS and resistance $R(P,T)$ studies [3] have shown the onset of a Mott transition above 50 GPa corroborating with the structural transition with a symmetry change. The Mott transition has been manifested by a sharp insulator-metal transition corroborating with an onset of the nonmagnetic state. Meanwhile, a XES study [4] has shown the existence of a residual signature of finite spin of Fe at P~70 GPa, suggesting a transition from a high- to a low-spin HP state. Other controversy exists regarding which transition precedes the other [5-7]. Our recent thorough XRD and MS studies undoubtedly show that the electronic transition in Fe_2O_3 takes place within the HP structure. Another important observation is the discovery of a two-stage Mott transition and a collapse of magnetism in Fe_2O_3. It wasshown that there is an intermediate pressure region, $53<P<70$ GPa, in which two equally abundant Fe^{3+} species co-exist, one HS antiferromagnetic and one non-magnetic. Only above 70 GPa the complete collapse of magnetism is observed. The structure of the observed HP polymorphs will be discussed.

References

[1] W.B. Holzapfel, , *J. Chem. Phys.* **56,** 712–715 (1972).
[2] P. Loubeyre et al., *Nature* **397**, 503-506 (1999).
[3] M. P. Pasternak et al., *Phys. Rev. Lett.* **82**, 4663 (1999).
[4] J. Badro et al., *Phys. Rev. Lett.* **83**, 4101 (1999).
[5] G. Kh. Rozenberg et al., *Phys. Rev. B* **65**, 064112 (2002).
[6] J. Badro et al., *Phys. Rev. Lett.* **89**, 205504 (2002).
[7] J. Kunes et al., *Phys. Rev. Lett.* **102**, 146402 (2009).

* erangre@gmail.com

Pressure-induced magnetic phase transition in Cr_2O_3 determined by second harmonic generation measurements

L. Bayarjargal[1] and B. Winkler[1]*

[1]Institut für Geowissenschaften, Goethe-Universität, Frankfurt a.M., Germany

At ambient conditions Cr_2O_3 has a corundum-type crystal structure and is an antiferromagnetic insulator with an acentric magnetic structure. The antiferromagnetic phase transition in Cr_2O_3 at 308 K has attracted significant attention for a long time and has been extensively investigated with numerous experimental approaches [1]. However, there is an open controversy with respect to the pressure dependence of the Neel temperature, dT_N/dP. The experimental study by Worlton *et al.* [2] of dT_N/dP was based on neutron diffraction, and found dT_N/dP = -16(3) K/GPa. A second study using magnetoelectric susceptibility measurements [3] found that dT_N/dP = +15.0(5) K/GPa. A third study [4] based on thermal expansion measurements using a strain gauge in a gas pressure cell yielded dT_N/dP = +5.0(5) K/GPa. Alberts *et al.* [5] combined ultrasound spectroscopic measurements and temperature-dependent x-ray diffraction to dT_N/dP = +2.2(5) K/GPa. Here we demonstrate that pressure-induced magnetic phase transitions can be detected by optical second harmonic generation (SHG) measurements [6] in diamond anvil cells.

For our experiment we loaded compacted powder samples of Cr_2O_3 and Ar in a diamond anvil cell. Lasers with wavelengths of 1054 nm and 920 nm were used as a fundamental pump wave. The fundamental wave at 920 nm was generated with an Optical Parametric Oscillator from a Q-switched Nd:YAG laser system. The SHG signal was separated with a short pass filter and with a monochromator from the fundamental wave. The SHG intensity was collected with a photo-multiplier and photon counter at pressures up to 20 GPa. The SHG intensity at both pumping wavelengths decreases continuously on increasing pressure and disappears above 10 GPa [6]. This indicates a transition from an acentric magnetic structure to a centrosymmetric arrangement of the magnetic order at this pressure. Measurements at more than one pumping wave length allow us to exclude that the pressure-induced diminishing of the SHG signal is due to a pressure-induced increase in the optical absorption. We can now, based on the diffraction study by Dera *et al.* [7], exclude that these changes are due to a structural phase transition. Our experiment show that the transition from an acentric to a centrosymmetric magnetic structure occurs in Cr_2O_3 at 10(1) GPa. The pressure dependence of the Neel temperature, dT_N/dP = -1.0(5) K/GPa from our SHG measurements. This result is consistent with results obtained by Raman measurements [8, 9] , which show a significant change in the Raman spectra at 13 - 15 GPa.

The authors acknowledge financial support from the Deutsche Forschungsgemeinschaft (DFG), Germany, within SPP1236 (projects Ba4020; Wi1232) and the FOKUS program of the Goethe University.

References

[1] M. Fiebig, D. Fröhlich, B. B. Krichevtsov, and R. V. Pisarev, Phys. Rev. Lett. **73**, 2127 (1994).
[2] T. G. Worlton, R. M. Brugger, and R. B. Bennion, J. Phys. Chem. Solids **29**, 435 (1968).
[3] G. Gorodetsky, R. M. Hornreich, and S. Shtrikman, Phys. Rev. Lett. **31**, 938 (1973).
[4] H. L. Alberts, J. Phys. Soc. Jpn. **38**, 1541 (1975).
[5] H. L. Alberts and J. C. A. Boeyens, J. Magn. Magn. Mater. **2**, 327 (1976).
[6] L. Bayarjargal and B. Winkler, Appl. Phys. Lett. 102, 182403 (2013);
[7] P. Dera, B. Lavina, Y. Meng, and V. B. Prakapenka, J. Solid State Chem.**184**, 3040 (2011).
[8] J. Mougin, T. L. Bihan, and G. Lucazeau, J. Phys. Chem. Solids **62**, 553 (2001).
[9] S.-H. Shim, T. S. Duffy, R. Jeanloz, C.-S. Yoo, and V. Iota, Phys. Rev. B **69**, 144107 (2004).

* *bayarjargal@kristall.uni-frankfurt.de*

High pressure studies of structural and electronic properties of lead selenide

P. Bhambhani[1] and G. Sharma[2]*

[1]Department of Physics, Banasthali University, Banasthali-304022, India

[2]Department of Pure & Applied Physics, University of Kota, Kota-304010, India

In this article, using the linear combination of atomic orbitals (LCAO) method, pressure induced phase transition, structural parameters and pressure dependent electronic properties of PbSe are studied. In the present investigations, two exchange and correlation approximations, the generalized gradient (GGA) and local density (LDA) are considered. It is observed that PbSe is stable in NaCl type (B1) phase and exhibits a transition from B1 phase to an orthorhombic Pnma (B27, FeB type) phase at 6.24 GPa, and further from Pnma phase to the CsCl type (B2) phase at 16.39 GPa. The variation of electronic band structure, theoretical directional anisotropies and covalent nature of PbSe under pressure are also reported. The calculated results are found in good agreement with previous theoretical and experimental results.

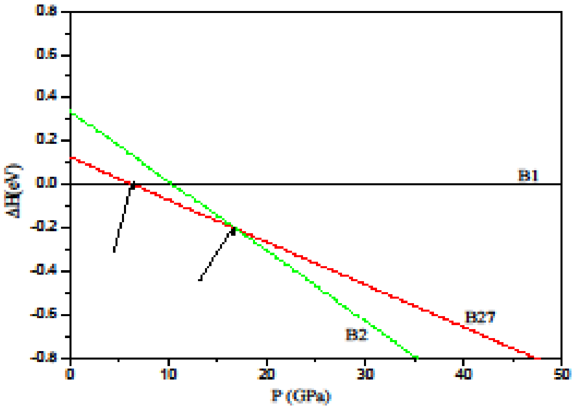


Figure 1: Enthalpy calculated from first-principles total energy for the B1, B27 and B2 structures of PbSe using the PBE correlation functional.

References

[1] R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, B. Civalleri, K. Doll, N.M. Harrison, I. J. Bush, Ph. D'Arco and M. Llunell, CRYSTAL06 User's manual, University of Torino, Torino, 2006.

[2] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.

[3] J.P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77 (1996), pp. 3865-3868.

[4] U. von Barth and L. Hedin, J. Phys. C: Solid State Phys. 5, 1629 (1972)

* poojagoklani@gmail.com

High Pressure and Low Temperature Studies on Raman Spectra and Resistivity on Bi_2Se_3 Single Crystals

Sandip V. Bhatt[*1], *M. P. Deshpande*[1], *Vasant Sathe*[2] *and S.H. Chaki*[1]

[1]*Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388 120, Gujarat, India*
[2]*UGC-DAE Consortium for Scientific Research, Khandwa Road, Indore 452017, India*

Bi_2Se_3 is a layered chalcogenide belonging to V_2-VI_3 compound with a narrow bandgap of 0.3eV having tremendous impact for thermoelectric applications, which are critical components for solid state power generation and refrigerating devices [1]. Very recently, it has regenerated great interest by being predicted to be a three-dimensional topological insulator [2]. Taking this aspect into consideration, we here report Raman spectra and electric resistivity measurement on Bi_2Se_3 single crystal under high pressure and low temperature conditions. Single crystals of Bi_2Se_3 were grown by vapor phase technique using ammonium chloride (NH_4Cl) as a transporting agent. Lattice vibration under hydrostatic high pressure, upto 12 GPa, was investigated in the Bi_2Se_3 single crystal by Raman scattering which provides the evidence that Bi_2Se_3 single crystal undergoes first order phase transition above 10 GPa. Isobaric and isothermal mode Gruneisen parameter have been determined from the temperature and pressure dependent Raman spectra for both Raman active modes of Bi_2Se_3 single crystal respectively. Pressure and temperature dependent Raman spectra was used to carry out an anharmonicity analysis in which implicit contributions and explicit contributions to the total observed frequency shifts (with pressure and temperature) have been evaluated and compared. The variation of electrical resistance under pressure upto 8 GPa was monitored in a Bridgman anvil set-up to indentify occurrence of any structural transition. Finally, results obtained and their discussion will be discussed in detail during the presentation.

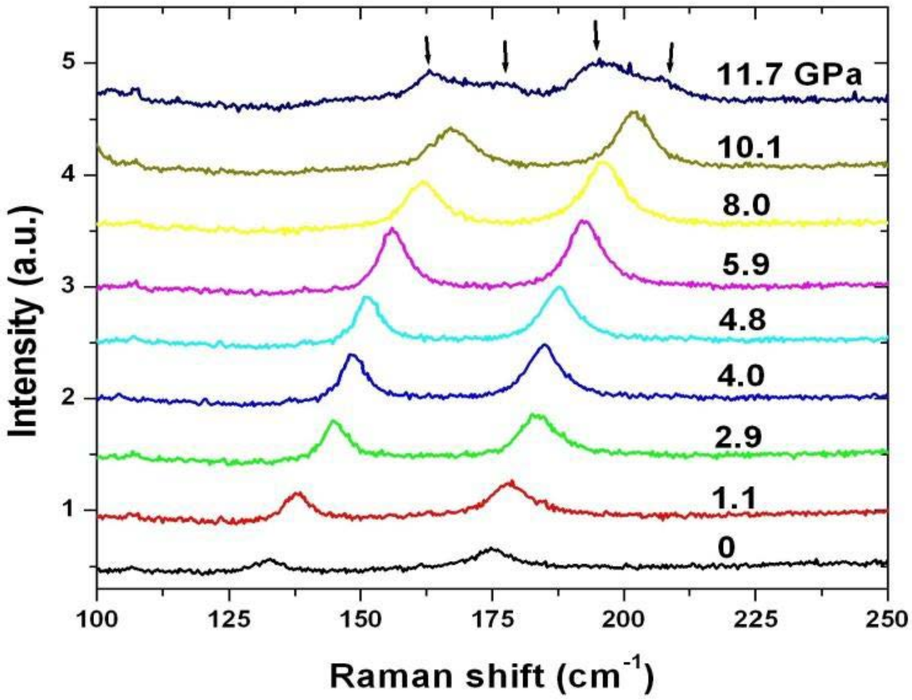


Figure 1: Raman spectra of Bi_2Se_3 single crystal at different pressures

Reference

[1] D. Wang, D. Yu, M. Mo, X. Liu, Y. Qian, Journal of Crystal Growth **253**, 445–451(2003)

[2] R. Vilaplana, D. Santamaria-perez, O. Gomis, F.J.manjon, J. Gonzalez, A. Segura, A. Munoz, P. Rodriguez-Hernandez, E. Perez-Gonzalez, V. Marin-Borras, V. Munoz-Sanjose, C. Drasar and V. Kucek, Physical Review B **84,** 18411001-14 (2011)

* presenter email : sandip.bhatt08@yahoo.com

Zeolite host-guest systems under pressure: towards the high pressure synthesis of zeolite/polymer nanocomposites

J. Haines[1], F. Alabarse[1], J. Rouquette[1], O. Cambon[1], B. Coasne[1,2], A. van der Lee[3], M. Santoro[4], F. G. Gorelli[5], R. Bini[5] and C. Paulmann[6]*

[1]Institut Charles Gerhardt Montpellier, UMR 5253 CNRS-Université Montpellier 2, Montpellier, France
[2]MultiScale Material Science for Energy and Environment (UMI CNRS/MIT), MIT, Cambridge, USA
[3]Institut Européen des Membranes, UMR-CNRS 5635, Université Montpellier 2, Montpellier, France
[4]IFAC-CNR, Sesto Fiorentino, Firenze, Italy
[5]European Laboratory for non Linear Spectroscopy (LENS), Sesto Fiorentino, Firenze, Italy
[6]Department Geowisssenschaften, Universität Hamburg, Hamburg, Germany

Microporous materials exhibit low-density structures built up of corner-sharing tetrahedra (SiO_4, AlO_4, PO_4) and are extensively used in important technological applications as molecular sieves and catalysts. Guest insertion in porous materials is of particular interest with respect to mechanical properties for possible applications as molecular springs and bumpers [1]. The insertion of Ar or CO_2 guest species in the pure SiO_2 zeolite, silicalite, was found to strongly increase the bulk modulus and deactivate pressure-induced amorphization [2]. In order to obtain more detailed structural information on the effect of guest species on the mechanical properties of zeolite systems, large-pore $AlPO_4$-54 was studied by single crystal x-ray diffraction at high pressure at DESY. Superhydration effects are observed and no decrease in the unit cell volume is observed up to 0.9 GPa in H_2O due to insertion of the H_2O molecules. Structure refinements were successfully performed and the analysis of the effect of pressure and H_2O insertion on the pore size and the positions of the oxygen atoms in the H_2O network provides a detailed understanding of the compression mechanism in this material. These results are found to be in very good agreement with the mechanical properties and the density maps obtained from Monte Carlo simulations. Based on the study of these zeolite-guest systems and in order to design new materials with targeted mechanical properties, the possibility of forming host-guest systems, which can be retained after pressure release was envisaged by polymerizing the guest species under high pressure in the pores of the host zeolite. Ethylene was thus photopolymerized in the pores of silicalite at 0.5-1.5 GPa in order to obtain a unique nano-composite material with drastically modified mechanical properties [3]. The structure obtained contains single polyethylene chains, which adapt very well to the confining channels based on vibrational spectroscopy and single-crystal x ray diffraction. The formation of this nanocomposite results in significant increases in bulk modulus and density and the thermal expansion coefficient changes sign from negative to positive with respect to silicalite. These results open the way to the high pressure, catalyzer free synthesis of a unique generation of functional materials based on simple hydrocarbons polymerized in microporous solids.

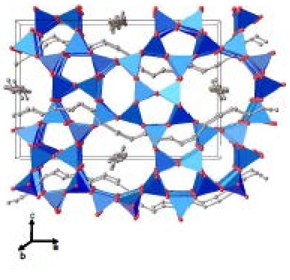


Figure 1: Structure of the silicalite/polyethylene nanocomposite synthesized at high pressure.

References

[1] V. Eroshenko, R.-C. Régis, M. Soulard, J. Patarin, *J. Am. Chem. Soc.* **123**, 8129 (2001).
[2] J. Haines et al., *J. Am. Chem. Soc.* **132**, 8860 (2010).
[3] M. Santoro et al., *Nature Commun.* **4**, 1557 (2013)

*Julien.Haines@univ-montp2.fr

Copious in Polymorphs Dabco Monosalts

Anna Olejniczak and Andrzej Katrusiak*

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 64-614 Poznań

1,4-Diazabicyclo[2.2.2]octane (dabco) monosalts are a fascinating group of compounds, which exhibit exceptional dielectric properties. They can be described by a general formula: dabcoHX, where X= Br^-, I^-, ClO_4, BF_4 and ReO_4. It was found, that the dabcoHX complexes are prone to exist in polymorphic forms. DabcoHI undergoes a large number of transformations at elevated pressure and temperature, forming at least ten phases [1], however its analogue dabcoHBr exists only in three forms [2]. These two compounds are ferroelectric relaxors, which are desired for practical applications in miniature electronic devices or capacitors. Moreover, the organic relaxors are environment friendly and easier to produce and to dispose off than inorganic relaxors, which are mainly mixed perovskites and lead-containing ceramics. Exceptionally rich phase diagram ten phases was also revealed for dabco perchlorate [3].

At normal conditions in the monosalts structures the $dabcoH^+$ cations are $NH^+\cdots N$ bonded into linear chains. Pressure can considerably modify the structure of $NH^+\cdots N$ bonded compounds. For example, in all dabcoHI polymorphs the $NH^+\cdots N$ bonded chains of $dabcoH^+$ cations are retained, whereas in dabcoHBr only phase III is $NH^+\cdots N$ bonded. Phase II of $dabcoHClO_4$ is isostructural with phase II of $dabcoHBF_4$, however it behaves differently on lowering temperature than it was observed in its analogue - $dabcoHBF_4$.

References

[1] A. Olejniczak, A. Katrusiak, and M. Szafrański, Cryst. Growth&Des. **10**, 3537 (2010).

[2] W. Nowicki, A. Olejniczak, M. Andrzejewski and A. Katrusiak, CrystEngComm **14**, 6428 (2012).

[3] A. Olejniczak, M. Anioła, M. Szafrański, A. Budzianowski, and A. Katrusiak, Cryst. Growth&Des.**DOI:**10.1021/cg400276c (2013).

* aniao@amu.edu.pl

Advancing from static to dynamic diffraction studies on the high pressure melting of materials

R. Briggs[1], D. Daisenberger[2], A. Salamat[3], G. Garbarino[4], M. Mezouar[4], V. Prakapenka[5], P.F. McMillan[6]*

[1]SUPA School of Physics and Astronomy & Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, UK

[2] Diamond Light Source Ltd., Diamond House, Harwell Science Campus, Didcot, Oxfordshire OX11 0DE, UK

[3] Lyman Laboratory of Physics, Harvard University, Cambridge, MA 02138, USA

[4]ID27, European Synchrotron Radiation Facility, BP 220, 38043 Grenoble Cedex, France

[5] GeoSoilEnviroCARS, University of Chicago, Argonne National Laboratory, Argonne, IL 60439, USA

[6] Chemistry and Institute of Shock Physics, University College London, 20 Gordon Street, London WC1H 0AJ, UK

The melting of the elements and compounds is of fundamental interest to earth and planetary sciences as well as for fundamental physics. The melting temperature (T_m) as a function of pressure has been traditionally determined *via* dynamic shock compression experiments and several static techniques (e.g. resistivity measurements [1], direct visual observations in laser speckle [2] or *in situ* X-ray diffraction techniques [3]), often providing excellent agreements with each other. Nevertheless, in some studies there are controversially different values for T_m that give discrepancies of several thousand kelvin at the highest pressures [4,5]. With the advancement of next generation synchrotron sources for 'time-resolved' X-ray diffraction on the ms and s timescale [6] as well as state-of-the-art laser facilities such as LCLS providing the capability of X-ray diffraction on the femtosecond time scale [7], the possibilities of implementing crystallographic measurements for the study of melting curves into the megabar range and beyond become increasingly tantalising. To be able to study the crystalline state of the sample below the melt curve, one must be able to provide high quality crystallographic data with reliable background subtraction, to accurately show a representative X-ray diffraction pattern of the sample. Diffraction data collected at ID27, ESRF and GSECARS, APS will be presented from 3 different melting experiments, with implications on designing and performing melting experiments at these new generation laser-facilities using laser-ramp / laser-shock techniques discussed.

References

[1] S. T. Weir, M. J. Lipp, S. Falabella, G. Samudrala, and Y. K. Vohra, J. Appl. Phys. **111**, 123529 (2012).

[2] B. Schwager, M. Ross, S. Japel, and R. Boehler, J. Chem. Phys. **133**, 084501 (2010).

[3] R. Briggs, D. Daisenberger, A. Salamat, G. Garbarino, M. Mezouar, M. Wilson, and P. F. McMillan, J. Phys.: Conf. Ser. **377**, 012035 (2012).

[4] J. Ruiz-Fuertes, A. Karandikar, R. Boehler, and D. Errandonea, Physics of the Earth and Planetary Interiors **181**, 69 (2010).

[5] A. Dewaele, M. Mezouar, N. Guignot, and P. Loubeyre, Physical Review Letters **104**, 255701 (2010).

[6] V. B. Prakapenka, A. Kubo, A. Kuznetsov, A. Laskin, O. Shkurikhin, P. Dera, M. L. Rivers, and S. R. Sutton, International Journal of High Pressure Research **28**, 225 (2008).

[7] H. J. Lee, Bulletin of the American Physical Society **Volume 58, Number 7**, (2013).

* richard.briggs@ed.ac.uk

High-Pressure Mixing in the Water-Ammonia System

C.W.Wilson[1], C. L. Bull[1,2], G.Stinton[1], D.Amos[1], J. S. Loveday[1]

[1]*SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK*
[2]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK*

The ammonia water system provides the basis of the ‘mineralogy’ of the outer solar-system. At ambient and low pressures ammonia water are extremely miscible in the liquid and form three solid hydrates at low temperature with 2:1, 1:1 and 1:2 water ammonia ratios. At higher pressures the liquids remain highly miscible, but above ~2.5 GPa liquids of the ammonia dihydrate and ammonia monohydrate composition crystalise to form ammonia hemihydrate-II and the relevant phase of ice [1,2]. Ammonia hemihydrate-II is then stable up to at least 30 GPa at room temperature [2]. This view is complicated by the existence at high pressure of a unique form of molecular solid in which ammonia and water are substitutionally disordered so that a given molecular centre may contain either an ammonia or a water molecule with the probability determined by the composition. This disordered molecular alloy (DMA) structure has been observed in samples of ammonia dihydrate and ammonia monohydrate which have been compressed to ~ 5 GPa at 180 K and then warmed to room temperature [3,4]. In contrast samples of the same composition compressed to 5 GPa at room temperature form ammonia hemihydrate-II and ice VII [2]. There thus arises a question as to which is the stable form of ammonia water above 5 GPa.

We have recently carried x-ray and neutron diffraction studies at pressures above 10 GPa and temperatures above room temperature. These show direct transformation of ammonia hemihydrate-II into the DMA structure and reveal the formation of DMA from the melt at ~7 GPa. These suggest that across a wide range of the high pressure phase diagram DMA is the stable structure and that a solid solution between water and ammonia exists.

*Corresponding author: j.loveday@ed.ac.uk

[1]A.D.Fortes et al, J. Appl. Cryst., **42**, 846-866 (2009).
[2] C.W.Wilson et al, J. Chem. Phys., **136**, 09456 (2012).
[3]J.S.Loveday et al, High Press. Res.**, 29** 396 (2009).
[4]J.S.Loveday and R.J.Nelmes, Phys. Rev. Lett. ,**83**, 4329 (1999).

Order-Disorder and Intra-phase Transitions in Incommensurate Host-Guest Potassium

E. E. McBride[1] K. A. Munro[1] and M. I. McMahon[1]*

[1]*SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, U.K.*

Complex crystal structures have unexpectedly been observed in many elemental systems at extreme compressions [1]. These phases are stabilised by the increase of electron interactions – both core-core and core-valence – at extreme compressions. The alkali elements, well understood at ambient conditions, all exhibit complex behaviour at high pressure, and are hence ideal systems to investigate this phenomenon [1-3].

Rubidium (Rb), sodium (Na) and potassium (K) have a common complex low symmetry phase at high pressure – an incommensurate host-guest structure (*tI*19) which is comprised of a 16-atom tetragonal host sub-structure with *c*-axis channels that contain linear chains of guest atoms. The host structure is common to all three elements – spacegroup *I4/mcm*, yet the guest structure for each is unique. In Rb, the guest crystallises into a body-centred tetragonal arrangement, in Na it adopts a monoclinic arrangement, and in K it crystallises into a *C*-centred tetragonal structure [2,4]. Over its 30 GPa stability range, *tI*19-K undergoes re-entrant intra-phase transitions in both the host and guest components of the structure [5].

In *tI*19-Rb, an additional pressure-induced phenomenon has been observed [6]. The guest reflections, sharp and Bragg-like at 18 GPa, broaden significantly when pressure is decreased, and disappear almost entirely at 16.2 GPa, indicating that the guest structure has become disordered. Interestingly, the guest reflections in *tI*19-Na are almost fully disordered at room temperature and show no significant sharpening over the entire stability field of the phase [4].

In a previously reported melting study of K, it was observed that the guest peaks broaden significantly upon heating at constant pressure, whereas the host structure remained unchanged, indicating a temperature- induced order-disorder transition in the guest component of the structure [7]. By combining diamond anvil cell techniques with *in-situ* synchrotron x-ray diffraction and external resistive heating we have conducted quasi-single crystal and polycrystalline studies to investigate the pressure and temperature dependence of this order-disorder transition. This transition exists over a wide range of pressures, and, interestingly, the temperature at which the guest chains disorder appears to be strongly influenced by the structure of the guest component. Furthermore, a single-crystal of *tI*19-K was grown at ~20 GPa and its structure was fully characterised by synchrotron x-ray diffraction. The influence of temperature on the inter-chain correlation length and atomic displacement parameters will be presented.

References

[1] McMahon & Nelmes, Chem. Soc. Rev. 35, 943 (2006).
[2] Marqués *et al.*, Phys. Rev. Lett. 106, 095502 (2011)
[3] Gregoryanz *et al.*, Science 320, 1054 (2008).
[4] Lundegaard *et al.*, Phys. Rev. B, 79, 064105 (2009).
[5] Lundegaard *et al.*, submitted to Phys Rev B (2013).
[6] McMahon & Nelmes, Phys. Rev. Lett. 93, 5 (2004).
[7] McBride *et al.*, Jour. of Phys.:Conf. Ser. 377, 012040 (2012).

* e.mcbride@ed.ac.uk

Networks under Pressure

Philip S. Salmon[1], Kamil Wezka[1], Anita Zeidler[1], Keiron J. Pizzey[1], Dean A. J. Whittaker[1],
James W. E. Drewitt[1], Ruth F. Rowlands[1], Stefan Klotz[2], Henry E. Fischer[3], Craig L. Bull[4],
Matthew G. Tucker[4], Martin C. Wilding[5], Malcolm Guthrie[6]
[1]Department of Physics, University of Bath, Bath BA2 7AY, UK
[2]IMPMC, Universit´e Pierre et Marie Curie, 75252 Paris, France
[3]Institut Laue Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble, France
[4]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, UK
[5]IMPS, Aberystwyth University, Aberystwyth SY23 3BZ, UK
[6]Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

The structural changes in glasses and liquids induced by high-pressure and/or high-temperature conditions can alter substantially their dynamical and transport properties. A notable example is pro- vided by so-called polyamorphic transitions where the variation of a state parameter such as pressure or temperature leads to an abrupt transformation between two phases having the same composition but different densities. Unravelling the mechanisms by which these transformations occur is, however, a formidable task owing to the nature of structural disorder and the experimental difficulties associated with the investigation of materials under extreme conditions.

This talk will focus on recent advances to measure the structure of network-forming glasses using in situ neutron diffraction with a Paris-Edinburgh press at pressures up to 17.5(5) GPa [1-4]. In particular, the mechanisms of density-driven structural collapse in glasses such as GeO_2 and $GeSe_2$ will be considered, where the debate is informed by the results obtained from the first applications of the method of high-pressure neutron diffraction with isotope substitution. The diffraction data are complemented by the results obtained from new molecular-dynamics simulations.

[1] A. Zeidler et al., J. Phys.: Condens. Matter 21, 474217 (2009)
[2] J. W. E. Drewitt et al., Phys. Rev. B 81, 014202 (2010)
[3] P. S. Salmon et al., J. Phys.: Condens. Matter 24, 415102 (2012)
[4] K. Wezka et al., J. Phys.: Condens. Matter 24, 502101 (2012)

Contact: p.s.salmon@bath.ac.uk

Structural Behaviour of Metallic Glasses under High Pressure

N. Mattern

IFW Dresden, Institute for Complex Materials, Helmholtzstr.20, 01069 Dresden
e-mail: n.mattern@ifw-dresden.de

High pressure has influence on the structure, the glass transition, and the crystallization of metallic glasses. Pressure induced phase transition were recently reported for some metallic glasses e.g. [1-3], which is surprising for such densely packed systems with a high coordination number $N_1 > 12$. In the first part, current status of high pressure studies on metallic glasses will be reviewed. We then report recent results of our investigations on the structural behaviour of glassy $Pd_{40}Cu_{30}Ni_{10}P_{40}$ under high pressure [4]. In situ high energy diffraction patterns were recorded as a function of pressure at the PETRA III extreme condition beam line P02.2. From the diffraction data the structure factors were extracted and the atomic pair correlation functions in real space were calculated. Up to the highest pressure of 47.4 GPa, a monotonic change of the structure factor is observed without any indication of a phase transition. In real space all maxima of the atomic pair correlation function including the nearest neighbour distance are lowered and scale with pressure. The volume function is extracted from the diffraction data and the bulk modulus K= 181GPa was obtained. The dependence of volume on pressure of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ metallic glass can be well described by the Birch – Murnaghan equation of state [5]. Challenges of temperature dependent X-ray diffraction experiments at high pressure will be pointed out and first results will be discussed.

[1] Sheng HW et al. : “Polyamorphism in a metallic glass”. Nat Mater 2007;6:192.

[2] Zeng QS et al. : “Origin of pressure-induced polyamorphism in Ce75Al25 metallic glass”. Phys Rev Lett 2010;104:105702.

[3] Li G et al. : “Electronic structure inheritance and pressure-induced polyamorphism in lanthanide-based metallic glasses”. Phys Rev Lett 2012;109:125501.

[4] N. Mattern, J. Bednarcik, H.P. Liermann, J. Eckert: ”Structural behaviour of $Pd_{40}Cu_{30}Ni_{10}P_{20}$ bulk metallic glass under high pressure” Intermetallics 2013; 38: 9

[5] W. B. Holzapfel, “Equations of state for solids under strong compression”, High Pressure Research 16;1998; 16:81

* N.Mattern@ifw-dresden.de

In-situ high-pressure XRD studies of Co-Zr metallic glass

J. Bednarcik[1*], J. Gamcova[1], L.F. Kiss[2], Z. Konopkova[1], H.P. Liermann[1]

[1] Deutsches Elektronen-Synchrotron (DESY), Notkestr. 85, D-22603 Hamburg, Germany
2 Institute for Solid State Physics and Optics, Wigner Research Centre for Physics, HAS, H-1525 Budapest, P.O.Box 49, Hungary

Room temperature pressure dependence of compressibility of the $Co_{91}Zr_9$ metallic glass was measured using a diamond anvil cell (DAC) at the Extreme Condition Beamline P02.2 of PETRA III (Hamburg, Germany). Neon was used as a pressure medium. Pressure inside the sample was determined using a ruby fluorescence. Pressure was increased in small steps up to 35 GPa using a pressure membrane. At each pressure point diffraction patterns were acquired in transmission mode. The energy of the synchrotron radiation was set to 42.72 keV, which corresponds to the wavelength of λ=0.2902 Å. Kirkpatrick-Baez (KB) mirrors were used to focus photon beam down to 2×2 μm^2. Two-dimensional XRD patterns were collected using a fast image plate detector Perkin Elmer 1621 (2048×2048 pixels, 200×200 μm^2 pixel size, intensity resolution of 16 bit) carefully mounted orthogonal to the X-ray beam. The volume changes were determined from the position of the first diffuse peak appearing in diffraction pattern. Obtained compressibility curve shows significant change of the slope around $p = 5$ GPa. Same behavior was observed when repeating compressibility measurements up to 10 GPa with higher photon energy (59.92 keV). Analyzing diffraction data in real space by means of pair distribution function suggests that observed changes in compressibility are associated with structural changes occurring in short and medium range order of CoZr metallic glass.

*Jozef.Bednarcik@desy.de

Pressure-induced structural change in molten basalt

C. Sanloup[1], J. Drewitt[1], P. Dalladay-Simpson[1], D. Morton[1], N. Rai[2], Z. Konôpková [3], W. van Westrenen[2], W. Morgenroth[4]*

[1]SUPA School of Physics and Astronomy & Centre for Science at Extreme Conditions, The University of Edinburgh, Edinburgh, UK

[2]Faculty of Earth and Life Sciences, VU University Amsterdam, Netherlands

[3]Photon Science, DESY, Hamburg Germany

[4]Goethe–Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany

Magmas are produced at depth in the Earth, and occurrences of their presence at greater depths are reported based on seismological information, such as the 410 disconti- nuity or atop the core-mantle boundary. Understanding the presence and eventual stability of magmas in the deep mantle requires a knowledge of their physical properties. However, this has been impeded for a long time due to the challenging nature of the experiments. In the recent years, structural and density information on silica glass have been obtained up to record pressures of up to 100 GPa, a first major step towards obtaining data on the molten state. Here, the structure of molten basalt is reported up to 60 GPa by means of in situ x-ray diffraction, and structural changes are evidenced. Silicon coordination increases from 4 at ambient conditions to 6 at 35 GPa, similarly to what has been reported in silica glass. Compressibility of the melt above completion of Si coordination change is lower than at lower pressure conditions, implying that a 4th order equation of state is needed to describe density evolution of silicate melts over the whole mantle P-range. It also implies that melts were buoyantly stable at the base of both upper and lower mantles during the magma ocean era.

Contact: chrystele.sanloup@upmc.fr

Defect chemistry and Si-diffusion in forsterite

T. Katsura[1], H.-Z. Fei[1], M. Wiedenbeck[2] and D. Yamazaki[3]*

[1]*Bayerisches Geoinstitut, University of Bayreuth, D95440 Bayreuth, Germany*
[2]*Helmholtz Centre Potsdam, Potsdam D14473, Germany.*
[3]*Institute for Study of the Earth's Interior, Okayama University, Misasa, Tottori 682-0193, Japan*

Fei et al. [1] demonstrated that the Si self-diffusion coefficient (D_{Si}) is proportional to 1/3 power of the water content (C_{H2O}) in forsterite with C_{H2O} up to 800 ppm. If the C_{H2O} is low and the oxygen fugacity is low, the charge neutrality condition of olivine in the water incorporation is considered to be $[(\mathrm{OH})_{\mathrm{O}}^{\bullet}] = 2[\mathrm{V}_{\mathrm{Me}}'']$. This charge neutrality condition leads to the relation of $[\mathrm{V}_{\mathrm{Si}}''''] \propto (C_{\mathrm{H2O}})^{2/3}$. If the Si self-diffusion coefficient is simply proportional to the $[\mathrm{V}_{\mathrm{Si}}'''']$, the water content exponent of 1/3 cannot be explained in view of the defect chemistry.

Here we propose a new model for Si diffusion in forsterite. A Si^{4+} site is tightly surrounded by four O^{2-} ions in the olivine structure. Namely, a Si ion is trapped in an oxygen cage. If one oxygen is missing, namely a $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$ associates a $\mathrm{V}_{\mathrm{Si}}''''$, the hopping probability of a $\mathrm{V}_{\mathrm{Si}}''''$ should become much higher, because the trapping cage is broken. This model suggests that D_{Si} is proportional not only to the $[\mathrm{V}_{\mathrm{Si}}'''']$ but also to the $[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}]$. Since $[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}] \propto (C_{\mathrm{H2O}})^{-1/3}$, $D_{\mathrm{Si}} \propto (C_{\mathrm{H2O}})^{2/3} \times (C_{\mathrm{H2O}})^{-1/3} = (C_{\mathrm{H2O}})^{1/3}$. Thus, this model well explains our new data about the water content dependence of Si self-diffusion coefficient.

A question is whether a significant proportion of $\mathrm{V}_{\mathrm{Si}}''''$ is associated with $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$ or not. Since both of the $[\mathrm{V}_{\mathrm{Si}}'''']$ and $[\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}]$ are low, the probability of association would be very low. However, the $\mathrm{V}_{\mathrm{Si}}''''$ and $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$ have excess negative and positive charges, the large Coulomb potential should greatly enhance the association. On the other hand, if all $\mathrm{V}_{\mathrm{Si}}''''$ are associated with $\mathrm{V}_{\mathrm{O}}^{\bullet\bullet}$, D_{Si} should be simply proportional to $[\mathrm{V}_{\mathrm{Si}}'''']$ only. The present model should be examined by computational simulation in order to assess its appropriateness.

References

[1] H-Z. Fei, M. Wiedenbeck, D. Yamazaki and T. Katsura, *Nature* 498, 213 (2013)

* tomo.katsura@uni-bayreuth.de

Advances in high-pressure materials rheology:

from single-crystal to aggregate plasticity

P. Raterron[1], C. Bollinger[1], O. Castelnau[2], P. Cordier[1], F. Detrez[2†], G. Fraysse[1,2], S. Merkel[1]*

[1] Unité Matériaux et Transformations (UMET), CNRS / Université Lille 1, France
[2] Procédés et Ingénierie en Mécanique et Matériaux (PIMM), CNRS / Arts et Métiers ParisTech, France
[†] Now at: Modélisation et Simulation Multi Echelle (MSME), CNRS / Université Paris-Est 2, France

The past decade abounded in technical and theoretical developments allowing new approaches in the investigation of materials rheology at high pressure (P) and temperature (T). New or improved devices set at synchrotron facilities [1], such as the Deformation-DIA apparatus (D-DIA) or radial diffraction in diamond anvil cells with external heater [2], allow quantifying high-T materials plasticity at P in excess of 35 GPa. While specimens are strained, d-spacing are measured in situ by X-ray diffraction in grains with different orientations, leading to the quantification of both differential stress and stress-field geometry in the cell assembly; these measurements benefit from developments in elastoplastic self-consistent (EPSC) modeling of strained aggregates. While specimen strain rates are measured by radiography, texture developments are quantified using diffraction lines intensities [3]. At the grain level, the effects of P, T, and other parameters on dislocation slip-system activities are investigated in single crystals, using polycrystalline materials to constrain stresses in the cell compression column [4]. Together with estimates of lattice friction based on first-principles calculations and theoretical modeling of crystal plasticity, these data are incorporated into viscoplastic self-consistent (VPSC) schemes [5] in order to assess aggregate microstructure evolution and plastic response in relevant rheological contexts.

We will present some of these recent advances as well as their application to the investigation of Earth upper-mantle plasticity. Minerals (i.e., olivine and pyroxenes) and aggregates representative of the upper mantle were deformed at P and T conditions prevailing in the Earth (e.g., 8 GPa and 1673K), in the D-DIA that equipped the X17B2 beamline of the NSLS. Experimental data were interpreted in terms of critical resolved shear stress (CRSS) for the active slip systems and integrated, together with theoretical CRSS estimates and an isotropic mechanism (accounting for diffusion at grain boundaries), into a VPSC model for olivine + pyroxenes aggregates. Result from the modeling allows better constraining upper-mantle plastic response during natural deformations, e.g., texture developments and flow stresses, as a function of P, T and phase proportions.

References

[1] P. Raterron and S. Merkel, Journal of Synchrotron Radiation **16**, 748 (2009).
[2] H.P. Liermann et al., Review of Scientific Instruments **80**, 104501 (2009).
[3] C. Bollinger, S. Merkel, and P. Raterron, Journal of Applied Crystallography **45**, 263 (2012).
[4] P. Raterron, S. Merkel, and C. Holyoke III, Review of Scientific Instruments **84**, 043906 (2013).
[5] O. Castelnau et al., Comptes Rendus Physique **11**, 304-315 (2010).

* Paul.Raterron@univ-lille1.fr

In-situ observation of crystallographic preferred orientation of olivine deformed in simple shear

T. Ohuchi[1], Y. Nishihara[1], Y. Seto[2], T. Kawazoe[3], M. Nishi[1], G. Maruyama[4], Y. Higo[5], K. Funakoshi[5], and T. Irifune[1]*

[1] *Geodynamics Research Center, Ehime University, Matsuyama, Ehime 790-8577, Japan*
[2]*Senior Research Fellow Center, Ehime University, Matsuyama, Ehime 790-8577, Japan*
[3]*Department of Earth and Planetary Sciences, Kobe University, Kobe, Hyogo 657-8501, Japan*
[4]*Bayerisches Geoinstitut, University of Bayreuth, 95440 Bayreuth, Germany*
[5]*Japan Synchrotron Radiation Institute, Sayo, Hyogo 679-5198, Japan*

In Earth's upper mantle, characteristics of the seismic anisotropy vary depending on the types of crystallographic preferred orientation (CPO) of olivine. Therefore, the pattern of the seismic anisotropy has been interpreted by taking into account the water- and pressure-induced olivine fabric transitions [1,2]. The fabric strength of olivine aggregates is also important when we evaluate the magnitude of the seismic anisotropy in the upper mantle. In the actual upper mantle, the steady-state fabric strength of olivine is expected to be achieved due to geological time-scales of flows. The dependency of the fabric strength of olivine aggregates on strain has been evaluated in only limited numbers of experimental studies (e.g., [3]). Bystrikcy et al. [3] showed that total shear strains higher than 4 are needed to achieve the steady-state fabric strength of olivine (D-type fabric) at 0.3 GPa and 1473 K. However, it has been difficult to evaluate the detailed processes of the developments of fabrics because fabrics of recovered samples have been used. Recently, we have developed experimental techniques for in-situ simple-shear deformation experiments using a D-DIA apparatus. In this paper, we briefly show that our recent experimental results on in-situ observations of stress, strain, and fabric developments in olivine samples.

Simple-shear deformation experiments on olivine aggregates at pressures P = 1-2 GPa, temperatures T = 1290-1490 K, and shear strain rates of 3E-4 s^{-1} were performed using a deformation-DIA apparatus installed at SPring-8. A sectioned sample of anhydrous olivine aggregates (diameter = 1.5 mm; thickness = 300-500 um) was placed into a nickel capsule and then sandwiched between two alumina pistons. Shear strain (up to 5) was measured by the rotation of a platinum strain-marker, which was initially placed perpendicular to the shear direction. Differential stress, generated pressure, and CPO patterns of olivine samples were determined from two-dimensional X-ray diffraction patterns using software (IPAnalyzer, PDIndexer, and ReciPro: Seto et al., [4]).

A-type olivine fabric was developed at high temperatures (1490 K). The fabric strength increased with strain (< 3), and steady-state fabric strength was achieved at shear strains about 3. Strain softening was observed in most of samples due to the developments of CPO of olivine. Developments of B-type and C- type-like fabric were observed at low temperatures (< 1440 K) in relatively wet samples.

It has been reported that the developments of the A-type fabric, which is the most commonly observed olivine fabric in natural peridotites. The threshold shear strain of 3, which is needed for the achievement of steady-state fabric strength, corresponds to 100 Myr of mantle flow (under the assumption of a shear strain rate of 1E-15 s-1). Our results implies that overwriting of an olivine CPO pattern due to a change of the deformation condition requires a long time-scale (i.e., 100 Myr or longer).

References

[1] H. Jung, and S. Karato, Science **293**, 1460-1463 (2001). [2]
T. Ohuchi et al., Earth Planet Sci. Lett. **304**, 55-63 (2011). [3]
M. Bystricky et al., Science **290**, 1564-1567 (2001).
[4] Y. Seto et al., Rev. High Pressure Sci. Technol., **20**, 269-276 (2010).

* ohuchi@sci.ehime-u.ac.jp

In Situ Stress-Strain Measurements on Ringwoodite at 18 GPa and 1700K Using a Deformation-DIA Apparatus Combined with Synchrotron Radiation

T. Kawazoe[1,2], *Y. Nishihara*[1], *T. Ohuchi*[1], *G. Maruyama*[1,3], *Y. Higo*[4], *K. Funakoshi*[4] *and T. Irifune*[1]

[1] *Geodynamics Research Center, Ehime University, Ehime 790-8577, Japan*
[2] *Bayerisches Geoinstitut, University of Bayreuth, Bayreuth D-95440, Germany*
[3] *Earthquake Research Institute, University of Tokyo 113-0032, Japan*
[4] *Japan Synchrotron Research Institute, Hyogo 679-5198, Japan*

Technical development has been made for deformation experiments with a deformation-DIA (D-DIA) apparatus in order to study rheology of solid materials at pressures up to 18 GPa and high temperature. We optimized dimensions of anvil truncation, a pressure medium and gasket to achieve the deformation experiments at 18 GPa at relatively low press load (0.5 MN) to minimize damage of X-ray transparent second-stage anvils. Stress and strain of a sample were determined quantitatively by means of *in situ* X-ray radial diffraction and radiography, respectively, in conjunction with synchrotron radiation at BL04B1 beamline, SPring-8 [1]. We adopted low X-ray absorption materials (e.g. cubic BN anvils, graphite window in a $LaCrO_3$ heater) along an X-ray path to enable the *in situ* stress-strain measurements. Based on the developed technique, the deformation experiments on ringwoodite were carried out in uniaxial geometry at pressures of 17-18 GPa and temperatures of 1500-1700 K with strain rates of $3.38\text{-}5.56 \times 10^{-5}\ s^{-1}$ and strains up to 26.0 % (Fig. 1). In the present study, the pressure condition of the *in situ* stress-strain measurements in the D-DIA apparatus was successfully expanded from 14.5 GPa [2] to 18 GPa at temperatures of 1500 - 1700 K. The present technical improvements in the *in situ* stress-strain measurements with the D-DIA apparatus should greatly contribute to studies on rheology of deep Earth materials.

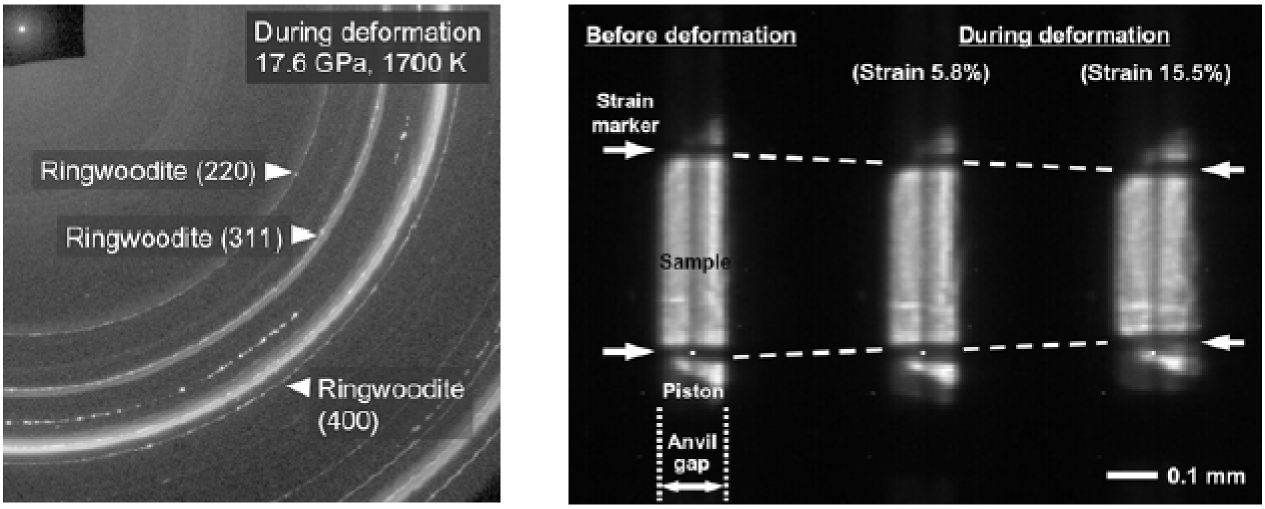


Figure 1: A representative X-ray diffraction pattern of ringwoodite collected at 17.6 GPa and 1700 K during the deformation (left) and X-ray radiographs during the deformation experiment at 18 GPa and 1500 K (right).

References

[1] Y. Nishihara et al, Phys. Earth Planet. Inter. **183**, 164-174 (2010).
[2] T. Kawazoe et al, Am. Mineral. **96**, 1665-1672 (2011).

* presenter email: takaaki.kawazoe@uni-bayreuth.de

Brillouin Scattering and X-ray Diffraction of Solid Argon to 65 GPa and 700 K: Shear Strength of Argon

H. Marquardt[1], S. Speziale[1], A. Gleason[2], S. Sinogeikin[3], I. Kantor[4] and V. B. Prakapenka[5]*

[1] *German Research Center for Geosciences (GFZ), Telegrafenberg, 14473 Potsdam*
[2] *Department of Geological & Environmental Sciences, Stanford University, CA 94305*
[3] *High Pressure Collaborative Access Team (HPCAT), Geophysical Laboratory, Carnegie Institution of Washington, Argonne, Illinois, 60439, USA*
[4] *European Synchrotron Radiation Facility, 38043 Grenoble, BP 220, France*
[5] *Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, USA*

The experimental study of noble gases provides a basis for the development and improvement of theoretical models [1-4]. Knowledge of the physical properties of argon at non-ambient conditions is also of significance in designing high-pressure experiments carried out in the diamond-anvil cell (DAC), where argon is commonly used as pressure-transmitting medium. Despite the longstanding interest in the high-pressure/high-temperature (HP/HT) elastic properties of argon, experiments at combined P/T were only performed to 500 K at 3.5 GPa [5]. Here, we present results of combined Brillouin scattering and synchrotron x-ray diffraction experiments on solid argon to 700 K and 65 GPa, performed in an externally heated diamond-anvil cell. From the measured acoustic velocities and densities, we derive the bulk elastic properties of solid argon up to 700 K and 65 GPa. Our HP-/HT-data show that the bulk modulus is almost insensitive to an increase of temperature (within the P-T-range of our study), whereas the shear modulus G measurably decreases with increasing temperature. We use our results to estimate the shear strength of argon at HP/HT, which we find to be 0.8 GPa at 65 GPa, substantially lower than found in a previous study. Increasing temperature to 700 K reduces the shear strength to 0.5 GPa at 65 GPa (Fig. 1). Based on our findings, argon might be a competitive candidate pressure-transmitting medium for HP/HT-experiments up to at least 65 GPa.

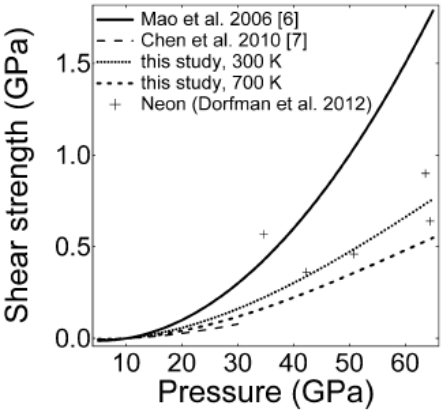


Figure 1: Estimated shear strength of argon at HP/HT

References

[1] M. Grimsditch, P. Loubeyre, and A. Polian, Phys. Rev. B **33**, 7192 (1986).
[2] E. Pechenik, I. Kelson, and G. Makov, Phys. Rev. B **78**, 134109 (2008).
[3] H. Shimizu, H. Tashiro, T. Kume, and S. Sasaki, Phys. Rev. Lett. **86**, 4568 (2001).
[4] T. Tsuchiya, and K. Kawamura, J. Chem. Phys. **117**, 5859 (2002).
[5] R. Jia, F. Li, M. Li, Q. Cui, et al., J. Chem. Phys. **129**, 154503 (2008).
[6] H.-k. Mao, J. Badro, J. Shu, R.J. Hemley, et al., J. Phys.: Condens. Matter **18**, S963 (2006).
[7] B. Chen, A.E. Gleason, J.Y. Yan, K.J. Koski, et al., Phys. Rev. B **81**, 144110 (2010).

* presenter email: hauke.marquardt@gfz-potsdam.de

Equations of state of metals from X-ray diffraction data at static pressures above 5 Mbar

L. Dubrovinsky[1], N. Dubrovinskaia[1], V. Prakapenka[2] and M. Hanfland[3]*

[1]*Bayreuth University, Germany*
[2]*GSECARS, APS, USA*
[3]*ESRF, France*

The impact of high-pressure studies on fundamental physics and chemistry, and especially on the Earth and planetary sciences, has been enormous. While experiments in diamond anvil cells (DACs) at pressures of ∼250 - 400 GPa are proven to be very difficult but possible, at higher static pressures any matter has not been investigated until very recently. We have developed a method of synthesis of balls and semi-balls (of 10 to 50 μm in diameter) made of nanodiamond (with individual nano-particles of linear dimensions below 30 nm) and used them as second-stage or indentor-type anvils in conventional DACs. In experiments on rhenium, osmium, gold, platinum, and tungsten we were able to generate pressures above 700 GPa and demonstrated crucial necessity of the ultra-high pressure measurements for accurate determination of the equation of state of materials at extreme conditions.

* Leonid.Dubrovinsky@uni-bayreuth.de

Time-resolved studies of phase transition dynamics in Bismuth and Krypton

J.-Y. Chen[1], H Cynn[1], J.T. Delitz[2], W.J. Evans[1], Zs. Jenei[1], Z. Konôpková[2], H.-P. Liermann[2], M.J. Lipp[1], W. Morgenroth[2] and C.S. Yoo[3]

[1]High Pressure Physics Group, Condensed Matter and Materials Division, Physical & Life Sciences, Lawrence Livermore National Laboratory. L-041, 7000 East Ave., 94650, Livermore, CA USA

[2]Extreme Conditions Beamline, PETRA III, Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany

[3]Chemistry Department, Washington State University. Pullman, WA

There is a wealth of unexplored physics in the dynamics of pressure-induced phase transitions. New diagnostic instruments and experimental platform are enabling us to increase the level of detail and sophistication beyond simply a transition pressure and the crystal structure of the phases. Time-resolved x- ray scattering measurements of transitions are enabling unprecedented studies of the dynamics of pressure- induced phase transitions. This includes the mechanics of the lattice transformation, nucleation, growth and the possibility of observing metastable phases. Many of these properties are also dependent on the compression rate. In this presentation we will discuss our use of the dynamic diamond anvil cell (dDAC) to study the dynamics of phase transitions undr vareied compression rates in simple metals, including krypton and bismuth. In particular, we will discuss our studies of the compression rate dependences of hcp versus fcc phases in krypton, and dynamics of host-guest lattices in solid phases of bismuth.

Portions of this work were performed under the auspices of the U.S. DOE by LNL under Contract DE-AC52-07NA27344. funded by the LLNL LDRD program under project tracking code 11-ERD-046. Portions of this research were carried out at Petra-III at DESY, a member of the Helmholtz Association (HGF). We thank the experimental support team lead by H.-P. Liermann for assistance in using the Extreme Conditions Beamline (ECB) P02.2.

* wjevans@llnl.gov

Melting Studies of iron from *in-situ* XRD at megabar pressures with short laser pulses

Z. Konôpková[1], A. Goncharov[2] and H-P. Liermann[1]*

[1]DESY Photon Science, Notkestr. 85, 22607 Hamburg, Germany
[2]Geophysical Laboratory, Carnegie Institution of Washington, 5251 Broad Branch Road NW Washington D.C., 200015

Recent improvements and growing technical capabilities of synchrotron sources enable us to investigate matter on shorter time scales, partially bypassing problems with sample contaminations and reaching increasingly higher temperatures at higher pressures.

High quality x-ray diffraction data are nowadays feasible to obtain in several tens of milliseconds thanks to the high photon flux and efficient large area detectors. *In-situ* XRD experiments were conducted at the Extreme Conditions Beamline, P02.2, PETRAIII in Hamburg. The short laser pulses keep the heating time at minimum, which proves to be less destructive to the diamonds and the sample.

Measuring diffraction of iron at Earth's core conditions is technically difficult to achieve, which leads to contradictory results. We have followed the above strategy to study iron at over megabar pressures using 200-500 ms laser pulses with synchronized x-ray diffraction and pyrometric temperature measurements. Onset of melting has been determined when the diffuse scattering signal from the hot sample first appeared in the x-ray diffraction patterns. Further studies on melting and phase transition will be conducted on iron and other metals in future.

* zuzana.konopkova@desy.de

Novel high-pressure Fe_2O_3 polymorph

E. Bykova[*1,2], *M. Bykov*[2], *V. Prakapenka*[3], *Z. Konôpková*[4], *H.-P. Liermann*[4], *N. Dubrovinskaia*[2] *and L. Dubrovinsky*[1]

[1]*Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany*
[2]*Laboratory of Crystallography / Material Physics and Technology at Extreme Conditions, University of Bayreuth, Bayreuth, Germany*
[3]*Center for Advanced Radiation Sources, Argonne National Laboratory, Argonne, USA*
[4]*Deutsches Elektronen-Synchrotron, Hamburg, Germany*

We report a novel high-pressure polymorph of iron sesquioxide, m-Fe_2O_3, revealed by means of single crystal synchrotron X-ray diffraction. On compression of a single crystal of hematite, α-Fe_2O_3, in a diamond anvil cell, the transition occurs at pressure of about 54 GPa and results in ~10 % volume reduction. The crystal structure of the new phase was solved by the direct method (monoclinic space group $P2_1/n$, a= 4.588(3), b = 4.945(2), c = 6.679(7) Å and β = 91.31(9)°) and refined. It belongs to the cryolite double-perovskite structure type and consists of corner-linked FeO_6 octahedra and FeO_6 trigonal prisms filling the free space between the octahedra (see Fig. 1). Upon compression up to ~71 GPa at ambient temperature no further phase transitions were observed. Laser heating to ~2100±100 K promotes a transition to *Cmcm* $CaIrO_3$-type (post-perovskite, PPv) phase. On decompression the PPv-Fe_2O_3 phase fully transforms back to hematite between ~25 and 15 GPa.

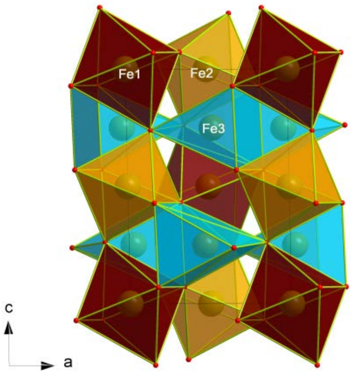


Figure 1: High-pressure polymorph of Fe_2O_3 with cryolite double-perovskite structure type.

* knilav@gmail.com

Newly Developed Micro X-ray Focusing Optics for High-pressure X-ray Diffraction at SPring-8

Y. Ohishi[1], N.Hirao[1], T. Matsuoka[2], K. Shimizu[2] and K. Hirose[3]*

[1]*Japan Synchrotron Radiation Research Institute (JASRI/SPring-8), Sayo, Hyogo 679-5198, Japan.*

[2]*Center of Quantum Science and Technology under Extreme Condition, Osaka University, Toyonaka, Osaka 560-8531, Japan.*

[3]*Department of Earth and Planetary Science, Tokyo Institute of Technology, Meguro, Tokyo 152-8551, Japan.*

Recently, at SPring-8, a combination of a laser-heated diamond anvil cell (DAC) technique and highly intense monochromatic x-ray beam allows us to perform in-situ x-ray diffraction (XRD) experiments under high-pressure of hundreds GPa and high-temperature of thousands Kelvin, corresponding to the condition of the center of the Earth. In order to enhance more precise analysis, such as partial grains/elements distribution, melting, solution and/or chemical reactions in the sample chamber of DAC, as well as to collect high-quality XRD data on materials subjected to extreme pressures over 300 GPa, we are committed to upgrading of x-ray micro-beam technique. However, high-flux hard x-ray micron-size beam generation for XRD is particularly challenging, because the third-generation synchrotron radiation undulator x-ray source has fundamentally a few hundreds micron size in horizontal. Here we report unique x-ray focusing optics by using compound x-ray refractive lens (CRL) at high-pressure XRD beamline BL10XU of SPring-8.

As usual, K-B mirror is an optical device for x-ray focusing, but we consider that CRL is more versatile for high-pressure facility. The CRL offers many advantages [1, 2]: capability of focusing and collimating x-rays in the high-energy range of 20–60 keV, good efficiency, compactness, easy operation, and especially in-line focusing element that allows one to combine XRD and other equipment, for example the laser-heating optics. We have installed the newly developed x-ray focusing optical system consisting of two CRL devices and a pinhole in tandem. The CRLs are sets of planar cross-lenses with a quasi-parabolic profile for focusing in two directions, and are fabricated from SU-8 polymer by deep x-ray lithography at the IMT in Germany [3]. The set of the upstream lens and the pinhole as a virtual source are used for generation of homogeneously divergent beam. The downstream lens, which is placed between a virtual source and a focal point (sample position), is utilized for focusing the x-ray towards the micron size. The focused beam size is defined by the relationship between a pinhole diameter and the ratio of source-lens versus lens-focal point distances.

We obtained the successful result, as we had designed, for focusing down to 2.4 microns in vertical and 2.1 microns in horizontal under the following conditions: 30 keV x-ray, 10-micron pinhole in diameter and 11:1 ratio of source-lens: lens-sample distances. Using the focusing optical system, we checked that clearly districted XRD profiles from the sample of several microns size and/or micro-structures such as electrodes for electrical resistance measurement, micro-anvils settled in the sample chamber of DAC and so on, were observed. We consider that sub-micron beam focusing is potentially achievable, and will be a key-technique for a probe of a scanning XRD microscope.

References

[1] A. Snigirev, V. Kohn, I. Snigireva, and B. Lengeler, Nature **384**, 49–51 (1996).

[2] Y. Ohishi, A. Q. R. Baron, M. Ishii, T. Ishikawa, O. Shimomura, Nucl. Instrum. Methods A **467–468**, 962–965 (2001).

[3] V. Nazmov, E. Reznikova, A. Somogyi, J. Mohr, and V. Saile, Proc. SPIE **5539**, 235–243 (2004).

---

* presenter email: ohishi@spring8.or.jp

New perspectives for dynamic high-pressure research: the high-energy density instrument at the European XFEL

K. Appel[1], M. Nakatsutsumi[1] and Th. Tschentscher[1]*

[1]*European XFEL GmbH, Notkestrasse 85, 22607 Hamburg, Germany*

Free-electron laser facilities provide new applications in the field of dynamic high-pressure research. The European X-ray Free Electron Laser (XFEL) [1] will start user operation in 2016 and will provide photon energies of up to 25 keV. With a photon flux of ca 10^{12} photons/pulse, a pulse duration of 2 – 100 fs and a repetition rate of up to 4,5 MHz, this facility will provide unique opportunities to study fast processes such as dynamic compression in solids.

The high-energy density instrument (HED) [2] is one of the six baseline experiments at the European XFEL and now has entered the technical design phase. For this instrument, it is planned to integrate a high-energy nanosecond pulse duration laser system to enable studies of materials at extremely high pressures. Ramp-compression [3-5] by nanosecond shaped laser pulses will enable to extend the range of high-pressure conditions accessible at hard X-ray sources up to 10 Mbar at comparatively low temperatures. A suitable optical laser system with repetition rates of 0.1 and 10 Hz was recently proposed by an international consortium. Probing of the laser generated excited states will be performed with the high energy X-ray free electron laser (FEL). In the energy range between 5 and 25 keV, it will be possible to study samples by X-ray diffraction, X-ray spectroscopy and imaging techniques. Due to the high excitation energies, diffraction patterns will have excellent quality and a wide range of elements ($Z > 22$) will be accessible by X-ray absorption spectroscopy. The high intensity and time structure will enable time-resolved studies of the samples generated during dynamic compression. In addition, the high brilliance and coherence of the FEL radiation will enable spatially resolved studies.

In this contribution, the X-ray instrumentation and foreseen X-ray techniques at HED will be presented as well as prototype experiments in the field of dynamic high-pressure research as proposed during a recent user consortium meeting for this instrument. These include dynamic compression and shock compression experiments as well as experiments in the dynamically driven diamond anvil cell (dDAC) and laser heated diamond anvil cells.

References

[1] for detailed information about European XFEL see www.xfel.eu.

[2] M. Nakatsutsumi, and Th. Tschentscher, Conceptual Design Report: Scientific instrument HED, http://www.xfel.eu/documents/technical_documents/, (2013).

[3] J.-P. Davis, J. Appl. Phys. **99**, 103512 (2006).

[4] R. Smith et al., Phys. Rev. Lett. **102**, 075503 (2009).

[5] A. Higginbothom et al., Phys. Rev. **B 85**, 024112 (2012).

* karen.appel@xfel.eu

Proton dynamics in Shewanella oneidensis at high pressure

F. Foglia[1], R. Hazael[1], G. Simeoni[2], M.-S. Appavou[2], T. Forsyth[3], M. Moulin[3], M. Haertlein[3], I. Daniel[4], F. Meersman[1,4] and P.F. McMillan[1]*

[1]Dept of Chemistry, University College London, UK
[2]Jülich Center for Neutron Science, FRMII, Garching bei Munich, Germany
[3]Deuteration Lab, ILL, Grenoble, France
[3]Dept of Earth Sciences, Université Claude Bernard Lyon 1, France
[4]Rousselot-Expertise Center, Gent, Belgium

Studies of the Earth's deep biosphere have revealed a remarkable array of bacteria and other organisms existing down to at least 10 kilometres below the ocean as well as several kilometres below the rocky seafloor and continental subsurface. The pressures attained reach at least 100 MPa. In laboratory experiments live organisms are shown to survive to even higher pressures, even into the GigaPascal range in some cases. One of the fundamental questions currently under investigation is how cells function under extremely high pressure conditions. Water is a key component of all cells and how it behaves and is transported inside the cells and across the cell membrane is fundamental to understanding biological function. Quasi-elastic neutron scattering is a powerful technique that gives detailed information on dynamic processes involving protonated species especially including water that can be "free" or confined within nanoscale environments. The diffusional vs confined motions can be identified by considering their momentum and energy transfer ranges. Isotopic contrast experiments using D- vs H-substituted molecules can be used to give precise information on the location of the proton dynamics taking place. Here we investigate proton dynamics including the kinetics of water diffusion under pressures up to 200 MPa for a model microbe system *Shewanella oneidensis MR-1*.

* p.f.mcmillan@ucl.ac.uk

Crystallographic structure of neuroglobin under high hydrostatic pressure. A tribute to Roger Fourme

Nathalie Colloc'h[1*], Eric Girard[2], Anne-Claire Dhaussy[3], Giovanna Avella[4],
Sophie Sacquin-Mora [5], Thierry Prangé[6], Beatrice Vallone[4], Roger Fourme[7]

1. ISTCT UMR 6301 CNRS –université de Caen, centre Cyceron, Caen, France
2. IBS, UMR 5075 CEA-CNRS-UJF, Grenoble, France
3. CRISTMAT, ENSICAEN, Caen, France
4. Department of Biochemical Sciences, University of Rome, La Sapienza, Rome, Italy
5. LBT-IBPC, UPR CNRS 9080, Paris, France
6. LCRB UMR 8015 CNRS – université Paris Descartes, Paris
7. Synchrotron SOLEIL, Gif-sur-Yvette, France

Neuroglobin (Ngb) is a heme protein belonging to the globin family which is expressed in neurons. The structure of murine Ngb has been determined for both the deoxy and carbonmonoxy forms, revealing the presence of a very large internal cavity which is functional, and involved in a structural transition that takes place upon ligand binding. The internal cavity and its plasticity are key features to Ngb function (1). Since pressure promotes high energy mechanistic conformers (2-5), we expect by determining the structure of Ngb under pressure to reach high-energy sub-states of Ngb.
Diffraction data have been collected on murine Ngb crystals submitted to high pressure in a diamond anvil cell on CRISTAL beamline at the synchrotron SOLEIL. Full data collections have been performed at ambient pressure, at 2700 bar and at 3150 bar, at a resolution around 2Å, which allow precise comparison between the three structures.
The most striking features between the three structures is the large diminution of the volume of the internal cavity behind the heme, with a disruption of the connection between the back of the cavity and the heme. There is also a shift of a helix and a loop toward the heme in both high pressure structures. Residues close to the heme are destabilized by pressure (B-factor increased by pressure) while residues on the opposite side are stabilized by pressure (B-factors decreased by pressure).

Roger Fourme, deceased in December 2012, was a pioneer in many domains, like in phase determination using MAD or xenon isomorphous derivatives. He was also a pioneer in high pressure macromolecular crystallography, developing for this purpose specially designed diamond-anvil cells with large aperture (2). He was convinced and convinced everybody that pressure is a wonderful tool to catch high-energy substates to allow to study conformational landscape (3-5).

References

[1] (a) B. Vallone, K. Nienhaus,M. Brunori, G.U. Nienhaus, *Proteins*, **56**, 85-92 (2004);
(b) B. Vallone , K. Nienhaus, A. Matthes, M. Brunori, G.U. Nienhaus, *Proc. Natl. Acad. Sci. USA*, **101**, 17351-17356 (2004)
[2] E. Girard, A.C. Dhaussy, B. Couzinet, J.C. Chervin, M. Mezouar, R. kahn, I. Ascone, R. Fourme, Applied Cryst., **40**, 912-918, (2007)
[3] R. Fourme, E. Girard, R. Kahn, A.C. Dhaussy, I. Ascone, *Ann. Rev. Biophys*., **38**, 153-171 (2009)
[4] E. Girard, S. Marchal, J. Perez, S. Finet, R. Kahn, R. Fourme, G. Marassio, A.C. Dhaussy, T. Prangé, M. Giffard, F. Dulin, F. Bonneté, R. Lange, J.H. Abraini, M. Mezouar, N. Colloc'h, *Biophys. J.*, **98**, 2365-2373 2010
[5] R. Fourme, E. Girard, K. Akasaka, Curr. Opin. Struct. Biol., **22**, 636-642, (2012)

*Presenter email : colloch@cyceron.fr

The Effect of Water on an Imidazolium Based Ionic Liquid

S. Saouane and F. P. A. Fabbiani*

GZG, Abteilung Kristallographie, Georg-August-Universität Göttingen, Göttingen, Germany

The sphere of interest in room-temperature ionic liquids (RTILs) has been steadily growing for the past three decades. Indeed, through the virtually infinite mix and match combinations of cations and anions, a broad and tunable spectrum of physical and chemical properties is accessible [1]. RTILs are used in a variety of applications. With their negligible vapour pressure, RTILs are considered to be novel and environmentally sustainable crystallisation media for active pharmaceutical ingredients [1-3]. In this context, imidazolium based RTILs are common solvents. Their liquid structure has been the subject of several experimental and computational investigations; however, due to the challenges of crystal growth, their solid-state structure and polymorphism have been less widely investigated.

We have recently reported on [4] the structures of the elusive low-temperature and high-pressure polymorphs of the RTIL 1-butyl-3-methylimidazolium hexafluorophosphate $[C_4mim][PF_6]$. We have extended our investigations to related systems; in this contribution, we focus on hydrate formation of the hygroscopic and water miscible 1-decyl-3-methylimidazolium chloride $[C_{10}mim][Cl]$. Water, which for RTILs is usually considered to be an undesirable impurity [5-7], is the main driving force for the crystallisation of the compound. At low temperature, the gradual incorporation of atmospheric water drastically affects crystal formation. The application of high-pressure crystallisation techniques favours a controlled environment and facilitates the elucidation of up to three hydration states of $[C_{10}mim][Cl]$ by single-crystal X-ray diffraction.

References

[1] P. D. McCrary, P. A. Beasley, G. Gurau, A. Narita, P. S. Barber, O. A. Cojocaru and R. D. Rogers, New J. Chem. (2013).

[2] H. Mizuuchi, V. Jaitely, S.Murdan, and A. T. Florence, Eur. J. Pharm. Sci. **33**, 326–331 (2008).

[3] J-H. A and W-S. Kim, Cryst. Growth Des. **13**, 31–39 (2013).

[4] S. Saouane, S. E. Norman, C. Hardacre and F. P. A. Fabbiani, Chem. Sci. **4**, 1270-1280 (2013).

[5] Y. Kohno and H. Ohno, Chem. Commun. **48**, 7119–30 (2012).

[6] K. R. Seddon, A. Stark and M-J. Torres, Pure Appl. Chem. **72**, 2275–2287 (2000).

[7] T. Takamuku, Y. Kyoshoin, T. Shimomura, S. Kittaka, and T. Yamaguchi, J. Phys. Chem. B **113**, 10817–24 (2009).

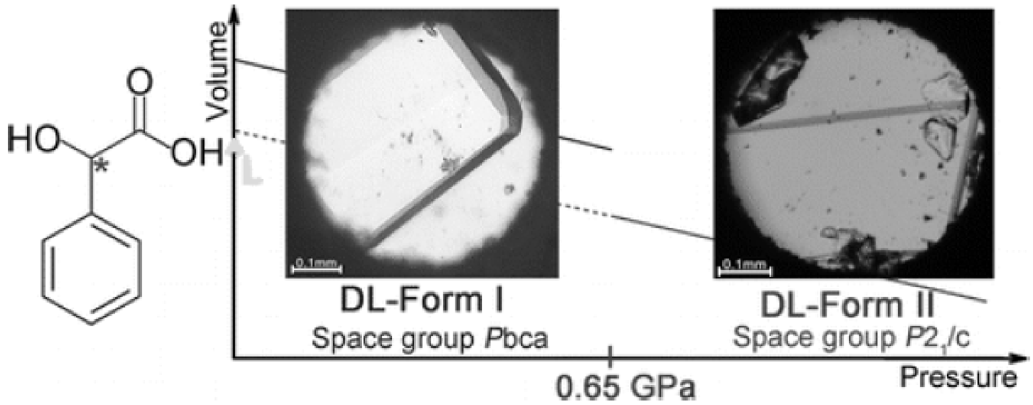
* ssaouan@gwdg.de

Pressure effect on D,L-mandelic acid racemate crystallization

Weizhao Cai[1], *Jędrzej Marciniak**[1], *Michał Andrzejewski**[1], *Andrzej Katrusiak*[1]

[1]*Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland*

Mandelic acid, $C_6H_5CHOHCOOH$, (MA) is one of frequent exempts from the Wallach's rule, as its racemate DL-MA is less dense than the enantiomers. This relation appears to be unfavorable for the racemate stability at high pressure; however, the racemate remains more stable than the conglomerate of enantiomers up to 1.36 GPa at least. The isochoric crystallization of DL-MA yields its orthorhombic form I, space group *Pbca*, and above 0.65 GPa, another centrosymmetric polymorph of monoclinic DL-MA form II, space group $P2_1/c$, becomes stable. Their structures have been determined by X-ray diffraction of the single crystals in situ grown in a diamond-anvil cell up to 1.36 GPa. Lattice-energy calculations by the semiempirical PIXEL method demonstrate that DL-MA form II is more stable than DL-MA form I, and both of these racemates are more stable than their enantiomer counterpart L-MA [1].



Acknowledgements:

This work was supported by the Foundation for Polish Science, research project TEAM 2009-4/6.

References:

[1] W. Cai, J. Marciniak, M. Andrzejewski, and A. Katrusiak, *J. Phys. Chem. C*, **117** (14), 7279–7285, 2013.

*jedrzej.marcin@gmail.com, mand@amu.edu.pl

Conformationally Assisted Compression in Methyl Benzoate

Weizhao Cai and Andrzej Katrusiak*

Faculty of Chemistry, Adam Mickiewicz Universityi, Umultowska 89b, 61-614 Poznań, Poland.

Methyl benzoate (MB) is widely applied in perfumery and pesticides industries. It is traditionally synthesized via Fischer esterification of benzoic acid with methanol and sulphuric acid as the catalysts. MB freezes at 261 K and its crystal structure at 100 K is orthorhombic, space group *P*bca, with the phenyl and ester moieties twisted by over 23° about the C1−C7 bond from the stable planar conformation (Figure 1a) [1]. The substantially non-planar conformation was associated with the effects of crystal packing. By using *in situ* isochoric crystallization in a diamond anvil-cell (DAC), we obtained MB phase α and its new phase β either from the pure substance or from benzoic acid dissolved in methanol after the esterification [2].

MB freezes isothermally at 296 K above 0.35 GPa in phase α, with the molecules in energetically unfavorable twisted conformation. Phase α exhibits negative linear compressibility along the *b* axis, with the magnitude of −16.5(3) TPa^{-1}. At 0.54 GPa, phase α undergoes a most unusual isostructural transition (same space group *P*bca, with very similar unit-cell dimensions) to a new β phase with the molecular-volume is compressed by −1.5 cm^3 mol^{-1} only along [*x*], while crystal exhibits negative area compressibility along the CH$\cdots$O bonded sheets perpendicular to [*x*]. The molecules in β phase assume the planar conformation, by 2.80 kJ mol^{-1} more stable than the twisted conformation at ambient-pressure (Figure 1b). The transition also involving the changes in CH$\cdots$O bonds pattern and shifts of molecular layers by *c*/6 along [*z*]. To our knowledge, it is the only reported compound with the molecules is in the unfavorable conformation in low-pressure phase, and in the favored conformation in high-pressure phase. This unusual direction of conformational changes has been explained by intermolecular interactions and crystal packing forces, significantly more energetic than the conformational change. The combination of strained molecules and exceptional compressibility can be applied for shock-absorbing and shock-damping buffers, as well as in energy-converting materials.

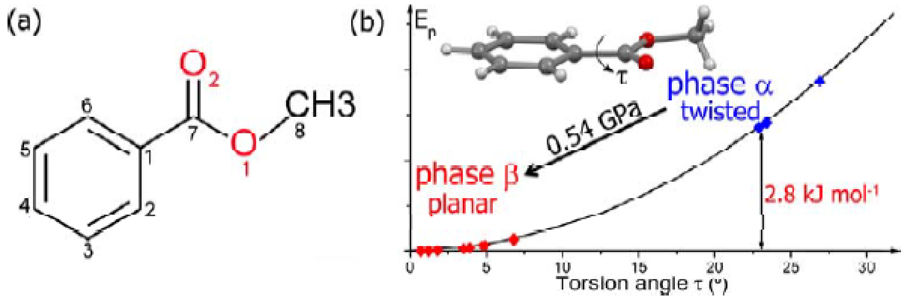


Figure 1: (a) The molecular structure of methyl benzoate (MB) and its atomic labels; (b) potential energy E_p curve of MB as a function of torsion angle τ. The potential energy of conformers in phases α and β are plotted on this curve with full red triangles and full blue squares.

References

[1] (a) A. A. Yakovenko, J. H. Gallegos, M. Y. Antipin, A. Masunov and T. V. Timofeeva, *Cryst. Growth Des.*, **11**, 3964 (2011); (b) N. Sundaraganesan and B. D. Joshua, *Spectrochim. Acta, Part A.*, 2007, 771.

[2] W. Cai and A. Katrusiak, *CrystEngComm*, **14**, 4420 (2012).

* Presenter email: wzhcai@gmail.com

Density Functional Theory: Applications to High-Pressure Crystallography

*M. Mattesini**[1,2]

[1]*Departamento de Física de la Tierra, Astronomía y Astrofísica I, Universidad Complutense de Madrid, Madrid E-28040, Spain*

[2]*Instituto de Geociencias (UCM-CSIC), Facultad de Ciencias Físicas, Plaza de Ciencias 1, Madrid E-28040, Spain*

Density functional theory (DFT) methods are representing an important computational tool for the high-pressure crystallography. In this presentation, I'll first review some key applications of DFT spanning from the general high-pressure phase stability problem, the search for potential light absorbers in solar-energy conversion (high-pressure cubic TiO_2 polymorphs), and the case of intermediate valence *f*-electron systems (Yb metal under pressure). I'll close the paper by disclosing a specific case study: the high-pressure behaviour of Ca and BaSn phases. Theoretical calculations [1] of the electron-localization function (ELF) show that, at the volumes of the two CaO phases (rocksalt and CsCl type), the parent Ca structures (fcc: face-centred cubic and sc: simple cubic, respectively) exhibit charge concentration zones which coincide with the positions occupied by the O atoms in their oxides. Similar features, also observed for the pairs Ca/CaF_2 and BaSn/$BaSnO_3$, are supported by recent high-pressure experiments as well as ELF calculations, carried out on elemental K. At very high pressures, the elemental K adopts the *h*P4 structure, topologically identical to that of the K atoms in high-pressure K_2S and high-temperature α-K_2SO_4. Moreover, the ELF for the *h*P4 structure shows charge concentration (~ 2 electrons) at the sites occupied by the S atoms in the high-pressure K_2S phase. All these features confirm the oxidation/high-pressure equivalence as well as the prediction of how cation arrays should be metastable phases of the parent metals. For the first time to our knowledge, the structure type, dimension and topology of several oxides and fluorides (CaO, CaF_2 and $BaSnO_3$) are explained in univocal physical terms.

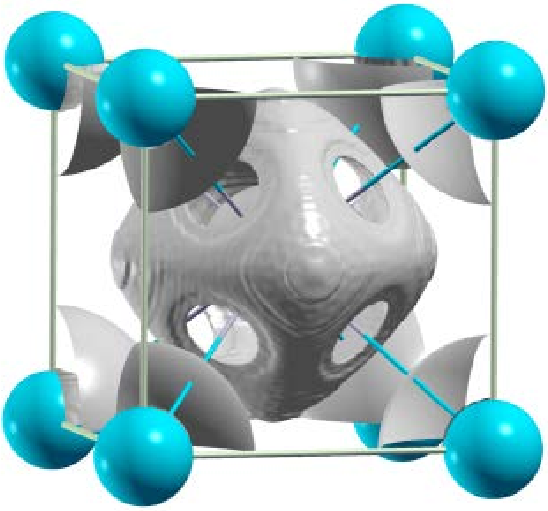


Figure 1: ELF with an isovalue of 0.50 for the BaSn structure with a lattice constant of 4.070 **Å**. Note the formation of a free-electron density at the oxygen positions of the $BaSnO_3$ perovskite phase. Blue spheres represent Ba atoms. The Sn atom is centring the cell and is hidden by the octahedral ELF.

References

[1] A. Vegas, M. Mattesini, Acta Cryst. B **66**, 338 (2010).

* mmattesi@ucm.es

Melting Curve and Atomic Diffusion in Solid Molecular Hydrogen at Extreme Pressures

*A. B. Belonoshko[1], M. Ramzan[*2], H.-K. Mao[3] and R. Ahuja[2,4]*

[1]*Condensed Matter Theory, Department of Theoretical Physics, AlbaNova University Center, KTH Royal Institute of Technology, SE-106 91 Stockholm, Sweden*
[2]*Condensed Matter Theory Group, Department of Physics and Astronomy, Box 516, Uppsala University, SE-751 20, Uppsala, Sweden*
[3]*Geophysical Laboratory, Carnegie Institution of Washington, Washington DC 20015, USA*
[4]*Applied Materials Physics, Department of Materials Science and Engineering, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden*

We have performed ab initio molecular dynamics (AIMD) simulations of the C2c and Cmca-12 phases of hydrogen at extreme pressures, starting from 210 GPa and proceeding upto 350 GPa. These phases were already demonstrated by Pickard *et al.*[1], to be stable at 0 K and pressures above 200 GPa. However (to the best of our knowledge), systematic studies of temperature impact on the properties of these phases have not been performed so far. For the complete understanding of these phases and filling up this gap, we have studied these phases by simulating the ab initio molecular dynamics calculations as implemented in VASP code. We observed that on temperature increase diffusion sets in the Cmca-12 phase, being absent in C2c phase. We explored the mechanism of diffusion and computed melting curve of hydrogen at extreme pressures. Our results suggest that the recent experiments by Eremets *et al.*[2], claiming conductive hydrogen at the pressure around 260 GPa and ambient temperature might be explained by the diffusion. The diffusion might also be the reason for the difference in Raman spectra obtained in recent experiments.

References

[1] C. J. Pickard, and R. J. Needs, Nature Physics **3**, 473 (2007).
[2] M. I. Eremets, and I. A. Troyan, Nature Materials **10**, 927 (2011).

* ramzanrao@gmail.com

Creation of bulk nanostructured ultra-hard materials by extreme conditions

Y. Le Godec[1], O.O. Kurakevych[1] and V.L. Solozhenko[2]*

[1]*IMPMC-CNRS, Université P&M Curie, 75005 Paris, France*
[2]*LSPM-CNRS, Université Paris Nord, 93430 Villetaneuse, France*

Superhard materials are widely employed in industry for production of cutting and polishing tools, as well as anti-abrasive coatings. The synthesis of man-made superhard phases started from the early 1950s, as soon as the development of high-pressure techniques allowed reaching the pressures necessary for diamond synthesis. However, the experimental and theoretical design of novel superhard materials still remains a great challenge to materials scientists.

To this aim, experimental observations and simulations suggest that for many polycrystalline materials there is an optimal grain size (usually in the range of dozens of nanometers) which results in a significant, up to 50–70%, increase of hardness of the material in comparison with that of its coarse grain counterpart. This increase in hardness is known as the Hall–Petch effect. That's why the synthesis of bulk nanostructured materials remains the least-explored but challenging domain that allows combining of desired physical, chemical, and mechanical properties and gives rise to nanoelectronics, nanomechanics, bandgap engineering, etc.

In this talk, I will show that the use of very high pressures and temperatures combined with the *in situ* probe by synchrotron X-ray diffraction is the methodological key to control the composition and microstructure of new materials in the B-C-N system.

* yann.legodec@impmc.upmc.fr

The local view of materials under pressure @ ISIS and Diamond

Matt Tucker *[1,2]

[1] *Diamond Light Source, Harwell Campus, Didcot, Oxfordshire, OX11 0DE, U.K*

[2] *ISIS facility, Harwell Campus, Didcot, Oxfordshire, OX11 0QX, U.K*

Increasingly it is being recognised that the properties of many important materials are governed by their local structure. For this reason, studies using total scattering (*aka* the PDF method) are becoming increasingly popular and necessary. In these measurements, the diffraction data are corrected onto an absolute scale and then both the Bragg and diffuse scattering are carefully analysed. The accurate background characterisation required for these measurements make them fairly complicated at ambient pressure and therefore extremely complicated at high pressure. However, the structural detail available makes the increased effort worthwhile, and indeed where the long range average structure is lost during pressurisation, there is no comparable alternative.

Here I will introduce the existing and future facilities available, at the ISIS neutron spallation source and the Diamond x-ray synchrotron, to study the local structure of materials under high pressure and those recovered from high pressure. I will also describe the experimental and computational developments that have been necessary to obtain total scattering at high pressure.

Finally, I will illustrate the use of total scattering by presenting a neutron and x-ray study of the pressure induced amorphisation of ZrW_2O_8, a negative thermal expansion material. This study started with a neutron and x-ray total scattering investigation of samples recovered from high pressure. The data was analysed using the RMCProfile[1] program to produce an atomistic model that is consistent with all the data available. This model gives an intriguing picture of the amorphisation process and the structure of the final material. Following this, an *in situ* x-ray total scattering measurements were carried out to understand the structure at pressure and how it develops.

References

[1] RMCProfile: reverse Monte Carlo for polycrystalline materials M G Tucker, D A Keen, M T Dove, A L Goodwin, Q Hui J. Phys.-Condes. Matter **19** 335218 (2007) – also more information and the program available at www.rmcprofile.org.

* matt.tucker@diamond.ac.uk

High-pressure behavior of unconventional spin-Peierls compounds TiOCl and $TiPO_4$

M. Bykov[1], E. Bykova[1,2], L. Dubrovinsky[2], H.-P. Liermann[3], M. Hanfland[4], R.K. Kremer[5], and S. van Smaalen[1]*

[1]*Laboratory of Crystallography, University of Bayreuth, Bayreuth, Germany*
[2]*Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany*
[3]*Photon Sciences, FS-PE, DESY, Hamburg, Germany*
[4]*ESRF, Grenoble, France*
[5]*Max Planck Institute for Solid State Research, Stuttgart, Germany*

The complex interplay between spin, charge, orbital, and lattice degrees of freedom has made low-dimensional quantum spin magnets with strong antiferromagnetic (AF) spin-exchange coupling prime candidates for studying unusual magnetic phenomena. A progressive spin-lattice dimerization in one-dimensional AF Heisenberg chains, which occurs below a critical temperature and induces a singlet ground state with a magnetic gap, is commonly referred to as spin-Peierls (SP) transition. Recently, the compounds TiOX (X = Cl, Br) and $TiPO_4$ have been intensively investigated due to their unconventional behavior [1, 2]. Unlike standard SP systems, TiOX and $TiPO_4$ showed two successive phase transitions at remarkably high temperatures. The SP transition temperature is related to the direct exchange interactions between Ti ions, which increases strongly with decreasing the distance between the Ti ions, and therefore is very sensitive to the applied hydrostatic pressure. Recent powder X-ray diffraction under pressure combined with *ab initio* calculations showed that the application of high-pressure enhances the formation of the dimerized phase at room temperature in the vicinity of 15 GPa [3]. However, our studies of isostructural *M*OCl (*M* = Cr, Fe) showed that structural phase transitions take place in the same pressure region, and are unrelated to the transition metal atom and to electronic or magnetic effects. Thus, the phase diagram of TiOCl may be complicated due to the nontrivial coupling of several mechanisms. That is indirectly suggested by a number of discrepancies between the interpretations of the powder X-ray diffraction data from different sources [3, 4]. On contrary, $TiPO_4$ is an excellent candidate for studying a pure pressure-induced SP phase transition, while it is separated from possible structural phase transitions on the pressure scale.

We have performed pressure-dependent single-crystal X-ray diffraction of TiOCl and $TiPO_4$ loaded into diamond anvil cells. The phase transition in $TiPO_4$ towards a dimerized phase was detected already at 7 GPa. This phase is analogous to the SP phase at low temperatures, and it is stable up to 45 GPa, whereupon it transforms to denser high-pressure phases. In case of TiOCl we have shown that structural phase transition similar to those of FeOCl and CrOCl closely follows the incommensurate phase where SP dimerization is frustrated by the interchain elastic interactions, while the pure SP phase was not detected. In this contribution we will present the detailed discussion of the sequence of the phase transitions, similarities and differences of phase diagrams of TiOCl and $TiPO_4$ and discrepancies between predicted and observed phases. The treatment of incomplete high-pressure data for the analysis of high-pressure superstructures with the use of the superspace formalism will be discussed.

References

[1] A. Seidel *et al.*, Phys.Rev. B **6**7, 020405(R) (2003).
[2] J.M. Law *et al.*, Phys. Rev. B **83**, 180414(R) (2011).
[3] S. Blanco-Canosa *et al.*, Phys. Rev. Lett. **102**, 056406 (2009).
[4] J. Ebad-Allah *et al.*, Phys. Rev. B **82**, 134117 (2010).

* maxim.bykov@uni-bayreuth.de

Pressure-Temperature Phase Diagram of $LuFe_2O_4$

J. Rouquette[1], J. Haines[1], M. Poienar[1], Ph. Papet[1], J. Bourgeois[2,3],
F. Damay[3], C. Martin[2]

[1]Institut Charles Gerhardt, UMR CNRS 5253, Université Montpellier II, Place Eugène Bataillon, 34095 MONTPELLIER CEDEX 5, France

[2]Laboratoire CRISMAT, CNRS UMR 6508, 6 bvd Maréchal Juin, 14050 CAEN CEDEX, France

[3]Laboratoire Léon Brillouin, CEA-CNRS UMR 12, 91191 GIF-SUR-YVETTE CEDEX, France

Recently, owing to their great technological and fundamental importance, multiferroic materials which are simultaneously ferroelectric and magnetic have attracted particular interest. Among them, charge ordered transition metal oxides in which the electronic ferroelectricity is determined by the charge ordering constitute a special class and $LuFe_2O_4$ is often cited as the prototype. $LuFe_2O_4$ crystallizes at room temperature in the *R-3m* space group and exhibits a layered structure (2D), described as the 1:1 stacking along the *c* axis of $[LuO_2]$ and $[Fe_2O_4]$ bilayers. The average iron valence in this compound is +2.5 and the Fe^{2+}/Fe^{3+} charge ordering (CO) that occurs at T_{CO} 330K induces ferroelectricity, with a quite large value of the ferroelectric polarization, *i.e.* about 26 $\mu C/cm^{-2}$ [1]. The pyroelectric signal shows an unusual step around 250 K, which is very close to the spin ordering temperature of 240K [2]. The CO state and the magnetic behaviour of $LuFe_2O_4$ are rather complex and still controversial in the literature.

In this study, the crystal structure of a polycrystalline sample of $LuFe_2O_4$ was investigated by synchrotron X-ray diffraction, neutron diffraction, resistivity measurements and X-ray absorption Spectroscopy. The Synchrotron X-ray diffraction data at 300 K as a function of pressure shows an irreversible structural transition to a high-pressure phase at ~18 GPa, which is recoverable at atmospheric pressure in agreement with our previous report [3]. This transition pressure decreases at high temperature (~13.5 GPa at 373 K) whereas it occurs at about 22 GPa at 50 K**.** The high pressure form of $LuFe_2O_4$ exhibits a new antiferromagnetic ordering ($T_N \approx 400K$), which makes this recovered compound a multiferroic (magnetic-dielectric) material at ambient conditions.

* presenter email: Jerome.Rouquette@um2.fr

References

[1] N. Ikeda, H. Ohsumi, K. Ohwada, K. Ishii, T. Inami, K. Kakurai, Y. Murakami, K. Yoshii, S. Mori, Y. Horibe, H. Kito, Nature, **436,** 1136 (2005).
[2] J. Iida, M. Tanaka, Y. Nakagawa, S. Funahashi, N. Kimizuka, S. Takekawa, J. Phys. Soc. Jpn., **62,** 1723 (1993).
[3] J. Rouquette, J. Haines, A. Al-Zein, P. Papet, F. Damay, J. Bourgeois, T. Hammouda, F. Dore, A. Maignan, M. Hervieu, C. Martin, Phys. Rev. Lett., **105**, 237203 (2010).

Pressure induced water insertion in synthetic clays.

S.You[1], D. Kunz[2], M. Stöter[2], H. Kalo[2], B. Putz[2], J.Breu[2*], and A.V.Talyzin[1*]

[1]*Department of Physics, Umeå University, SE-901 87 Umeå (Sweden)*
[2]*Lehrstuhl für Anorganische Chemie I, Universität Bayreuth, Universitätsstrasse 30, 95447 Bayreuth, Germany*

Synthetic smectites immersed in water or methanol liquid media were studied at high pressure using *in situ* synchrotron X-ray diffraction in diamond a anvil cell [1]. A reversible phase transition due to the insertion of an additional water layer was observed for Na- fluorohectorite (Na-hect) at 1.7 GPa but no similar transition was found when methanol was used as a pressure medium. The structures of 1 WL and 2 WL hydrates of Na-Hect were recently solved using single crystal methods. Hectorites with interlayer cations of higher hydration enthalpy than Na$^+$, e.g. Mg- hectorite are known also to adopt the 3 WL hydration state. The Na-Hect sample loaded into the DAC exhibited, as expected, the 2 WL structure at low pressure (0.2 GPa). At 1.7 GPa a sharp and step-like increase of interlayer distance was observed. The change in d(001)-spacing is about 2Å and corresponds to pressure-induced insertion of one additional layer of water thus resulting in 3WL structure. It should be noted that the water media surrounding the tactoids remained liquid at this pressure point and did not solidify until around 2.2 GPa. Pressure induced swelling of clay materials reported here is very similar to earlier discovered pressure induced swelling of graphite oxide, thus suggesting that it is a general phenomenon typical for certain types of hydrophilic layered compounds. It can be expected that other clay materials, including some natural clay minerals will also exhibit a similar pressure induced increase of hydration level at high pressures.

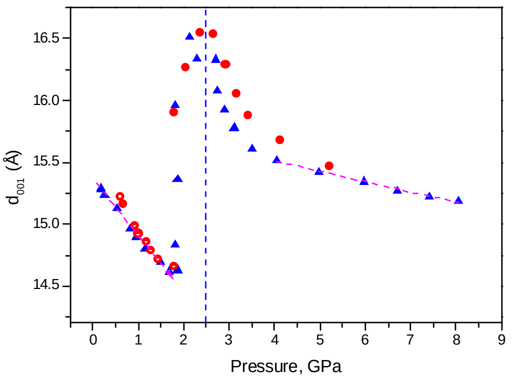


Figure 1. Pressure dependence of d(001) on compression (blue) and decompression (red) runs.

[1]. S.You, D.Kunz, M. Stçter, H. Kalo, B. Putz, J. Breu, A.V. Talyzin, Pressure-Induced Water Insertion in Synthetic Clays, *Angewandte Chemie*, *Int.Ed,* 52, 3891 –3895, (2013).

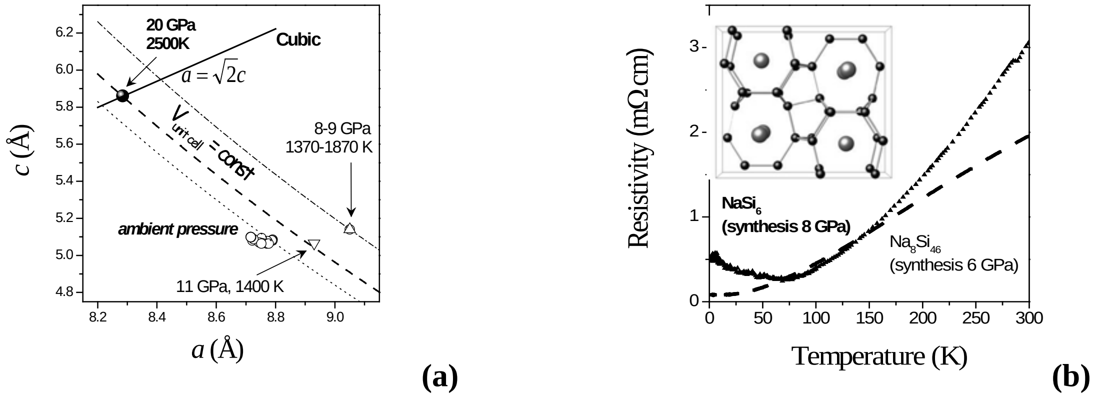
* Alexandr.Talyzin@physics.umu.se

High-Pressure Chemistry of Light Elements: New Compounds and Crystal Structures

O.O. Kurakevych[*1,2], *Y. Le Godec*[1], *T.A. Strobel*[2], *V.Z. Turkevich*[3] *and V.L. Solozhenko*[4]

[1]*IMPMC-CNRS, Université P&M Curie, 75005 Paris, France*
[2]*Geophysical Lab, CIW, 20015 Washington DC, USA*
[3]*ISM, NAS of Ukraine, 04074 Kiev, Ukraine*
[4]*LSPM-CNRS, Université Paris Nord, 93430 Villetaneuse, France*

This presentation will be devoted to recent achievements in crystal chemistry of boron, carbon and silicon. A number of new crystal forms and compounds has been recently synthesized under high pressure (HP), such as tetragonal allotrope of boron (a set of t-B_{52} phases) [1], pseudo-cubic boron (pc-B_{52}) [2], rhombohedral $B_{13}N_2$ [3], novel magnesium carbides (e.g. antifluorite Mg_2C) [4], a number of tunnel-like silicon clathrates Na_xSi_6 ($0 < x < 1$) [5], etc. Crystal structures, HP physical properties and chemical bonding have been studies from both experimental and theoretical points of view [2, 4-7]. HP equilibrium phase diagrams of boron [8], and binary systems such as B-BN [9], Mg-C and Na-Si will be discussed. The reported materials have a high potential for advanced applications as superhard, thermoelectric, extreme-condition electronics, methane storage, optoelectronics, etc.



(a) **(b)**

Figure 1: (a) Lattice parameters of tetragonal boron phases (*p-T* parameters correspond to synthesis). (b) Electrical resistance of tunnel clathrate $NaSi_6$ as compared to cage clathrate Na_8Si_{46} (Insert - crystal structure of $NaSi_6$).

References

[1] O.O. Kurakevych, Y. Le Godec, et al, High Press. Res. **32**, 30 (2012).
[2] O.O. Kurakevych, and V.L. Solozhenko, J. Superhard Mater. **35**, 60 (2013).
[3] O.O. Kurakevych, and V.L. Solozhenko, Acta Crystallogr. C **63**, i80 (2007).
[4] O.O. Kurakevych, T.A. Strobel et al, Angew. Chem. DOI: 10.1002/anie.201303463 (2013).
[5] O.O. Kurakevych, T.A. Strobel et al, Cryst. Grow. Design **13**, 303 (2013).
[6] Y. Le Godec, O.O. Kurakevych et al, Solid State Comm. **149**, 1356 (2009).
[7] O.O. Kurakevych, and V.L. Solozhenko, Solid State Comm. **149**, 2169 (2009).
[8] V.L. Solozhenko, and O.O. Kurakevych, *under review* Sci. Rep. (2013).
[9] V.L. Solozhenko, O.O. Kurakevych et al, J. Phys. Chem. B **114**, 5819 (2010).

* Presenter email: oleksandr.kurakevych@impmc.jussieu.fr

Recent Advances in the High-Pressure Chemistry of Alkali Metal Borates

*H. Huppertz**[1], *S.C. Neumair*[2] *and G. Sohr*[1]

[1]*Institut für Allgemeine, Anorganische und Theoretische Chemie, Leopold-Franzens-Universität Innsbruck,*
Innrain 80-82, A-6020 Innsbruck, Austria
[2]*Tyrolit Schleifmittelwerke Swarovski K.G., Swarovskistraße 33, A-6130 Schwaz, Austria*

Investigating borates under high-pressure/high-temperature conditions, we were able to synthesize several new high-pressure modifications in the field of alkali metal borates. The first example is the lithium borate HP-LiB_3O_5, which is built up from layers of corner-sharing BO_4 tetrahedra [1]. These layers are interconnected *via* trigonal-planar BO_3 units. As not uncommon for high-pressure phases, the crystal structure comprises also threefold coordinated oxygen atoms ($O^{[3]}$). With sodium as the alkali metal, HP-$Na_2B_4O_7$ could be synthesized at 6 GPa and 1000 °C consisting of BO_3 and BO_4 units that are connected alternatingly forming layers of "sechser" rings [2]. The layers are interconnected to a three-dimensional network structure, forming channels along the *c*-axis in which the sodium ions are located. One of the most interesting discoveries in our research were the syntheses of the isotypic alkali metal borates HP-KB_3O_5 [3] and HP-RbB_3O_5. As a matter of fact, high-pressure conditions favor the formation of tetrahedrally coordinated boron atoms, the edge-sharing of BO_4 tetrahedra, an increased coordination number of the bridging oxygen atoms ($O^{[3]}$), and often an enhanced coordination of the metal cations as can be expected from the pressure coordination rule. Both compounds fulfill these expectations, as can be seen in Figure 1.

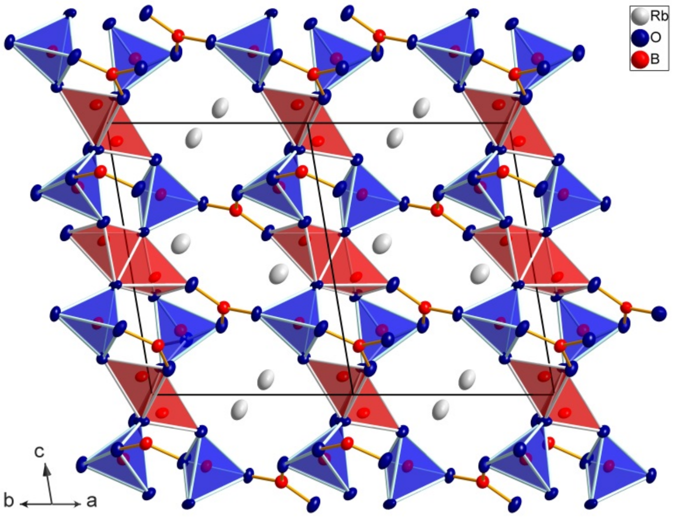


Figure 1: Projection of the crystal structure of HP-MB_3O_5 (M = K, Rb) along [110]. Spheres: 90 % thermal elipsoides.

In this context, the question concerning the existence of a high-pressure cesium borate is of highest interest; the results of our investigations will stand in the focus of this presentation.

References

[1] S.C. Neumair, S. Vanicek, R. Kaindl, D.M. Többens, K. Wurst, and H. Huppertz, J. Solid State Chem. **184**, 2490–2497 (2011).
[2] S. C. Neumair, G. Sohr, S. Vanicek, K. Wurst, R. Kaindl, and H. Huppertz, Z. Anorg. Allg. Chem. **638**, 81–87 (2011).
[3] S.C. Neumair, S. Vanicek, R. Kaindl, D.M. Többens, C. Martineau, F. Taulelle, J. Senker, and H. Huppertz, Eur. J. Inorg. Chem. 4147–4152 (2011).

* Hubert.Huppertz@uibk.ac.at

Metal Hydrides at Extreme Conditions

E. Gregoryanz[1], T. Scheler[1], R. Howie[1], C. Guillaume[1]*

M. Marques[2]

Z. Konôpková[3]

[1]CSEC, School of Physics and Astronomy, U. of Edinburgh, Edinburgh, UK
[2]MALTA Team and Dpto. Química Física y Analítica. U. de Oviedo, Oviedo, Spain
[3]DESY Photon Science, Notkestr. 85, 22 607 Hamburg, Germany

The application of extreme conditions offers a general route for the synthesis of materials under thermodynamic equilibrium. By finely tuning the thermodynamic variables of pressure and temperature one can manipulate matter on an atomic scale, creating novel compounds or improve the properties of existing materials. In particular, the study of hydrogen and hydrogen alloys has attracted the attention of researchers in the past. Although hydrogen reacts readily with many materials at ambient conditions, a significant "hydride hole" is apparent in the periodic table covering most of the transition metals between the chromium and copper group elements. At elevated pressures however, the chemical potential of hydrogen rises steeply and the hydrogen molecules eventually overcome the dissociation barrier on the metal surface. Atomic hydrogen diffuses into the metal to occupy available interstitial sites, forming a binary metal hydride and significantly altering the material's physical properties. Effects include increased toughness, structural phase transitions accompanied by drastic changes in the microstructure and hydrogen mediated superconductivity. Most of the d-metals have been found to exhibit hydride phases under certain conditions. However, besides rhenium, the 6th row metals between tungsten and gold, as well as silver, have long eluded the formation of a bulk hydride.

Here, we present a review of our most recent advancements and discoveries in the field of metal hydrides at extreme conditions. Synchrotron based in-situ x-ray diffraction techniques were used to study novel structures, their equation of state and, in combination with transmission electron microscopy, microstructure. Particular emphasis will be on the discoveries of the elusive hydrides of the 6th row elements.

* e.gregoryanz@ed.ac.uk

Chemical reactions at extreme conditions – polymerisation of CO and decomposition of SF_6 in the diamond anvil cell

N. Rademacher[1], L. Bayarjargal[1] , W. Morgenroth[1], J. Ciezak-Jenkins[2], S. Batyrev[2]*
and B. Winkler[1]

[1]*Institut für Geowissenschaften, Goethe-Universität, Frankfurt am Main, Germany*
[2]*US Army Research Laboratory, Aberdeen Proving Grounds, USA*

Chemical reactions at high pressures and temperatures are of interest because these extreme conditions can lead to reaction pathways which result in novel compounds with unusual structural features [1]. This study presents the investigation of the polymerisation of CO at high pressures and the decomposition of SF_6 in the presence of glassy carbon.

The chemical reaction of CO at high pressures has been studied extensively since a first report in 1983 and stability or phase diagrams as well as possible reaction products have been proposed [2,3]. However, structural information from total scattering experiments is lacking. We have performed diamond anvil cell (DAC) experiments with mixtures of 25 vol% CO in He and collected X-ray diffraction data at the Extreme Conditions Beamline P02.2 at PETRA III. Here, powder diffraction data of liquid and polymerised CO (p-CO, see figure 1) suitable for pair distribution function (PDF) analysis were obtained. The PDFs directly show the local structural changes before and after the polymerisation of CO and the behaviour during compression of p-CO up to pressures of 30 GPa.

The behaviour of SF_6 at high pressures and temperatures is less well studied. Sasaki *et al.* [4] investigated the high pressure phase diagram up to 10 GPa by Raman spectroscopy. We explored the stability field of SF_6-He mixtures up to 25 GPa and induced the decomposition of SF_6 at 10 GPa and around 2000 K by laser heating (LH) with glassy carbon as absorbing material. Figure 1 shows the sample chamber before and after laser heating. Clearly, a chemical reaction must have occured, since the black glassy carbon is no longer visible after the heating but a yellow and red coloured material instead. The reaction products will be characterised using powder X-ray diffraction at the Extreme Conditions Beamline P02.2 and Raman spectroscopy in Frankfurt.

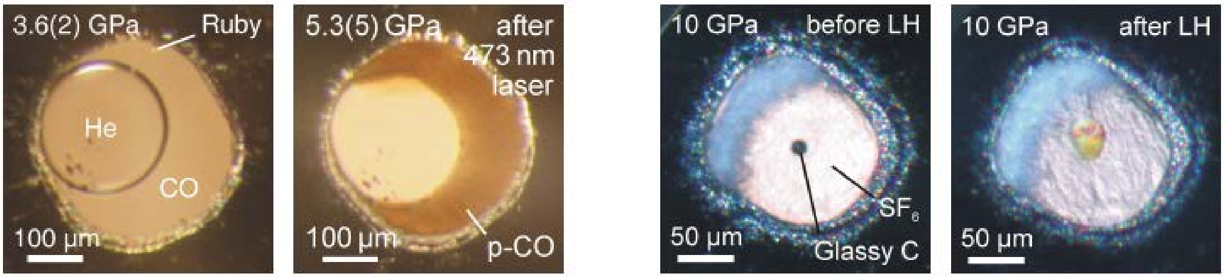


Figure 1: Left: Phase separation of CO and He in the DAC and the red polymerisation product p-CO. Right: Glassy carbon and SF_6-He in the DAC before laser heating and the reaction product after heating.

References

[1] R. Bini, M. Ceppatelli, M. Citroni, and V. Schettino, Chemical Physics **398**, 262 (2012).
[2] W.J. Evans, M.J. Lipp, C.-S. Yoo, H. Cynn, J.L. Herberg, and R.S. Maxwell, Chem. Mater. **18**, 2520 (2006).
[3] M. Ceppatelli, A. Serdyukov, R. Bini, and H.J. Jodl, J. Phys. Chem. **B113**, 6652 (2009).
[4] S. Sasaki, Y. Tomida, and H. Shimizu, J. Phys. Soc. Jpn. **61**, 514 (1992).

* Rademacher@kristall.uni-frankfurt.de

High-(p,T) synthesis and stability of tantalum and rhenium nitrides and their characterization

A. Friedrich*

Institute for Geosciences (Crystallography), Goethe University Frankfurt, Altenhöferallee 1, D-60438
Frankfurt am Main, Germany

Transition-metal carbides, nitrides and borides have a high potential for industrial applications as they generally show higher hardness, lower compressibility and higher melting points than the pure metals. The formation of new materials with high density and hence potential for high hardness is promising at extreme pressures and temperatures [1]. Here are presented the results of reactions and phase stabilities in the systems tantalum – nitrogen and rhenium – nitrogen at high pressures and temperatures up to about 32 GPa and 3500 K [2-4].

Synthesis and stability experiments were conducted in situ at high pressure and temperature at both the ALS (beamline 12.2.2, Berkeley, U.S.A.) and PETRA III (beamline P02.2, DESY, Hamburg, Germany) using the laser-heated diamond anvil cell and powder synchrotron X-ray diffraction. The bulk moduli of the high-pressure phases were determined from the pressure dependence of their unit-cell volumes. Micro-Raman spectroscopy and quantum-mechanical ab initio calculations based on density functional theory were performed at ambient and high pressures for validation of the structural models proposed from X-ray diffraction and for better characterization of the synthesis products [5,6]. Novel rhenium nitrides were further characterized using single-crystal synchrotron X-ray Laue microdiffraction at the ALS beamline 12.3.2 [3].

The examples presented show how the combination of micro-techniques like micro-Laue X-ray diffraction and micro-Raman spectroscopy with the power of quantum-mechanical calculations can be used for crystallographic characterization of novel high-(p,T) materials.

Financial support from the DFG, Germany, within priority program SPP1236 (projects Wi1232, Fr2491/2-1) and the BMBF, Germany (projects 05K10RFA, 05KS7RF1) is gratefully acknowledged. I thank ALS, HASYLAB, DESY, STFC E-Science facility, COMPRES, Goethe University and the VFF of the Goethe University for beamtime, computing time and financial support, as well as my colleagues, co-workers and the ALS and PETRA III beamline scientists for their contributions and help.

References

[1] A. Friedrich, B. Winkler, E.A. Juarez-Arellano, and L. Bayarjargal, Materials 4, 1648 (2011).
[2] A. Friedrich et al, Journal of Alloys and Compounds 502, 5 (2010).
[3] A. Friedrich et al, Physical Review Letters 105, 085504 (2010).
[4] A. Friedrich et al, High Pressure Research (2013), in press.
[5] A. Friedrich, B. Winkler, K. Refson, and V. Milman, Physical Review B 82, 224106 (2010).
[6] A. Friedrich, B. Winkler, K. Refson, and V. Milman, Physical Review B 86, 014114 (2012).

* friedrich@kristall.uni-frankfurt.de

Calcium – Hydrogen System under High Pressures

S. Besedin[*1,] *M. Eremets*[1], *I. Troyan*[1], *and A. Irodova*[2]

[1]*Max Plank Institut für Chemie, Hahn-Meitner-Weg 1, 55128 Mainz, Germany*
[2]*National Research Centre "Kurchatov Institute", Akademika Kurchatova pl. 1, 123182, Moscow, Russia*

Since year 2004 when Ashcroft suggested that hydrogen-dominant metallic alloys may posses superconductivity with high T_c [1] high-pressures studies of hydrogen rich compounds have gained considerable attention. Besides studies of three- and tetrahydrides, which are mostly hydrogen abundant among the saturated and stoichiometric hydrides it is found that even more hydrogen-rich compounds can be formed in the van der Waals systems such as SiH_4-H_2 [2] and Xe-H_2 [3]. H_2 molecules in these compounds remain essentially intact. In the SiH_4-H_2 system hydrogen exists both in atomic and in molecular-like states. Theory predicts that similar polyhydrides can be formed with alkali and alkali-earth metals. Examples are LiH_n (n=2-8) [4] and CaH_n (n=4-12) [5]. Ca-H system appears perhaps most interesting. It is predicted that CaH_6 compound should be stable above 150 GPa and is expected to be metal with critical superconducting temperature T_c as high as 220-235 K [5].

We present experimental study of calcium - hydrogen system in pressure range 0 - 160 GPa. The samples were probed by powder X-ray diffraction and Raman scattering. Kinetic of chemical reaction(s) appear slow leading to non-trivial phase behaviour. The X-ray data for at least one phase are consistent with formation of the predicted CaH_6 compound.

References

[1] N. W. Ashcroft, , Phys. Rev. Lett. **92**: 187002 (2004).
[2] T. A.Strobel, , M. Somayazulu , R. J. Hemley , Phys. Rev. Lett., **103**, 065701 (2009)
[3] M.Somayazulu, P. Dera, A. F. Goncharov, S. A. Gramsch, P. Liermann, W. Yang, Z. Liu, H-K. Mao, R. J. Hemley, Nature Chemistry, **2**, 50 (2010)
[4] E. Zurek, , R. Hoffmann , N.W. Ashcroft , A.R. Oganov , A.O. Lyakhov , PNAS, **106**: 17640 (2009).
[5] H. Wang, , J. S. Tse , K. Tanaka , T. Litaka , Y. Ma, PNAS, **109**, 6463 (2012).

* s.besedin@mpic.de

The high-pressure behaviour of the H_2O-CO_2 system

D. M. Amos[1], C. L. Bull[2], A. Falenty[3], W. F. Kuhs[3] & J. S. Loveday[1]*

[1]SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK
[2]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, UK
[3]GZG, Abt. Kristallographie, Universität Göttingen, Goldschmidtstrasse 1, 37077 Göttingen, Germany

Gas hydrates are a type of icy compound that are typically formed under the application of pressure and incorporate simple gas molecules into their crystal structures. These compounds are of broad interest as they occur widely in nature and have potential application in carbon capture and storage technologies, as well as other areas of the energy industry.

The existence of CO_2 clathrate hydrate formed at modest pressures (~30 bar) has been long known, with its transformation at a pressure of ~0.6 GPa into a new, currently unsolved, hydrate phase recently discovered [1]. The high-pressure behaviour of this binary system has, however, never previously been well studied and the reported absence of CO_2 hydrate phases above 1 GPa is in stark contrast to other gas hydrate systems, which are observed to undergo transition to more dense hydrate phases, with stability up to 100 GPa in some cases. We show the latest results of our comprehensive study of the H_2O-CO_2 system at high-pressure, in which a range of diffraction and spectroscopic techniques have been applied. Our studies provide new insight into the structure of the high-pressure phase reported by Hirai and co-workers, as well as new results on the properties of the molten system up to 5 GPa and the high-pressure chemistry of related ternary systems.

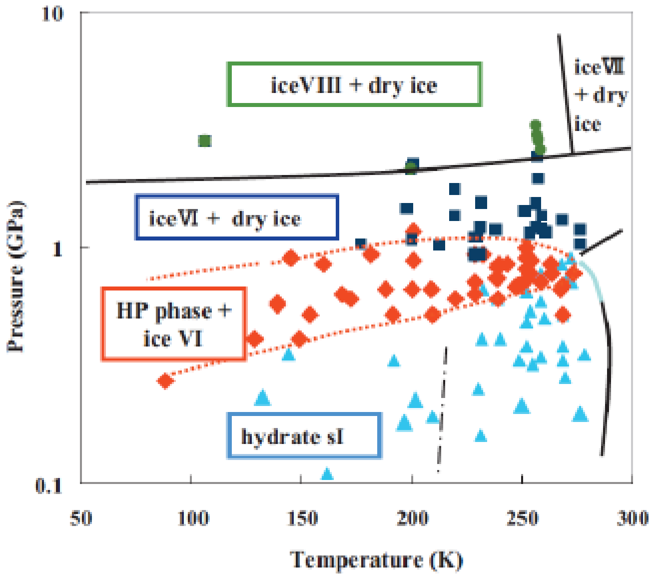


Figure 1: Phase diagram of the water-CO2 system, highlighting the high-pressure dissociation curve [1]

References

[1] H. Hirai, K. Komatsu, M. Honda, T. Kawamura, Y. Yamamoto, T. Yagi of J. Chem. Phys. 133, 124511 (2010).

* d.m.amos@ed.ac.uk

Poster Abstracts by 1st Author

The High Pressure Behaviour of Metallic Lithium Ammonia

C. L. Bull[1,2], J. S. Loveday[1*], R. J. Nelmes[1], D. Amos[1], C. Wilson[1], M.-E. Donelly[1], T. Hansen[3]

[1]*SUPA, School of Physics and Astronomy and Centre for Science at Extreme Conditions, University of Edinburgh, Edinburgh, UK*

[2]*ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire*

[3]*Institut Laue Langevin, 6, rue Jules Horowitz, Grenoble, France*

The "expanded" metal solutions formed by ammonia and the alkali metals are a remarkable group of compounds. These systems can be tuned from insulating to metallic state by varying the metal concentration. The lithium-ammonia system is one of the most interesting as it forms the lowest temperature liquid-metal known. The ambient pressure phase diagram shows the onset of the metallic state at 4 mol% of metal, with a eutectic point at 89 K and 20 mol% of metal. Above this concentration the freezing point rises rapidly and stoichiometric solid $Li(NH_3)_4$ forms. At ambient pressure, superconductivity has not been observed, but pressure has been proposed as a means to tune the electron density of states and induce superconductivity. Recent calculations indicated that the ambient pressure cubic structure remains stable up to 200GPa.

We will present recent results from high pressure neutron diffraction studies of $Li(ND_3)_4$. These studies show that at ~80 K the cubic phase II compresses strongly and at 2.5-3 GPa decomposes into a mixture of ammonia and lithium amide. The deuterium produced in this reaction is a fluid under these conditions. When compressed into the solid at ~160 K and 2.0 GPa or when warmed to these P and T conditions from solid phase below the melting line, a very different behaviour is observed. A new diffraction pattern is observed which cannot be explained by a mixture of any known lithium amide and ammonia phases. This thus appears to be a new phase of $Li(ND_3)_4$.

We acknowledge helpful insights from computations carried by Eva Zurek (University of Buffalo) and Chris Pickard (UCL).

The Counterintuitive High-Pressure Physics of Flexible Frameworks

A. B. Cairns[1], I. E. Collings[1], J. Adamson[1], S. Hunt[1], S. A. Hodgson[1], J. Ogborn[1], N. P. Funnell[1],
A. L. Thompson[1], H. Fang[2], A. E. Phillips[3], M. T. Dove[2,3], M. G. Tucker[4,5], D. A. Keen[4],
J. Parker[5], C. C. Tang[5], V. Dmitriev[6], P. Pattison[6], A. van der Lee[7], L. Peters[8], S. A. Moggach[9],
T. Lucas[10], J. Hriljac[10], J. Catafesta[11,12], C. Levelut[12], J. Rouquette[11], J. Haines[11], A. L. Goodwin[1]

[1] *University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, U.K.*
[2] *Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge CB2 3EQ, U.K.*
[3] *Centre for Condensed Matter and Materials Physics, Queen Mary University of London, Mile End Road, London E1 4NS, U.K.*
[4] *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire OX11 0QX, U.K.*
[5] *Diamond Light Source, Chilton, Oxfordshire OX11 0DE, U.K.*
[6] *Swiss-Norwegian Beamlines, ESRF, Polygone Scientifique Louis Néel, 6 rue Jules Horowitz, 38000 Grenoble, France.*
[7] *Institut Européen des Membranes, UMR-CNRS 5635, Univesité Montpellier 2, 300 Avenue Prof. E. Jeanbrau, 34095 Montpellier, Cedex 5, France.*
[8] *Institut für Kristallographie, RWTH Aachen, Jaegerstrasse 17-19, 52066 Aachen, Germany.*
[9] *Department of Chemistry, University of Edinburgh, Joseph Black Building, The King's Buildings, West Mains Road, Edinburgh EH9 3JJ, U.K.*
[10] *School of Chemistry, University of Birmingham, Edgbaston, Birmingham B15 2TT, U.K.*
[11] *Institut Charles Gerhardt, Equipe C2M, UMR-CNRS 5253, Université Montpellier 2, Place E. Bataillon, 34095 Montpellier Cedex 5, France.*
[12] *Laboratoire Charles Coulomb, UMR-CNRS 5221, Université Montpellier 2, Place E. Batallion, 34095 Montpellier Cedex 5, France.*

While the high-pressure behaviour of oxide-based framework materials (e.g. silicates, perovskites) has been the focus of an enormous collective body of research, much less is known regarding the behaviour of molecular framework materials. The fundamental consequence of using molecular — rather than single-atom — bridges from which to assemble a framework structure is an order-of-magnitude amplification of structural flexibility. The dominant energy regime of these materials is not that associated with usual bond stretching and bond bending deformations but another, much lower, energy scale associated with geometric flexing of the framework lattice. As a consequence, properties such as negative thermal expansion, negative compressibility, and pressure-induced mechanical softening appear to be vastly more common amongst molecular frameworks than is the case in longer-established ceramic phases. This poster will highlight some recent studies carried out in our laboratory, where we have attempted to characterise, optimise, exploit, and understand some of this unusual high-pressure physics of molecular framework materials [1-5].

[1] A. B. Cairns, *et al.*, *Nature Mater.* **12**, 212 (2013)
[2] J. M. Ogborn, *et al.*, *Chem. Sci.* **3**, 3011 (2012)
[3] I. E. Collings, *et al.*, *J. Am. Chem. Soc.* **135**, 7610 (2013)
[4] A. B. Cairns, *et al.*, *J. Am. Chem. Soc.* **134**, 4454 (2012)
[5] H. Fang, *et al.*, *arxiv:*1306.1909

The Behaviour of SiO_2 under Dynamic Loading and Unloading

E.-R. Carl[1], A. Danilewsky[1], G.Trullenque[2], T. Kenkmann[2] and H.-P. Liermann[3]*

[1]Crystallography, Institute of Geo- and Environmental Sciences, University of Freiburg, Hermann-Herder-Str.5, 79104 Freiburg, Germany
[2]Geology, Institute of Geo- and Environmental Sciences, University of Freiburg, Alberstr. 23b, 79104 Freiburg, Germany
[3]DESY, FS-PE, P02, Notkestr. 85, Bldg. 47c, Rm. L115, 22607 Hamburg, Germany

Little is known about phase transitions in the SiO_2 system under non-equilibrium conditions that occur at highly dynamic geological processes such as meteorite impacts. In a meteorite impact, high pressure polymorphs of quartz are formed given the non-hydrostatic stresses and temperatures produced by a shockwave.

In order to study phase transitions of quartz during fast compression and decompression, a series of experiments were carried out at the PETRA III "Extreme Conditions Beamline" (ECB) P02.2 at DESY, Hamburg. Thereby, coarse grained crystalline quartz powder (grain size > 1 micrometer) was placed in a membrane driven Diamond anvil cell (mDAC). Powder diffraction pattern were monitored every second by a detector flat panel XRD1621 from Perkin Elmer.

During compression under non-hydrostatic conditions, one non-identified phase is observed indicated by a peak splitting of the low-quartz (100) reflection (Figure 1). The new crystalline phase cannot be explained by any known high pressure SiO_2 polymorph. The obtained sample compression rates are 0.08 GPa per second, with a maximum applied pressure of 25 GPa. Furthermore, the experiments give evidence that the formation of the high pressure phase stishovite is related to higher pressures and slower loading rates than expected with respect to equilibrium conditions. However, further experiments at the ECB at different loading and unloading rates and at higher stresses using a piezoelectric-driven dynamic Diamond anvil cell (dDAC) need to be analysed to confirm systematic developments and to obtain further details. Moreover, the influence of amorphous intermediate needs to be considered as well.

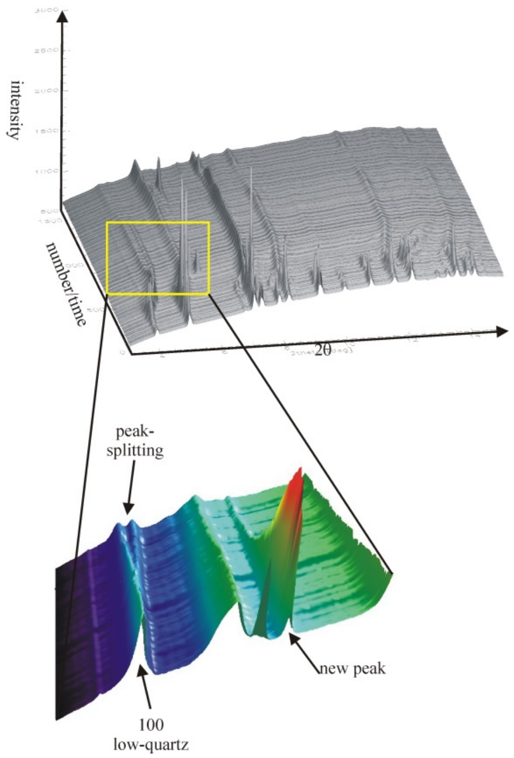


Figure 1: Stack of approx. 1600 diffractograms of SiO_2- powder during loading and unloading, maximum pressure of approximately 25 GPa and non-hydrostatic conditions.

* eva-regine.carl@krist.uni-freiburg.de

High Temperature Studies of Hydrogen and Deuterium at Extreme Pressures

Philip Dalladay-Simpson[1], Christophe Guillaume, Ross Howi[1] and Eugene Gregoryanz[1]

[1] *Centre for Science at Extreme Conditions and School of Physics and Astronomy, University of Edinburgh, Edinburgh, EH9 3JZ, United Kingdom*

Abstract

Melting characteristics is an essential diagnostic in studying the properties of the interactions within a material as well as differences between the solid and liquid states. Hydrogen despite being a simple system displays immense complexity and rich physics when under extreme pressures [1]; therefore it is important to broaden our understanding of quantum systems by studying hydrogen in extended pressure-temperature regimes. Previous experimental data alludes to a maximum in the melting curve [2], which has major implications for the existence of a ground state liquid at higher pressures [3]. Recent experimental advances have allowed us to probe melting in a new region of pressure-temperature space previously inaccessible due to the chemical reactivity of H_2. Through a series of high temperature Raman spectroscopic experiments we have investigated the melting curve of hydrogen and deuterium in excess of 1000K within the megabar range, conditions previously unattainable. This study not only will show the first experimental melting data on deuterium but also allow for much needed isotopic comparisons in the high temperature regime.

[1] R. T. Howie *et al. Phys. Rev. Lett.*, **108**, 2012.

[2] E. Gregoryanz *et al. Phys. Rev. Lett.*, **90**, 175701, 2003.

[3] E. Babaev *et al. Nature*, **431**, 666, 2004.

Effect of pressure on electrical resistance of CVT grown $ZrSe_3$ and ZrS_3 single crystals

A. Dasadia[1], B. Nariya [2] and A. Jani [3]*

[1,2,3]*Department of Physics, Sardar Patel University, Vallabh Vidyanagar-388120, Gujarat, India*

Single crystals of $ZrSe_3$ and ZrS_3 are grown by chemical vapour transport technique using iodine as a transporting agent. The grown crystals were characterized by energy dispersive analysis of X-ray (EDAX) for conformation of stoichiometric proportion of constituent elements and structure of grown crystals was determined by X-ray diffraction (XRD) technique. Pressure dependence of electrical resistance was studied using Bridgman opposed anvils experimental system up to 6 GPa for $ZrSe_3$ and up to 7 GPa for ZrS_3.

* abhi2physix@gmail.com

Using an innovative Vinet EoS approximation for parametric refinement of high pressure powder diffraction data

M. Etter[*1] *and R.E. Dinnebier*[1]

[1]*Max Planck Institute for Solid State Research, Stuttgart, Germany*

The relationship between the thermodynamic state variables pressure, volume and temperature can normally be described with so-called equation of states (EoS), which are semi-empirical determined and which are often used with an isothermal description (see also Fig. 1). Among this semi-empirical EoS, the Vinet EoS [1] is believed to be the most accurate [2], allowing to describe the behavior of most material systems under high pressure up to a compression of 40 %. Similar to other EoS like the Birch-Murnaghan EoS [3] or the natural strain EoS [4], the Vinet EoS has an pressure on volume dependency, which makes it unsuitable for parametric refinement of high pressure powder diffraction data, where the pressure is the independent variable and the volume is the dependent which is a refineable quantity.

Using an innovative Taylor series expansion of the Vinet EoS, it is possible to obtain an equation which is analytical invertible and therefore useful for a direct parametric refinement in analysis programs like TOPAS. By means of high pressure powder diffraction data of different material systems the validity of the newly developed EoS is evaluated and demonstrated.

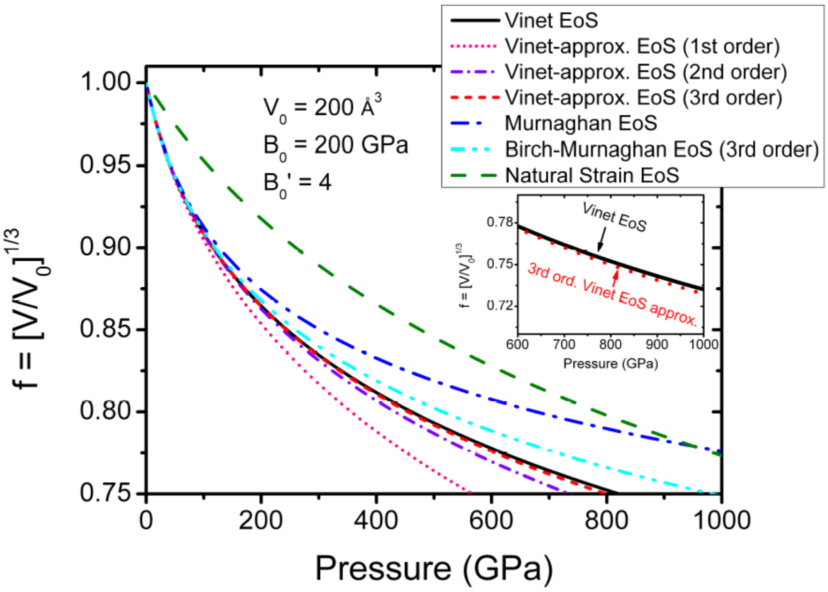


Figure 1: Theoretical calculated curves for different equation of states for fixed values of the volume at ambient pressure, the bulk modulus and the pressure derivative of the bulk modulus.

References

[1] P. Vinet, J.R. Smith, J. Ferrante and J.H. Rose, *Phys. Rev. B* **35**(4), 1945–1953 (1987).
[2] P. Vinet, J.H. Rose, J. Ferrante and J.R. Smith, *J.Phys.-Condens. Mat.* **1**, 1941–1963 (1989).
[3] F. Birch, *Phys. Rev.* **71**(11), 809–824 (1947).
[4] J.-P. Poirier and A. Tarantola, *Phys. Earth Planet. In.* **109**, 1–8 (1998).

* e-mail: M.Etter@fkf.mpg.de

Crystal structure and vibrational properties of the tetragonal Mn^{3+} hydrogarnet, henritermierite, up to 32 GPa

A. Friedrich, W. Morgenroth and B. Winkler*

Institute for Geosciences (Crystallography), Goethe University Frankfurt, Altenhöferallee 1, D-60438 Frankfurt am Main, Germany

Henritermierite is a rare Mn^{3+} silicate belonging to the hydrogarnet group of minerals with the end-member formula $Ca_3Mn_2[SiO_4]_2[OH]_4$. Due to the Jahn-Teller distortion of octahedrally coordinated Mn^{3+} henritermierite is tetragonal (space group $I4_1/acd$) [1]. This might also be the reason for its ordered arrangement of small SiO_4 and large H_4O_4 tetrahedra [1]. In an earlier study, the structural compression of henritermierite was studied at pressures up to 8.7 GPa [2]. There, a reduction of the Jahn-Teller distortion of the $Mn^{3+}O_6$ octahedra was observed and the bulk modulus was determined with $B_0 = 97.9(9)$ GPa and its pressure derivative $B' = 5.3(3)$ [2]. We were now interested whether the Jahn-Teller distortion could be suppressed at considerable higher pressure.

A small single crystal of henritermierite (40 × 30 × 10 µm³) was cut from the same crystals from the N'Chwaning II mine at the Kalahari manganese fields, Republic of South Africa, as were used by Armbruster et al. [2], with a composition $(Ca_{2.98}Na_{0.01}Mg_{0.01})^{VIII}(Mn_{1.95}Fe_{0.01}Al_{0.004})^{VI}[SiO_4]_{2.07}[H_4O_4]_{0.93}$ close to the end member. The crystal was pressurized in a diamond anvil cell up to 32(1) GPa using neon as pressure-transmitting medium and ruby for pressure determination [3]. Intensity data for crystal structure analyses were collected at the PETRA III synchrotron facility (beamline P02.2, DESY, Hamburg, Germany) using 42.78 keV radiation and a beam focused to $2 \times 3{-}4\ \mu m^2$ full width at half maximum. Diffraction images were acquired on a PerkinElmer XRD1621 area detector in step scans of 1° omega rotation, covering a cell opening of ± 39° at 6.7(1), 12.2(1), 22.1(1) and 31.7(1) GPa. After collection, the images were converted with an in-house software script to conform to the standard format of the program CrysAlis [4], which was used for data integration and reduction. Crystal structures were refined with the Shelx software [5] as implemented in WinGX [6]. On decompression, Raman spectra were collected from the same crystal with a Renishaw micro-Raman spectrometer in steps of about 2 GPa. Complementary quantum mechanical calculations based on density functional theory were performed using the program CASTEP [7].

The crystal structure remains stable up to the highest pressure obtained. Although the Jahn-Teller distortion of the $Mn^{3+}O_6$ octahedra is strongly reduced, it is not suppressed in this pressure range. Data analysis and investigations at even higher pressures are currently in progress.

Financial support from the DFG, Germany, within priority program SPP1236 (project Fr2491/2-1) and the BMBF, Germany (projects 05K10RFA, 05KS7RF1) is gratefully acknowledged. Portions of this research were carried out at the light source PETRA III at DESY, a member of the Helmholtz Association (HGF). We thank Z. Konôpková and H.-P. Liermann (PETRA III) for technical support at the beamline, and J. Gutzmer (Bergakademie Freiberg) for donating the sample crystals.

References

[1] A. Aubry et al, Bulletin de la Société Francaise de Minéralogie et de Cristallographie 92, 126 (1969).
[2] T. Armbruster et al, American Mineralogist 86, 147 (2001).
[3] H. K. Mao, J. Xu, and P. M. Bell, Journal of Geophysical Research 91, 4673
(1986). [4] Agilent Technologies, CrysAlis RED, version 171.36.28 (2013).
[5] G. M. Sheldrick, Acta Crystallographica A 64, 112 (2008).
[6] L. J. Farrugia, Journal of Applied Crystallography 32, 837 (1999).
[7] S. J. Clark et al, Zeitschrift für Kristallographie 220, 567 (2005).

* friedrich@kristall.uni-frankfurt.de

Isotopic Studies of Hydrogen and Deuterium Phase IV at Multi-Megabar Pressures

R.T. Howie[1], C.L Guillaume[1], T.S. Scheler[1] and E. Gregoryanz[1]

[1]*Centre for Science at Extreme Conditions and School of Physic and Astronomy, University of Edinburgh, Edinburgh, EH9 3JZ, United Kingdom*

The recent discovery of the mixed atomic and molecular phase IV of hydrogen (deuterium) is exemplary of how the studies of hydrogen at multi-megabar pressures is constitutive to the understanding of simple systems at extreme compressions[1]. Through a series of high pressure Raman spectroscopic experiments we have conducted an isotopic comparison between hydrogen and deuterium in phase I. Isotopic studies not only reveal differences in phase stability, imposing constraints on the P-T phase diagram, but also provide strong evidence for structural phenomena, such as proton (deuteron) tunnelling[2,3]. New data will be presented over a wide temperature range.

References

[1] R. T. Howie, C. L. Guillaume, T. Scheler, A. F. Goncharov and E. Gregoryanz, Phys. Rev. Lett., 108,125501 (2012).

[2] R. T. Howie, T. Scheler, C. L. Guillaume, and E. Gregoryanz, Phys. Rev. B., 86, 214104 (2012).

[3] A. F. Goncharov, J. S. Tse, H. Wang, J. Yang, V. V. Struzhkin, R. T. Howie and E. Gregoryanz, Phys. Rev. B., 87, 024101, (2013).

A Comparative Diffraction Study of Europium and Samarium

R. J. Husband[1], K. A. Munro[1], I. Loa[1] and M. I. McMahon[1]*

[1]SUPA, School of Physics and Astronomy, and Centre for Science at Extreme Conditions
The University of Edinburgh, Edinburgh, UK, EH9 3JZ

Europium (Eu), which is divalent at ambient pressure due to its half-filled 4f electron shell, is an anomalous element in the lanthanide series, in which the majority of the elements are trivalent. Consequently, Eu has a significantly larger atomic volume, and compressibility, than would be expected to be in keeping with the general trend across the lanthanide series [1]. Eu also does not fit in with the general trend of structural phase transitions observed in the trivalent lanthanide elements (hcp → Sm-type → dhcp → fcc → distorted-fcc (dfcc) → “collapsed”), and its behaviour is much more complex. Initial high-pressure x-ray diffraction studies were complicated by the presence of two pressure-induced contaminant phases [2,3]. Consequently, the behaviour of Eu above 18 GPa has only recently been determined and the Eu-IV phase, stable above 31.5 GPa, was identified as the only known incommensurate structure in the lanthanide series [4].

The high-pressure behaviour of divalent Eu has typically been compared with that of its neighbouring trivalent elements, samarium (Sm) and gadolinium (Gd), with the aim of producing a unified phase diagram of all the lanthanide elements. The fact that the atomic volume of Eu falls below that of neighbouring Gd between 10 - 20 GPa was taken as evidence that Eu was no longer divalent at this pressure, but rather mixed valent [1,5]. However, the observation of incommensurate structures in Eu, and the recent report that Eu remains divalent up to 87 GPa, questions this interpretation [6]. In addition, previous x-ray diffraction studies on Sm do not provide a complete description of the structural behaviour of Sm under pressure. In particular, the structure of the dfcc phase has not yet been definitively characterised.

We will present the results of our powder x-ray diffraction studies of Eu and Sm up to a pressure of 50 GPa. In Eu, we will report a transition to a second incommensurately-modulated phase, Eu-V, above 42 GPa. This transition is accompanied by an increase in modulation amplitudes and the appearance of higher-order satellite reflections. This is the first pressure-induced incommensurate-incommensurate (non-host-guest) transition to be observed in the elements at high pressure. In Sm, we have determined that the dfcc phase has the same *hR*24 structure observed in Pr, although the pressure dependence of this structure is different to that observed previously in Pr [7]. However, we saw no evidence of a transition to second dfcc phase, such as the transition to the *oI*16 phase observed in Pr and possibly also in Nd. Having fully characterised the structures observed in Eu and Sm up to 50 GPa, the compressibilities of the two elements will be compared.

References

[1] K. Takemura and K. Syassen, J. Phys. F: Met. Phys., **15**, 543 (1985).
[2] R. J. Husband *et al.*, J Phys Conf Ser. **377**, 012030 (2012).
[3] R. J. Husband *et al.*, High Press. Res. **33**, 158 (2013).
[4] R. J. Husband *et al.,* Phys. Rev Lett. **109,** 095503 (2012).
[5] W. Bi *et al.*, Phys. Rev. B. **83** 104106 (2011).
[6] W. Bi *et al.*, Phys. Rev. B. **85**, 205134 (2012).
[7] S. R. Evans *et al.*, Phys. Rev. B 80, 134105 (2009).

* R.J.Husband@ed.ac.uk

Pressure-induced Structural and Magnetic Transformations in $La_{0.75}Ca_{0.25}MnO_3$

*S. E. Kichanov *[1], D. P. Kozlenko [1], N. T. Dang[1], E. V. Lukin[1], Z. Jirák[2], L. S. Dubrovinsky[3],*
V. I. Voronin[4] and B. N. Savenko[1]

[1] *Frank Laboratory of Neutron Physics, JINR, 141980 Dubna, Russia*
[2] *Institute of Physics, Academy of Sciences, 16253 Prague, Czech Republic*
[3] *Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, D-95440, Germany*
[4] *Institute for Metal Physics, Ural Division of RAS, 620219 Yekaterinburg, Russia*

Doped manganites $R_{1-x}A_xMnO_3$ (R – rare earth, A - alkali earth elements) with perovskite-like structure exhibit a rich variety of fascinating physical phenomena extensively studied during last years – the colossal magnetoresistance, insulator-metal transition, charge and orbital ordering, mesoscopic phase separation [1]. It is widely accepted that interplay between magnetic, transport and electronic properties in these compounds results from a complicated balance of the ferromagnetic (FM) double exchange and the antiferromagnetic (AFM) superexchange interactions, coupled to lattice distortion effects and orbital degrees of freedom.

In present work the high pressure evolution of structural and magnetic properties of $La_{0.75}Ca_{0.25}MnO_3$ was studied by means of X-ray diffraction up to 39 GPa and neutron diffraction up to 7.5 GPa.

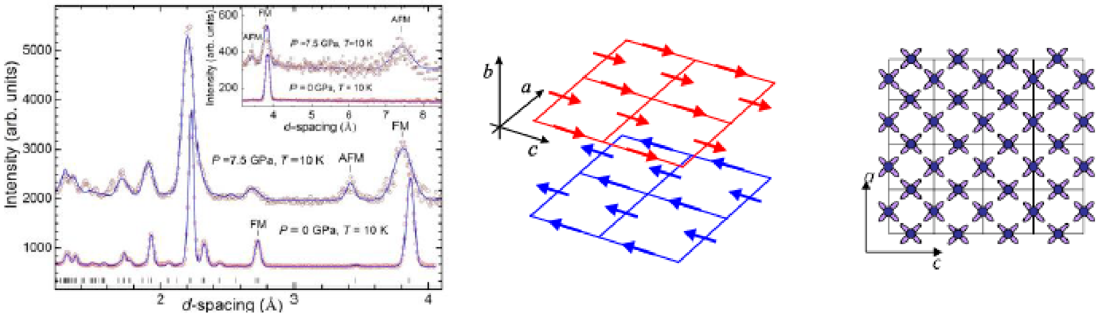


Figure 1: Neutron diffraction patterns of $La_{0.75}Ca_{0.25}MnO_3$ measured at different pressures and T = 10 K. The arrangement of Mn magnetic moments in the A-type AFM structure and characteristic $d_{x^2-z^2}$ orbital order are shown.

At normal pressure and temperature below T_C = 240 K, a ferromagnetic state (FM) is exist in $La_{0.75}Ca_{0.25}MnO_3$ [2]. The magnetic order in $La_{0.75}Ca_{0.25}MnO_3$ undergoes a continuous transition from the ferromagnetic metallic ground state to the A-type antiferromagnetic (AFM) state (Fig. 1) of assumedly 2D pseudo-metallic character under pressure, that starts at about ~1 GPa and extends possibly to 20-30 GPa. The initial FM metallic ground state becomes unstable under high pressure due to strongly anisotropic distortions of MnO_6 octahedra, and A-type AFM ground state with an e_g orbital polarization of the $d_{x^2-z^2}$ kind (Fig.1) is gradually developed instead.

The subsequent application of high pressure leads to the *Pnma* – *Imma* structural phase transformation in $La_{0.75}Ca_{0.25}MnO_3$, mediated by a change in the octahedral tilting and anisotropic lattice compression, coupled to orbital ordering effects.

References

[1] E. Dagotto, T. Hotta, and A. Moreo, Phys. Rep. **344**, 1 (2001).
[2] D. P. Kozlenko, S.E. Kichanov, V. I. Voronin and et al, JETP Lett. **82**, 447 (2005).

*ekich@nf.jinr.ru

The Role of Oxygen in Shockwave-Synthesized γ - Si_3N_4 Material

A. Köhler[1,3], T. Schlothauer[2], C. Schimpf[3], V. Klemm[3], M. Schwarz[1], G. Heide[2], D. Rafaja[3] and E. Kroke[1]*

[1]*Institute of Inorganic Chemistry, TU Bergakademie Freiberg*
[2]*Institute of Mineralogy, TU Bergakademie Freiberg*
[3]*Institute of Materials Science, TU Bergakademie Freiberg*

Spinel-type γ-Si_3N_4 is known as one of the hardest materials with a temperature stability of T > 1250 °C in air. It can be synthesized under high pressure only. Although γ-Si_3N_4 is thermodynamically stable above ~12 GPa, usually large overpressures are required for shockwave synthesis of this material. The application of amorphous precursors and peak shock pressures of 31 GPa (shock duration 1.1 to 1.5 µs) enabled us to manufacture spinel-type material without detectable amount of the low pressure modifications (e.g. α- or β-Si_3N_4) [1].

Samples were comprehensively investigated by Elementary Analysis by Carrier Hot Gas Extraction (CHGE), XRD, Neutron Diffraction and TEM including EELS and EDX. The shockwave-synthesis produces a nanopowder which consists of clusters of a size up to 500 nm containing nanocrystals of about 20 nm in diameter. XRD and high resolution TEM confirmed the expected spinel structure. However, the overall oxygen content measured by CHGE is about 7-8 wt% and an additional amorphous phase occurs. The incorporation of oxygen into the spinel-γ-Si_3N_4 lattice was investigated by Neutron Diffraction in a possible metastable solid solution series $Si_{3-y}O_xN_{4-x}$. The determined value of about $x = 0.4$ is similar to the value determined by CHGE after etching of the as-received powders by hydrofluoric acid. Thus, we conclude a small amount of oxygen can be incorporated in the spinel structure but an excess of oxygen leads to the formation of an amorphous phase.

References

[1] T. Schlothauer, M. R. Schwarz, M. Ovidiu, E. Brendler, R. Moeckel, E. Kroke, and G. Heide, Shock wave synthesis of oxygen-bearing spinel-type silicon nitride -$Si_3(O,N)_4$ in the pressure range from 30 to 72 GPa with high purity. In: *Minerals as Advanced Materials II*. Ed. by Krivovichev, S. V. Springer Berlin/Heidelberg, 389 (2012).

* anke.koehler@chemie.tu-freiberg.de

Synthesis and determination of the crystal structure of Sb_2Te_3 metastable phase

I. A. Kruglov[*1, 2], *N. R. Serebryanaya*[1, 2], *E. V. Tatyanin*[1], *N. A. Lvova*[1, 2], *S. G. Buga*[1, 2],
V. D. Blank[1, 2]

[1] *Technological Institute for Superhard and Novel Carbon Materials of Ministry of Education and Science of RF, 142190 Troitsk, Moscow region, Russian Federation*
[2]*Moscow Institute of Physics and Technology, 141700, 9, Institutskii per., Dolgoprudny, Moscow Region, Russia*

We have manufactured the metastable phase Sb_2Te_3_m using the method of quenching after treatment at P = 4.0 GPa and T = 400 – 850 ^{0}C [1]. The powder X-ray diffraction pattern of this phase is similar to that of monoclinic structure β - Sb_2Te_3 revealed *in situ* at high pressure and room temperature [2] and also it is similar to that of monoclinic α-As_2Te_3 crystal- structure-type. We propose that Sb_2Te_3_m structure has the space group C2/*m* with monoclinic distortion $\beta \sim 149\ ^0$. The preliminary calculated unit cell parameters are a ~ 15,6 Å, b ~ 4,3 Å, c ~ 18,2 Å. The crystal structure is layered, Sb-atoms have 7-fold and 8-fold distorted polyhedrons of Te-atoms. Calculations of atomic positions and unit cell parameters were made by methods of full profile analysis. Also we investigated the structure of Sb_2Te_3_m after P-T treatment using electron diffraction methods. It has been found that the diffraction patterns, obtained by specimen tilt, correspond to the proposed structure of Sb_2Te_3_m.

We also investigated the structure by *ab initio* simulation within the density functional theory. The structure of the relaxed configuration correlates with the data obtained from XRD analysis.

The electrical resistivity of this phase at room temperature is about $1{,}5\times10^{-3}$ Ohm cm. The Hall measurements show dominating electron conductivity with the density of charge carriers (n-p) about 4×10^{20} cm^{-3}. At heating to T=380K Hall coefficient changes sign. The p – type conductivity characterizes transformation to the initial phase.

The metastable Sb_2Te_3_m completely reverts to the initial rhombohedral structure α-Sb_2Te_3 after annealing during 2,5 hours at 400^0 C and after two years the process of reverse transformation to α-Sb_2Te_3 is beginning at ambient conditions.

References:

1. S. G. Buga, N. R. Serebryanaya, G. A. Dubitskiy, E. E. Semenova, V. V. Aksenenkov, V. D. Blank. “Structure and electrical properties of Sb_2Te_3 and $Bi_{0,4}Sb_{1,6}Te_3$ metastable phases obtained by HPHT treatment”. High Pressure Research, **Vol**. 31, No. 1, March 2011, 86 – 90.
2. J. Zhao, H. Liu, L. Ehm, Z. Chen, S. Sinogeikin, Y. Zhao, G. Gu. “Pressure-induced disordered substitution alloy in Sb_2Te_3”. Inorganic Chemistry, **Vol**. 50, 2011, p. 11291-11293.

* kruglov.mipt@gmail.com

High-pressure phase transitions of $[CuF_2(H_2O)_2(pyz)]$ in different pressure transmitting fluids

A. Lanza,[1,2] M. Fisch,[1,2] N. Casati,[2] C. Fiolka,[1] K. Krämer[1] and P. Macchi[1]*

[1]*Departement für Chemie und Biochemie – Universität Bern, Freiestrasse 3, 3012 Bern, Switzerland*
[2]*Swiss Light Source – Paul Scherrer Institut, 5232 Villigen PSI, Switzerland*

In recent years, several crystallographic, magnetic and spectroscopic investigations have been carried out on the linear coordination polymer $[CuF_2(H_2O)_2(pyz)]$ (pyz = pyrazine) at “extreme conditions”, which revealed the occurrence of many phase transitions. The room pressure structure consists of pyz-bridged chains of distorted Cu^{II} octahedra, which vertices are occupied by pairs of three different ligands in a *trans* arrangement. For its simplicity, $[CuF_2(H_2O)_2(pyz)]$ is an ideal candidate to investigate the variation of the material properties as a function of pressure induced modifications of the coordination environment. [1-3]

The variety of high-pressure phases reported in the literature[2,3], some of which show a switching in the direction of distortion of the coordination octahedron, prompted us to thoroughly investigate the influence of different pressure transmitting fluids and of the aggregation state of the sample (*i.e.* single crystal or powder) in directing the phase transitions. High-pressure X-ray diffraction experiments were repeated on single crystals and powders using polar and non-polar pressure transmitting fluids. A new triclinic phase was observed at 3.3 GPa, which resulted different from those found in the previous both single crystal and powder high-pressure crystallographic studies and in particular does not show the expected pressure-induced orbital reorientation.

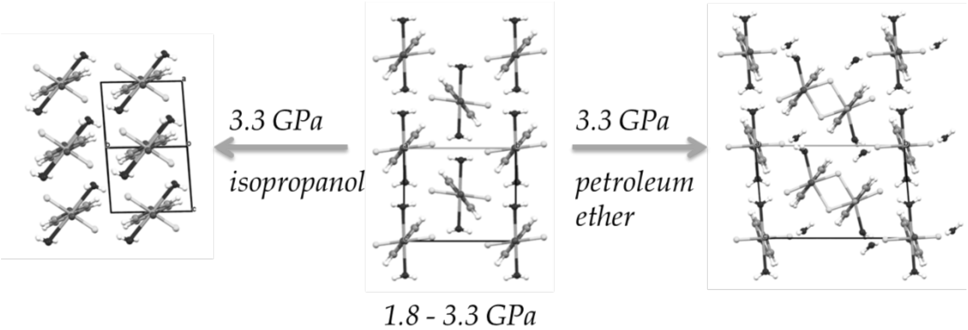


Figure 1: Two different phases observed at the same pressure by varying the pressure transmitting fluid.

References

[1] a) J.L. Manson, M.M. Conner, J.A. Schlueter, A.C. McConnell, H.I.Southerland, I.Malfant, T.Lancaster, S.J.Blundell, M.L.Brooks, F.L.Pratt, J.Singleton, R.D.McDonald, Changhoon Lee, Myung-Hwan Whangbo, Chem.Mater. **20**, 7408-7416 (2008). b) P.A.Goddard, J.Singleton, P.Sengupta, R.D. McDonald, T.Lancaster, S.J.Blundell, F.L.Pratt, S.Cox, N.Harrison, J.L.Manson, H.I.Southerland, J.A.Schlueter, New Journal of Physics, 10, 83025 (2008). c) J.A.Schlueter, H.Park, J.L.Manson, H.Nakotte, A.J.Schultz, Physica B **405**, S324-S326, (2010). d) J.L. Musfeldt, Z. Liu, S. Li, J. Kang, C. Lee, P. Jena, J.L. Manson, J.A. Schlueter, G.L. Carr, M.-H. Whangbo, Inorg. Chem. **50**, 6347-6352 (2011). e) C.H. Wang, M.D. Lumsden, R.S. Fishman, G. Ehlers, T. Hong, W. Tian, H. Cao, A. Podlesnyak, C. Dunmars, J.A. Schlueter, J.L. Manson, D. Christianson Phys. Rev. B **86**, 064439 (2012).

[2] G.J. Halder, K.W. Chapman, J.A. Schlueter, J.L. Manson, Angew. Chem. Int. Ed. **50**, 419–421 (2011).

[3] A. Prescimone, C. Morien, D. Allan, J.A. Schlueter, S.W. Tozer, J.L. Manson, S. Parsons, E.K. Brechin, S. Hill, Angew. Chem., Int. Ed. **51**, 7490-7494 (2012).

* arianna.lanza@dcb.unibe.ch

Capabilities of the Extreme Conditions Beamline at PETRA III, DESY

H.-P. Liermann[1], Z. Konôpková[1], K. Glazyrin[1], W. Morgenroth[2], A. Rothkirch[1], E. Wittich[1], J. T. Delitz[1], A. Ehnes[1]*

[1]Photon Sciences, Deutsches Elektronen Synchrotron, Hamburg, Germany.

[2]Department of Crystallography, University of Frankfurt, Frankfurt, Germany.

At the end of 2010 the Extreme Conditions Beamline (ECB) at PETRA III received first beam and entered the commissioning phase. Since 2012 we are offering beamtime to general users to conduct a variety of different experiments such as powder and single diffraction in the laser/resistive heated and cryogenically cooled Diamond Anvil Cell (DAC). Particularly attractive has been our ability to conducted diffraction experiments at high energies of 60 and 77 keV for pair distribution function (PDF) studies as well as possibility to preform time resolved powder diffraction experiments at 26 and 43 keV with a maximum time resolution of 15 Hz. Within we present some of the current capabilities of the beamline as well as future plans to promote single crystal diffraction at high pressures and temperatures using both monochromatic and pink beam. Finally, we emphasis the present and future time resolved capabilities to conduct powder and single crystal diffraction experiments under dynamic compression and heating conditions in the DAC.

* hanns-peter.liermann@desy.de

High pressure spectrometer DN-6

E. V. Lukin[1], D. P. Kozlenko[1], B. N. Savenko[1], S. E. Kichanov[1], E. S. Kuzmin[1], A. P. Sirotin[1], V. V. Zhuravlev[1], A. A. Bogdzel[1] and A. P. Bulkin[2]*

[1]Joint Institute for Nuclear Research, Dubna, Moscow reg., 141980, Russia
[2]Peterburg Nuclear Physics Institute, Gatchina, Leningrad reg., 188300, Russia

The results of the current work on developing of the new spectrometer DN-6 for crystal and magnetic structures high-pressure studies are presented. The mine parts of this spectrometer are described. The spectrometer is working by time-of-flight method, and neutron spread through long vacuumed curved neutron guide. The describing of mechanical unit for main part of spectrometer is presented. The helium filled detector system with additional neutron shielding and a neutron beam collimator are mounted.

The mine parameters of new spectrometer are obtained. In report the results of first neutron diffraction experiments especially with high pressure cell with sapphire anvils were obtained. The test experiments with high pressure cell with diamond anvils cell were performed. The noticeable for neutron diffraction experiments minimum sample volume was 0.003 mm^3.

* lukin@jinr.ru

Bifurcated S-H...O Hydrogen Bonds in Cysteine-Containing Crystal Structures on High Pressure

Vasily S. Minkov[a,b] & Elena V. Boldyreva[a,b]

[a]*Institute of Solid State Chemistry and Mechanochemistry SB RAS; [b]Novosibirsk State University, Novosibirsk, Russian Federation*
E-mail: vasilyminkov@yahoo.com

In a series of recent publications, the crystals of L- and DL-cysteine were shown to undergo multiple phase transitions upon variation of temperature and pressure. All these transitions are related to rotation of the amino acid side chain accompanied by switching the weak S-H...X hydrogen bonds. Accordingly, cysteine-containing crystal structures should be stabilized with respect to phase transitions by measures that reduce the mobility of the side chain in the crystalline environment. In the recent work, we show that this can be achieved by increasing the significance of the side chain –SH group as a participant in intermolecular hydrogen bonds, either by N-acetylation, which removes the strong $-NH_3^+$ donor of cysteine and leaves a system without strong charge-assisted interactions, or by co-crystallization with an acid that converts the amino acid to a cation and itself forms a strong anion H-bond acceptor, thus boosting the importance of potential –SH donors. The crystal structures of the three compounds N-acetyl-L-cysteine, DLcysteinium semioxalate, and bis(DL-cysteinium) oxalate have thus been studied with variation of temperature and pressure. Cooling down to 4 K and increasing pressure up to 9.5 GPa did not result in any structural phase transitions in N-acetyl-L-cysteine and bis(DL-cysteinium) oxalate. In case of DL-cysteinium semioxalate, increasing pressure caused a phase transition at a much higher pressure (~6 GPa), compared to the ranges of pressure-induced phase transitions observed earlier for both monoclinic and orthorhombic L-cysteine (2.5–3.9 GPa and 1.1–2.5 GPa, respectively) or DL-cysteine (0.1–5 GPa). This phase transition had a large hysteresis, so that the reverse transformation on decompression was observed at ~3.7 GPa only, and was accompanied by a change in molecular conformations, as well as by the reorganization in the N–H...O hydrogen bonds in the crystal structure.

The polarized Raman spectroscopy from oriented single crystals of N-acetyl-L-cysteine revealed anomalous changes in $(SH)_{str.}$, $(C{=}O)_{str.}$, $(CH_2)_{wagg.}$ bands on increasing pressure. Precise single crystal X-ray diffraction allowed us to follow the continuous changes in S-H...O hydrogen bond on increasing pressure resulting in formation of bifurcated S-H...O hydrogen bond where oxygens from carbonyl and carboxyl groups act as acceptors. The blue shift of stretching vibrations of -SH group in orthorhombic and monoclinic L-cysteine on increasing pressure at the shortening of S...O distance may be explained by formation of the bifurcated hydrogen bonds in crystal structures.

The work was partly supported by Integration Project of SB RAS No. 108 and the Ministry of Education and Science of the Russian Federation (agreement No. 14.B37.21.1093).

[1] Minkov, V.S., Krylov, A.S., Boldyreva, E.V., Goryainov, S.V., Bizyaev, S.N., Vtyurin, A.N. (2008) J. Phys. Chem. B Letters 112, 8851-8854.
[2] Kolesov, B.A, Minkov, V.S., Boldyreva, E.V., Drebushchak, T.N. (2008) J. Phys. Chem. B 112, 12827-12839.
[3] Minkov V. S., Tumanov N. A., Kolesov B. A., Boldyreva E. V. and Bizyaev S. N. (2009) J. Phys. Chem. B, 113, 5262–5272.
[4] Minkov, V.S., Goryainov, S.V., Boldyreva, E.V., Görbitz, C.H. (2010) J. Raman Spectrosc., 41, 1748-1758.
[5] Minkov V.S., Boldyreva E.V., Drebushchak T.N., Görbitz C.H. (2012) CrystEngComm, 14, 5943-5954.

Keywords: cysteine; hydrogen bonds; high pressure

Lattice Instability in Spin Ice Pyrochlore $Dy_2Ti_2O_7$

A. K. Mishra[1], H. K. Poswal [1], Surinder M. Sharma[1], R. Suryanarayanan[2], A. Revcolevschi[2] and A. K. Sood[3]*

[1]High Pressure & Synchrotron Radiation Physics Division, BARC, Mumbai 400085, India

[2]Laboratoire de Physico-Chimie de l' Etat Solidi, ICMO, CNRS, UMR8182, Universite paris-Sud, 91405 Orsay, France

[3]Department of Physics, Indian Institute of Science, Bangalore 560012, India

Pyrochlore compounds have gained a lot of attention over last several years [1] due to their interesting physical phenomena as well as technological relevance. For example, these materials are used as high permittivity ceramics, thermistors, thick film resistors and electrodes for solar cells etc. [2]. These materials are also potentially useful in nuclear engineering due to their utility for actinide rich waste immobilization. Pyrochlore lattice gives rise to a geometrically frustrated magnetic state in which the frustration of spins to order and minimize their exchange energies leads to a macroscopically degenerate ground state. High pressure can alleviate the delicate balance among various competing interactions and thus may lead to realization of different physical states [3]. Hence it will be interesting to study the high pressure behavior these compounds.

High-pressure angle dispersive x-ray diffraction (XRD) and Raman scattering studies have been carried out on a geometrically frustrated spin ice pyrochlore $Dy_2Ti_2O_7$ up to ~34.3 GPa and ~29 GPa respectively. Analysis of XRD data implies a discontinuity in the d_{hkl}'s as well as in the pressure induced variation of volume at ~ 9 GPa. At the same pressure, we have also observed a sudden change in the x-fractional coordinate of oxygen at 48f Wyckoff site with our Rietveld analysis. This implies a rearrangement of TiO_6 octahedra. The results obtained from analysis of our Raman scattering data are consistent with the XRD results. These results indicate the occurrence of a subtle structural distortion at ~9 GPa with a possible lattice instability at this pressure. The observed pressure induced variation of volume fitted with third order Birch-Murnaghan equation of state determines the bulk modulus to be 201.5 ± 6.9 GPa with its pressure derivative as 0.3 ± 1.9.

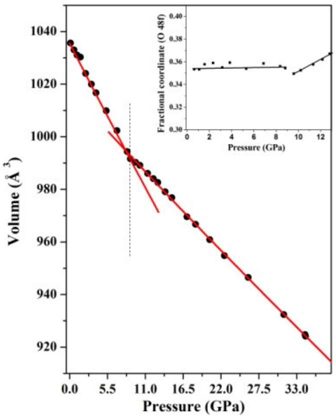


Figure 1: Observed P-V data (circle) fitted with 3rd order B-M equation of state (red line). The inset shows the variation of x-coordinate of oxygen at 48f wyckoff site.

References:

[1] R. Moessner and A. P. Ramirez, Phys. Today 59(2), 24 (2006).

[2] M. A. Subramanian, G. Aravamudan and G. V. Subba Rao, Pro. Solid State Chem. 15, 55 (1983).

[3] J. S. Gardner and et al. Phys. Rev. Letts. 82, 1012 (1999).

* akmishr@gmail.com

Pressure-induced phase transition in γ-MnOOH

W. Morgenroth[1], B. Winkler[1] and V. Milman[2]*

[1]*Goethe–Universität Frankfurt, Altenhöferallee 1, 60438 Frankfurt, Germany*
[2]*Accelrys, 334 Science Park, Cambridge CB40WN, UK*

At ambient conditions manganite, γ-MnOOH, crystallizes in space group $P2_1/c$ with parameters a = 5.304, b = 5.277, c = 5.304 Å and β = 114.38° [1]. A high-pressure study by Suzuki [2] up to 9 GPa gave a bulk modulus of 91(2) GPa, when the data was fitted with a 2nd order Birch-Murnaghan equation of state.

Preliminary DFT calculations based on the PBEsol exchange-correlation functional predicted a phase transformation to an orthorhombic space group at pressures above 15 GPa. In order to test the prediction, natural γ-MnOOH was ground to powder and compressed in a DAC up to 70 GPa. A rhenium gasket was pre-indented to 30 µm thickness and a hole of 80 µm diameter drilled by EDM as a sample chamber for the 300 µm diameter culet sized diamonds. We used helium as a pressure-transmitting medium.

Lattice parameters were determined from X-ray patterns recorded at the Extreme Conditions Beamline P02.2@PETRA III. A structural phase transition into an orthorhombic phase was observed at 47 GPa. The bulk modulus of the ambient pressure phase is 98(3) GPa with K' = 7.7(3). The poor agreement between experiment and theory implies a shortcoming of the latter. The most likely cause for the disagreement is an inaccurate description of the localisation of the *d*-electrons of Mn. Currently, we are therefore carrying out DFT+U calculations in order to test if this leads to an improved description of the high pressure behaviour. Once the reliability of the calculations is established, they will be employed to understand the details of the compression mechanism.

Funding by the BMBF (project 05K10RFA) is gratefully acknowledged. We thank DESY Photon Science for beam time and Hanns-Peter Liermann and his team for support.

References

[1] Th. Kohler, Th. Armbruster, and E. Libowitzky, J Solid State Chemistry **133**, 486-500 (1997).
[2] A. Suzuki, SPring-8 Exp. Report, 2006A1464 (2006).

* wolfgang.morgenroth@desy.de

Phase Transformations of Lanthanum at High Pressure

K. A. Munro[1], R. J. Husband[1], G. W. Stinton[1] and M. I. McMahon[1]*

[1]SUPA, School of Physics and Astronomy, and Centre for Science at Extreme Conditions, The University of Edinburgh, Mayfield Road, Edinburgh EH9 3JZ, U.K.

The high-pressure behavior of the lanthanide series of metals has been studied since the pioneering work of Bridgman [1]. The properties of these metals are strongly influenced by the electrons occupying the localized 4f shell. Applying pressure greatly influences the 4f electrons, which have a huge effect on the crystal structures and physical properties of the lanthanides. The trivalent lanthanide metals (La to Lu, excluding Eu and Yb) go through a general phase transition sequence on increasing pressure: hcp → Sm type → dhcp → fcc → distorted-fcc (d-fcc) [2]. Once this phase transformation sequence is complete there is a "volume collapse" transition to low-symmetry, highly complex crystal structures such as the α-U structure in praseodymium [3]. This large, discontinuous decrease in volume is attributed to the normally localised 4f electrons becoming delocalised [4].

Lanthanum is the first member of the lanthanide series and has unique physical properties and behavior. Firstly, lanthanum does not have any electrons occupying the 4f electron shell at ambient conditions. It does, however, still crystallize in the dhcp structure and follows the general phase transformation sequence observed in the other trivalent lanthanides. Lanthanum transforms to the fcc phase at ~2.5 GPa and into the d-fcc phase at ~7 GPa [5]. This latter phase is stable over a large pressure range up to 60 GPa, but once above that pressure, lanthanum diverges from the general transformation sequence by undergoing a re-entrant phase transition back into the same fcc structure seen at lower pressures [6]. Lanthanum's d-fcc phase is reported to have the hR24 structure (using Patterson notation) with space group R-3m, the same structure found in other low-Z lanthanides such as praseodymium and neodymium [7-9]. However, a recent preliminary diffraction study suggested that lanthanum undergoes a subtle d-fcc → d-fcc phase transition between 19 GPa and 28 GPa [10], with this new d-fcc phase reported to have the same orthorhombic oI16 structure found in praseodymium [11].

In order to investigate this possibility further, lanthanum has been studied using x-ray powder diffraction with the aim of resolving the dispute about the identity of the d-fcc phase between 7 and 60 GPa. The results of these new studies are presented, and the possibility of a previously-unidentified member of the general lanthanide transformation sequence is discussed.

References

[1] Bridgman, Proc. Am. Acad. Arts. Sci. **82**, 95 (1953).
[2] Errandonea *et al*., Phys. Rev. Lett. **85**, 3444 (2000).
[3] Mao *et al*., J. Appl. Phys. **52**, 4572 (1981).
[4] Fabbris *et al*., arXiv 1305.3852v1 (2013).
[5] Grosshans *et al*., Phys. Rev. Lett. **49**, 1572 (1982).
[6] Porsch *et al*., Phys. Rev. Lett. **70**, 4087 (1993).
[7] Seipel *et al*., High Pressure Res. **15**, 321 (1997).
[8] Hamaya *et al*., J. Phys. Condensed Matter **5**, L369 (1993).
[9] Akella *et al*., J. Less-Common Metals **116**, 313 (1986).
[10] S. R. Evans, PhD Thesis University of Edinburgh (2010).
[11] Evans *et al*., Phys. Rev. B **80**, 134105 (2009).

*K.A.Munro-1@sms.ed.ac.uk

Elastic and Inelastic Properties under Simulated Earth’s Mantle Conditions in Large Volume Apparatus in Conjunction with Synchrotron Radiation

Hans J. Mueller

GFZ German Research Centre for Geosciences, Telegraphenberg, D-14473 Potsdam, Germany

The interpretation of highly resolved seismic data from Earth’s deep interior require measurements of the physical properties of Earth’s materials under experimental simulated Earth’s mantle conditions. More than a decade ago seismic tomography clearly showed subduction of crustal material can reach the core mantle boundary under specific circumstances. That means there is no longer space for the assumption deep mantle rocks might be much less complex than deep crustal rocks known from exhumation processes. Considering this geophysical high pressure research is faced the challenge to increase pressure and sample volume at the same time to be able to perform in situ experiments with representative complex samples. High performance multi anvil devices using novel materials are the most promising technique for this exciting task. Recent large volume presses provide sample volumes 3 to 7 orders of magnitude bigger than in diamond anvil cells far beyond transition zone conditions. The sample size of several cubic millimeters allows elastic wave frequencies in the low to medium MHz range. Together with the small and even adjustable temperature gradients over the whole sample this technique makes anisotropy and grain boundary effects in complex systems accessible for elastic and inelastic properties measurements in principle. The measurements of both elastic wave velocities have also no limits for opaque and encapsulated samples. The application of triple-mode transducers and the data transfer function technique for the ultrasonic interferometry reduces the time for saving the data during the experiment to about a minute or less. That makes real transient measurements under non-equilibrium conditions possible. A further benefit is, both elastic wave velocities are measured exactly simultaneously. Ultrasonic interferometry necessarily requires in situ sample deformation measurement by X-radiography. Time-resolved X-radiography makes in situ falling sphere viscosimetry and even the measurement of elastic and inelastic properties in the seismic frequency range achievable. This way current geophysical high pressure research is more and more bridging the gap between indoor and outdoor seismology.

*hjmuel@gfz-potsdam.de

Limiting structure of expanded high density amorphous ice

R. J. Nelmes, C. L. Bull and J. S. Loveday

Centre for Science at Extreme Conditions and SUPA, School of Physics and Astronomy, The University of Edinburgh

The discovery that high density amorphous ice (HDA) expands when warmed at pressures below 0.5 GPa was unexpected and transformed our understanding of this important system [1]. Expanded high density amorphous ice (eHDA) appears to be the relaxed form of amorphous ice at low pressures and may be a hyperviscous liquid at temperatures around 140 K. As such its behaviour is very different from unrelaxed HDA (uHDA) which had generally been used for studies of amorphous ices. For example, eHDA has been shown to transform cleanly and discontinuously to and from low density amorphous ice (LDA) [1] and this result has ended debate about the nature of the LDA to HDA transition, and has provided support for the two liquids model of water [2].

Although the transition between LDA and eHDA has been well studied, there has to date been no detailed comparison of the two structures close to the transition, nor of the structural difference between eHDA and uHDA. We will present high-pressure neutron diffraction studies of eHDA carried out using the Paris-Edinburgh press. Data on the structure close to the transformation to LDA at 0.1 GPa provide insight into the limiting HDA structure and the structural changes at the transition.

[1] R. J. Nelmes et al, Nature Phys., **2**, 414-418, (2006).
[2] P. H. Poole et al, Nature, **360**, 324-328, (1992).

The Large Volume Press Beamline at the extension of PETRA III

N. Nishiyama[1]*, T. Katsura*[2]*, W. Drube*[1]*, E. Weckert*[1]*, H.-P. Liermann*[1]

[1]*Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany*
[2]*Bayerisches Geoinstitut, Universität Bayreuth, Bayreuth, Germany*

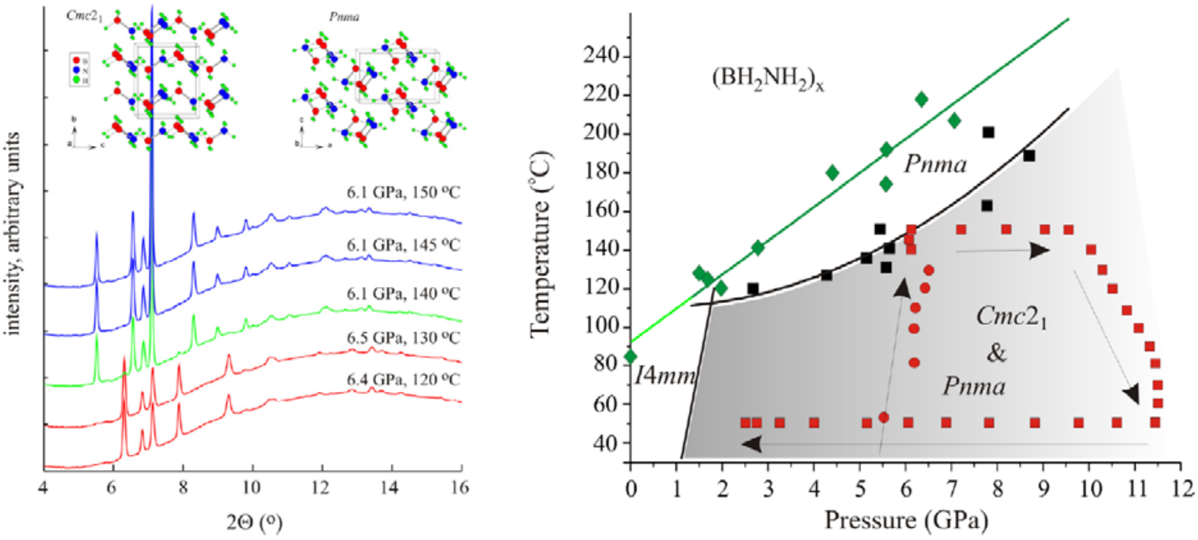
PETRA III is currently the brightest 3rd generation storage ring in the world. DESY decided to build a new experimental station dedicated to a combination of large volume press (LVP) technique and synchrotron radiation in the PETRA III extension project. This experimental hutch will be located at one of the 100 m long damping wiggler section of the storage ring. It offers the unique opportunity to study materials under high pressure and temperature conditions using high energy X-rays which allow us to study samples surrounded by pressure media and in sample capsules. Construction of the experimental halls will start in 2014 and beamline constructions are scheduled to begin in 2015. Here we report the conceptual design of this new beamline. X-rays from the damping wiggler will be filtered by exchangeable absorbers to cut X-rays below 40 keV and to adjust flux of X-rays depending on the beam size (0.01 - 10 mm) because the power and heat of the damping wiggler beam will be too high for optical components. The pink beam will be used for energy dispersive X-ray diffraction experiments under high pressure. We are planning to perform time-resolved X-ray diffraction study to observe nucleation and grain growth process separately under high PT conditions, which might give us useful information to design materials synthesized under extreme conditions. A 6-pistons LVP instrument will be installed in this beamline. The maximum load of each hydraulic ram is 500 tons, which is equivalent to 1500 ton-DIA apparatus. This instrument is suitable to carry out controlled deformation experiments under confining pressure up to 25 GPa by using a 6-6 anvil assembly. We believe that the instrumentation of the new LVP beamline will be very powerful for geosciences and material sciences.

High pressure, high temperature behavior of BH_3NH_3

J. Nylen[1] *and U. Häussermann**[1]

[1] *Department of Materials and Environmental Chemistry, Stockholm University, Arrhenius Laboratory, SE-10691 Stockholm, Sweden*

Ammonia borane or borazane, BH_3NH_3, has been extensively investigated as a potential candidate for chemical hydrogen storage [1]. The simultaneous presence of protonic N-bonded and hydridic B-bonded hydrogen gives rise to strong hydrogen bonding and – in contrast to isoelectronic ethane – BH_3NH_3 is a white, crystalline solid. In bulk form the compound undergoes an exothermic decomposition at temperatures between 80 and 105 ^{o}C. At elevated pressures (above 1.5 GPa) dihydrogen bonded BH_3NH_3 undergoes a solid-solid phase transition with increasing temperature. The high pressure, high temperature (HPHT) phase precedents decomposition [2] and evolves from the known high pressure, low temperature form with space group symmetry $Cmc2_1$ (Z=4) [3]. Structural changes of BH_3NH_3 with temperature were studied at around 6 GPa in a diamond anvil cell by synchrotron powder diffraction. At this pressure the $Cmc2_1$ phase transforms into the HPHT phase at around 140 ^{o}C. The crystal system, unit cell, and B and N atom position parameters of the HPHT phase were extracted from diffraction data, and a hydrogen ordered model with space group symmetry *Pnma* (Z = 4) subsequently established from density functional calculations. However, there is strong experimental evidence that HPHT-BH_3NH_3 is a hydrogen disordered rotator phase. A reverse transition to the $Cmc2_1$ phase is not observed. When releasing pressure at room temperature to below 1.5 GPa the ambient pressure (hydrogen disordered) *I4mm* phase of BH_3NH_3 is obtained.



X-Ray diffraction patterns (λ = 0.36940 Å) across the transition $Cmc2_1$ → *Pnma* and sketch of a p-T phase diagram.

References

[1] F. H. Stephens, V. Pons and R. T. Baker, Dalton Trans. **2007**, 2613.
[2] J. Nylén, T. Sato, E. Soignard, J. L. Yarger, E. Stoyanov, and U. Häussermann J. Chem. Phys. 131, 104506 (2009).
[3] Y. Filinchuk, A. H. Nevidomskyy, D. Chernyshov and V. Dmitriev, Phys. Rev. B 79, 214111 (2009).

* Ulrich.Haussermann@mmk.su.se

High pressure behavior of reduced graphene oxide

K. K. Pandey[1], H. K. Poswal[1], Hanns-Peter Liermann[2], S. Vasu[3], A .K. Sood[3] and Surinder M. Sharma[1]*

[1]High Pressure & Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India
[2]Photon Sciences, Deutsches Elektronen Synchrotron (DESY), Hamburg, Germany
[3]Department of Physics, Indian Institute of Science, Bangalore 560012, India

Graphene and its functional derivatives have been extensively investigated owing to their remarkable mechanical, optical electronic properties;[1] however its large scale productions for actual technological implementation still eludes scientific community. Chemically derived reduced graphene oxide (rGO) is an alternative viable solution, which closely competes with the mechanically exfoliated pristine graphene.[2] Despite enormous scientific exploration on these materials there are only a few investigations on their behavior under extreme conditions. With these motivations we have investigated the effect of high pressure on reduced graphene oxide up to 20 GPa using x-ray diffraction (XRD). The XRD measurements were carried out using perforated diamond anvil cell at ECB beamline at PETRA III synchrotron source, Hamburg, Germany. Our XRD measurements show 2-step reversible inter-layer compressional behavior of rGO whereas in-plane ordering exhibits a high pressure behavior similar to that of graphite up to 20.3 GPa. First, a huge compression of about 17 % has been observed along 'c' (inferred from 002 peak representing inter-layer spacing) axis up to 1 GPa which is followed by ~ 3% expansion attributed to pressure induced insertion of pressure transmitting medium. This is about 10% of the earlier reported expansion in graphite oxide due to pressure induced intercalation.[3] This lower expansion can be attributed to the lower concentration of oxygen functional groups attached to rGO. On subsequent higher pressures the 'c' axis exhibits similar behavior to that of graphite approaching critical interlayer separation of 2.8 Å at 20.3 GPa; however the 002 peak intensity gradually diminishes suggesting loss of long range order along 'c' axis. In order to explain the asymmetric shape of 100 peak, we propose a hypothesis of local out of plane distortions in reduced graphene oxide in the form of puckered regions in rGO multilayer sheets (fig. 1).This is in line with the recent high resolution transmission electron microscopic study of atomic structure of rGO.[4] The puckered regions can be modeled with a normal distribution of puckering angle with some standard deviation, σ. Our analysis suggests σ at ambient condition to be ~ 15.6° which progressively reduces to 10.4° at 20.3 GPa indicating flattening of rGO sheets as a function of pressure. On released pressures the standard deviation in puckering angle remains 10.4° exhibiting irreversible character. Relative intensities and positions of 002 and 100 peaks retrieve back on released pressure, suggesting high stability and healing ability of reduced graphene oxide under pressure cycling.

(a) (b)

Figure 1. a) pristine graphene sheet; b) puckered graphene sheet

[1] A. K. Geim and K. S. Novoselov, Nature Mater. 6 183-91 (2007)

[2] S. Stankovich, D. A. Dikin, R. D. Piner, K. A. Kohlhaas, A. Kleinhammes, Y. Jia, Y. Wu, S. T. Nguyen and R. S. Ruoff, Carbon 45 1558-65 (2007)

[3] A. V. Talyzi, B. Sundqvist, T. Szabó, I. Dékány and V. Dmitriev, Journal of the American Chemical Society 131 18445-9 (2009)

[4] C. Gómez-Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, K. Kern and U. Kaiser, Nano Letters 10 1144-8 (2010)

[*]Email Id: kkpandey@barc.gov.in

High pressure stabilization of labile hydroquinone acetone solvate

Kacper Rajewski[1], Jędrzej Marciniak[1], Michał Andrzejewski[1], Andrzej Katrusiak[1]*

[1]Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

According to the CSD [1] there are 24 different benzene-1,4-diol (hydroquinone) solvates. In most of the cases a solvent molecule fills an accessible space in a clathrate like β form (~ 5% of the unit cell volume) or α form (~ 1%) leaving a host structure unaffected. There are nine examples where the solvent forces a different molecular arrangements of hydroquinone molecules. We report the hydroquinone acetone solvate (*C*2/*c*), unstable under ambient conditions, previously obtained in a glass capillary [2], presently investigated in high pressure. Experiments at high pressure were performed in a modified Merrill-Bassett diamond-anvil cell (DAC). Hydroquinone interacts with an acetone molecule via OH···O bonds forming zigzag chains along the [101] direction (Fig. 1). Moreover, there is a significant influence of pressure on the c-parameter, which shortens approximately 0.4 Å up to 0.6 GPa and at approx. 0.7 GPa becomes shorter than the b-parameter. It is possible due to an alternating layer system with acetone and hydroquinone molecules. Assuming that the surface is not affected by defects, we can suppose that the top or bottom surface consists of either A or B layer in equilibrium with the solvent – acetone. When the crystal is exposed to air, the acetone layer evaporates quickly (acetone boiling point is 329-330 K, under standard conditions). Acetone evaporates also from the bulk of the crystal, which collapses.

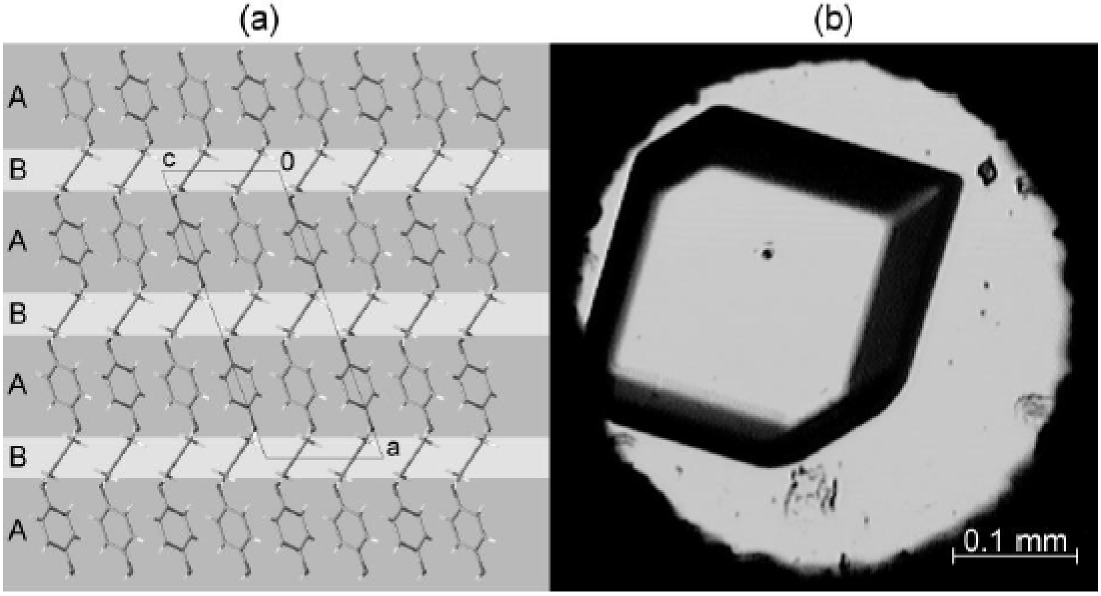


Figure 1. (a) Hydroquinone (A) and acetone (B) alternating layers and in the cocrystal structure, projected onto the (101) surface; (b) the cocrystal obtained at 0.63GPa, 296 K.

Acknowledgements:

This work was supported by the Foundation for Polish Science, research project TEAM 2009-4/6.

References

[1] F. H. Allen, *Acta Cryst.*, **B58**, 380-388, 2002.
[2] J. D. Lee, S. C. Wallwork, Acta Cryst., **12**, 210-216, 1959.

*kacper.rajewski@gmail.com

High-Pressure Modifications of Silicon for the Advances in Static and Dynamic High-Pressure Crystallography Meeting

J. Richter[1], A. Danilewsky[1], A. Cröll[1], P. McNally[2], D. Allen[2] and H.-P. Liermann[3]*

[1]*Crystallography, Institute of Geo- and Environmental Natural Sciences, University of Freiburg,*
Hermann-Herder-Str. 5, 79104 Freiburg, Germany
[2]*The RINCE Institute, School of Electronic Engineering, Dublin City University, Dublin, Ireland*
[3]*DESY, FS-PE, P02, Notkestr. 85, Bldg. 47c, Rm. L115, 22607 Hamburg, Germany*

In the semiconductor manufacturing industry micro-crack damage to silicon wafers occur during wafer handling, which may result in breakage of the wafers. The locally high-pressures during the handling may produce a high number of high-pressure phases including the by now not fully characterized phase Si XIII. To prevent high costs in the future, it is important to study the occurrence phase Si XIII in detail. For the investigation of high-pressure modifications of silicon, dynamic measurements were performed using powder diffraction with a diamond anvil cell at the beamline P2.02 at PETRA III, DESY. Samples at different pressure rates were measured and analyzed using the Rietveld method. The following phase transformations at room temperature are observed with increasing pressure (fig. 1):

$$Si\ I \rightarrow Si\ II \rightarrow Si\ XI \rightarrow Si\ V \rightarrow Si\ VI$$

The pressure ranges of the individual phases are shifted to lower pressures with increasing pressure rates. Analog, the stability fields of the phases Si XI, Si V and Si VI are shifted to lower pressures at pressure relief. It will be shown that the stability fields at near equilibrium and dynamic conditions are pretty similar and correspond well with the literature, whereas at dynamic and non-hydrostatic conditions they are slightly shifted to higher pressures. Only the phase Si II occurs in a strongly limited pressure range at dynamic conditions. Furthermore, the lattice parameters of the individual phases at the different pressure conditions are refined by the Rietveld method and are consistent with the literature values within the inaccuracy. For the by now little described phase Si VI, the lattice parameters are refined as a function of the pressure (at 36.29 GPa: a = 8.0128089 ± 0.0027966 Å, b = 4.7989741 ± 0.0027272 Å, c = 4.7841285 ± 0.0028203 Å). For the study of Si XIII phase, which was not found yet, higher temperatures are planned for the next experiments.

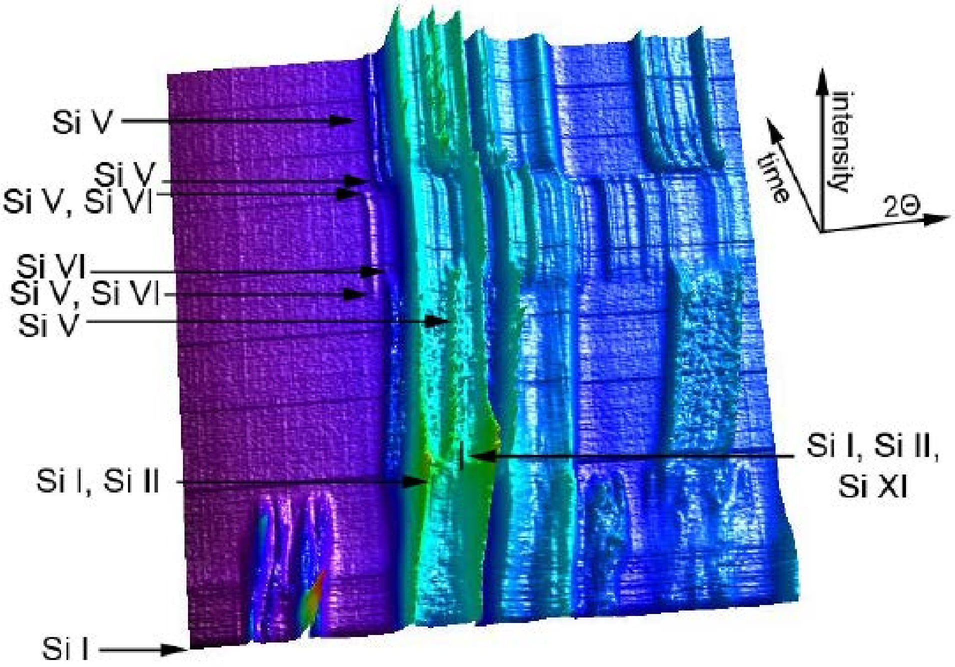


Figure 1: 3D graphics of an experiment at a pressure rate of 1.57 GPa/min at pressure build- up and 2.7 GPa/min at pressure relief from 5 to 11° 2Θ, the arrows mark the present Si phases at the respective positions

* jannik.richter@mars.uni-freiburg.de

In-situ pressure calibration for heated multianvil experiments and a complete re-design of multianvil assemblies for synchrotron and non-synchrotron experiments

*M. R. Schwarz *[1], T. Barsukova,[1] C. Schimpf[2], G. Li[1] and E. Kroke[1]*

[1]Freiberg High Pressure Research Centre, Institute of Inorganic Chemistry,
TU Bergakademie Freiberg, Leipziger Str. 29, D-09599 Freiberg, Germany

[2]Institute for Materials Science, TU Bergakademie Freiberg,
Gustav-Zeuner-Str. 5, D09599 Freiberg, Germany

A method that provides continuous monitoring of the sample pressure during loading and unloading of individual heated multianvil experiments while being independent from synchrotron sources has been devised. Based on previous results [1], we managed to accommodate one or more fixed-point calibrants together with a piezoresistive manganine gauge within octahedral pressure cells of various sizes, without interfering with the furnace assembly. The method gives the final pressure within the octahedron before heating, and moreover, yields important information on the unloading path of the experiment. It does not only offer the possibility to combine room- temperature and high-temperature pressure calibration within a single experiment, but also proved to be a useful tool to speed-up testing of new multianvil assemblies and configurations, e.g. in gasketing, without the need to use a synchrotron facility. Three commonly used octahedron sizes, 10, 14 and 18 mm (edge length) have been tested. The accuracy of the pressure calibration was cross-checked by simultaneous synchroton measurements and showed good agreement.

Other improvements in the design and assembly of 'on-line' and 'off-line' multianvil experiments are presented. This includes the development of a completely new gasketing scheme that allows easy and accurate assembly. Natural pyrophyllite gaskets werew substituted with a commercially available synthetic gasket material – hence improving reproducibility of the experiments and reducing the cost and effort for raw material purchase. Anvil failures could be reduced significantly while simultaneously increasing compression and decompression rates. A low-Z gasket material with high X-ray transmittance was developed, as well as amorphous and X-ray transparent, low thermal conductivity and high temperature-resistant window materials for the high pressure cells. First results on the performance of all-zirconia-based octahedra and precursor-based TiC-SiC heaters, that can be directly painted into the ZrO_2 insulator tubes are shown as well.

References

[1] M. R. Schwarz , J. Phys.:Conf. Series **215**, 012193 (2010).

---

* marcus.schwarz@chemie.tu-freiberg.de

Ab-Initio Study of Structural and Phase Transition Properties of Ytterbium Monopnictides Under High Pressure

Sanjay K. Singh[*1] *and U. P. Verma*[1]

[1]*School of Studies in Physics, Jiwaji University, Gwalior- 474011, India*

In present paper, we have investigated the structural properties of ytterbium monopnictides (YbX = N, P) and its phase transition behaviour under high pressure by using the full potential linear augmented plane wave plus local orbitals approach within the framework of density functional theory. In the study the generalized gradient approximation (GGA) is chosen for the exchange-correlation functional energy. The equilibrium properties viz., equilibrium lattice constants, bulk modulus, its pressure derivative and total energy are calculated in four different phases i.e. NaCl (B1), CsCl (B2), zinc blende(B3) and body centered tetragonal (BCT) phases and compared with previous calculations and available experimental data [1,2]. At ambient conditions YbX (X = N, P) stabilize in NaCl (B1) structure characterized by the space group Fm-3m. Under compression, both YbN and YbP undergo first-order structural transition from Fm-3m (B1) to Pm-3m (B2) at 164.0 and 337.0 GPa, respectively.

We have calculated total energy of the crystal at different volumes by means of Murnaghan's equation of state [3] at T= 0 K and P = 0 GPa. The variations of total energy with cell volume for B1, B2, B3, and BCT phases have been shown in Figure 1 for YbN compound. It is obvious from this curves that the B1 structure is the most stable at ambient pressure, which is consistent with the experimental results.

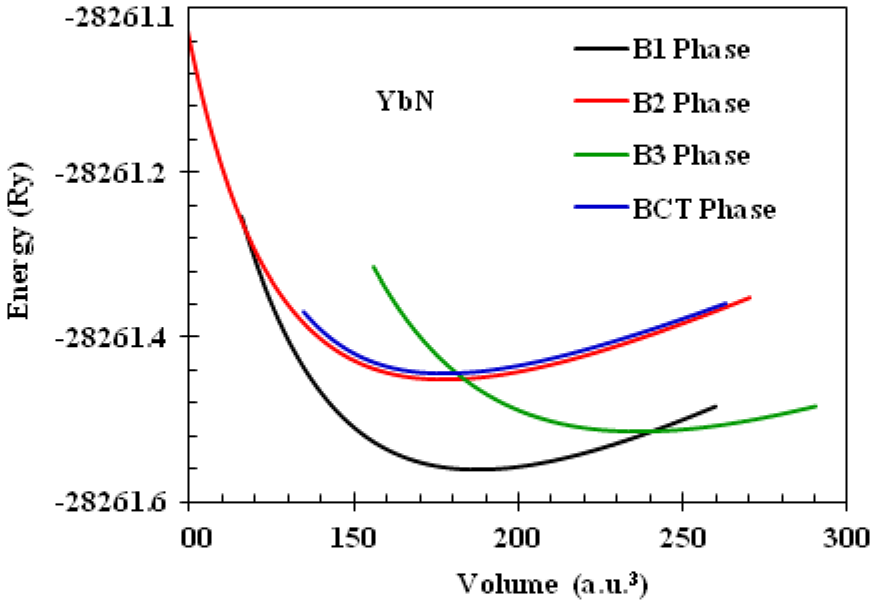


Figure 1: Energy *vs*. volume curves for YbN.

References

[4] L. Degiorgi, W. Bacsa and P. Wachter. Phys. Rev. B **42,** 530 (1990).
[2] F. D. Murnaghan, Proc. Nat. Acad. Sci. U.S.A., **30,** 244 (1944).

* presenter email : sanjayfizix@gmail.com

HP/HT Radial X-ray Diffraction and Brillouin Scattering Capabilities at the Extreme Condition Beamline of PETRA III

S. Speziale[1], H.-P. Liermann[2], H. Marquardt[1], L. Miyagi[3]*

[1]German Research Center for Geosciences (GFZ), Telegrafenberg, 14473 Potsdam, Germany
[2]Deutsches Elektronon Synchrotron (DESY), Hamburg, Germany
[3]Department of Geology and Geophysics, The University of Utah, Salt Lake City, UT 84112 U.S.A.

The Extreme Condition Beamline (ECB) P02.2 of PETRA III synchrotron in Hamburg provides a range of experimental tools to investigate the behaviour of materials at very high pressures and temperatures [1]. Here we present the features and the performance of two recently developed experiments developed at the ECB. The first experiment is designed to study texture development in-situ at Mbar pressures and $T > 1000$ K by radial X-ray diffraction in the diamond anvil cell (DAC). The second experimental setup allows one to perform combined measurements on both acoustic velocities by Brillouin scattering and density by X-ray diffraction on single-crystals and polycrystalline aggregates at high pressure in the DAC.

The combination of the DAC and X-ray diffraction performed in radial scattering geometry allows one to measure the development of texture and differential strain in polycrystals compressed at very high pressures [2]. Texture development in oxides and metals at very high pressures (HP) and temperatures (HT) is extremely attractive to materials science in terms of understanding the fundamental physics of deformation. It has a wide application in geophysics and planetary physics because it furnishes crucial information to model the internal dynamics of deep planetary bodies. A dedicated setup for HP-HT radial X-ray diffraction has been developed for general purpose experiment of the ECB. The setup employs a modified Mao-Bell piston-cylinder DAC with large lateral openings for radial X-ray diffraction. B-epoxy or cubic BN gaskets provide a X-ray transparent sample chamber. High temperatures are generated by external graphite heaters, which surround the sample chamber and the tips of the diamond. The assemblage is enclosed in a vacuum chamber to prevent the diamond anvils and DAC from oxidation at very high temperature. The chamber itself is water cooled as well as the piston of the DAC providing differential cooling preventing jamming of the DAC at very high temperatures. The system has been tested to a maximum 1100 K at 40 GPa compressing a mixtures of Mg-rich silicate perovskite and ferropericlase and within an B-epoxy gaskets. The experimental pressure range will be extended to the megabar (10^2 GPa) regime by using cubic BN gaskets.

The measurement of acoustic velocities is essential for characterizing the elastic properties of materials. In geophysics knowing the elastic properties of mantle minerals is crucial to interpret deep Earth seismic data in terms of a consistent mineralogical model. Brillouin scattering is a method of choice to study the effect of pressure on the elastic properties of deep Earth minerals compressed in the DAC [3]. The combined measurement of Brillouin scattering and X-ray diffraction allows one to simultaneously determine the pressure-volume equation of state of a material and both bulk and shear elastic moduli of a material independently of a secondary pressure scale [4]. A Brillouin scattering system is now available in the laser laboratory of the Infrastructure for Extreme Condition Research (ECR) next to the ECB beamline. The system is based on a Tandem Fabry-Perot interferometer and is specially designed to allow simple transfer of the sample to the ECB beamline without time-consuming alignment procedures. Combined Brillouin scattering and X-ray diffraction has been successfully conducted at high pressure on polycrystalline MgO and on Ar up to 50 GPa at ambient temperature. In addition to density, X-ray diffraction allows determination of grain-size heterogeneity and the orientation and spatial distribution of large grains in the sample. This additional information allows partial determination of the single-crystal elastic tensor from a polycrystalline sample. This technique has been applied to polycrystalline MgO and Ar [5].

References

[1] H.-P. Liermann, W. Morgenroth, A. Ehnes, A. Berghäuser, B. Winkler, H. Franz, and E. Weckert, J. Phys: Conf. Ser. **215**, 012029 (2010)

[2] S. Merkel, A. Kubo, L. Miyagi, S. Speziale, T. S. Duffy, H. K. Mao and H.-R. Wenk, Science **311**, 644 (2006); L. Miyagi, W. Kanitpanyacharoen, P. Kaercher, K. K. M. Lee, H.-R. Wenk, Science **329**, 1639 (2010)

[3] M. Murakami, Y.Ohishi, N. Hirao, K. Hirose, Nature **485**, 90 (2012); H. Marquardt, S. Speziale, H.J. Reichmann, D. J. Frost, F. R. Schilling, and E. J. Garnero, Science **324**, 224 (2009)

[4] C. S. Zha, H. K. Mao, and R. J. Hemley Proc. Natl. Acad. Sci. U.S.A. 97, 13494 (2000)

[5] S. Speziale, H. Marquardt, and H.-P. Liermann, High Press. Res. doi:10.1080/08957959.2013.806501 (2013)

Ab-initio studies of some actinide mono-nitrides under pressure

Ashok K. Verma

High Pressure and Synchrotron Radiation Physics Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

In recent years actinide mono-nitrides have been probed extensively because of their possible use as advanced fuels in the fourth generation nuclear reactors. In comparison to presently used oxide fuels, the nitride fuels have many superior properties: High thermal conductivity, high melting temperature, higher burn-up, easy re-processing and higher metal density.

A major advantage of ab-initio calculations is that they are entirely first-principles which, in principle, need only the atomic numbers as input. Starting with this limited information one can make detailed and quantitative predictions of various properties such as ground state volume, bulk modulus and its pressure derivative, equation-of-state, and phonon dispersion relations, etc.

In this talk we will present density functional theory based results of the electronic properties, phonon dispersion relations, elastic constants and structural phase transitions for mono-nitrides of thorium, protactinium and uranium under pressure. Though all these compounds crystallize in sodium chloride structure at ambient condition but their high pressure behaviour is found very different.

Email: hpps@barc.gov.in

High-Pressure phase transitions in multicomponent crystals of amino-acids: joint application of Raman spectroscopy and X-ray diffraction

B.A. Zakharov[a,b], E.A. Losev[a,b], B.A. Kolesov[b,c], E.V. Boldyreva[a,b]

[a]*Institute of Solid State Chemistry and Mechanochemistry SB RAS,* [b]*Novosibirsk State University,*
[c]*Institute of Inorganic Chemistry SB RAS, Novosibirsk, Russian Federation*
E-mail: b.zakharov@yahoo.com

Multicomponent crystals with components present in a well-defined stoichiometric ratio (salts and co-crystals) attract much attention. Multicomponent crystals containing amino-acids are of special interest for studies at non-ambient conditions. They are interesting for improving our understanding of factors determining the formation of a crystal structure and its variations *vs*. pressure, and are promising as new materials. A remarkable feature of most of these compounds is that very short O H...O hydrogen bonds are present in the crystal structures. The structure-forming units in these crystals are similar to those in biopolymers, therefore they can be used as biomimetics.

The main aim of this study was to follow the effect of increasing pressure on crystal structures of some selected multicomponent crystals of amino acids, such as *bis*(DL-serinium) oxalate dihydrate, DL-alaninium semi-oxalate monohydrate, and a co-crystal of glycine with glutaric acid. All these compounds were were shown to undergo phase transitions. They were studied at high pressures by X-ray diffraction and Raman spectroscopy to benefit from both techniques and their combination.

Bis(DL-serinium) oxalate dihydrate and a co-crystal of glycine with glutaric acid were shown to undergo phase transitions at high pressures (4.3 and 0.1 GPa respectively) with the formation of domains. Pressure-induced phase transitions were related to lowering the symmetry. High-pressure (0.1 GPa) and low-temperature (200 K) phases of glycine with a glutaric acid co-crystal were shown to have the same structures. During the phase transition in *bis*(DL-serinium) oxalate dihydrate, crystal structure was shown to disorder on increasing pressure, as was proven by Raman spectroscopy and confirmed by the appearance of diffuse scattering at diffraction patterns.

A single-crystal to single-crystal transition in DL-alaninium semi-oxalate monohydrate without changing a space group ($P2_1/c$) was detected at a pressure between 1.5 and 2.4 GPa. During the phase transition selected hydrogen bonds switch-over and become bifurcated, whereas the others are compressed continuously. The transition was accompanied by pronounced discontinuities in the changes of cell parameters and volume *vs*. pressure, although no radical changes in the molecular packing were induced and no crystal fragmentation was observed.

This work was supported by grants from RFBR (09-03-00451, 12-03-31541 mol_a), BRHE (RUX0-008-NO-06), by the Integration Projects Nos. 13 and 109 of the Siberian Branch of RAS (2009-2011), FASI Grants P2529 and 16.740.11.0166, by the Ministry of Education and Science of Russia (project 14.B37.21.1093), and by a grant of President of Russia for State support of Russian leading Scientific Schools (project NSh-221.2012.3).

[1] Zakharov, B.A., Losev, E.A., Boldyreva, E. V. (2013) *CrystEngComm* 15, 1693–1697
[2] Zakharov, B.A., Boldyreva, E. V. (2013) *Acta Cryst. B* 69, 271–280.

Keywords: phase transitions; amino-acid complexes; high pressure

Hydrogen bonds NH···N in compressed benzimidazole polymorphs

W. Zieliński and A. Katrusiak*

Faculty of Chemistry, Adam Mickiewicz University, Umultowska 89b, 61-614 Poznań, Poland

Compounds with switchable NH···N bonds are promising new ferroelectric and relaxor materials with desired dielectric properties.[1,2] Therefore the structure-property relation of NH···N bonds in different molecular environments are of primary importance for selecting chemical substances and engineering new materials of this kind. Molecular substitutes of ceramic ferroelectrics and relaxors are sought in connection to their envisaged improved characteristics – finer tuning of properties, easier production, deposition and utilization.

Two phase transitions in compressed benzimidazole (Figure 1) reveal a remarkable interplay of the H-site in NH···N hydrogen-bonded aggregates and the crystal structure. The ambient-pressure polar polymorph α, space group $Pna2_1$, at $p_1 = 0.26$ GPa transforms into centrosymmetric phase β, space group *Pccn*, and above $p_2 = 2.26$ GPa into another centrosymmetric polymorph γ, space group *Pbca*. Single crystals of forms α, β and γ have been *in-situ* grown in isothermal and isochoric conditions in a diamond-anvil cell and their structures determined by X-ray diffraction. Both at p_1 and p_2 the H-bond distance N···N increases in the higher-pressure phase. However, the H-atom always assumes the site for which the H···N distance in the homoconjugated NH···N bond is shorter.

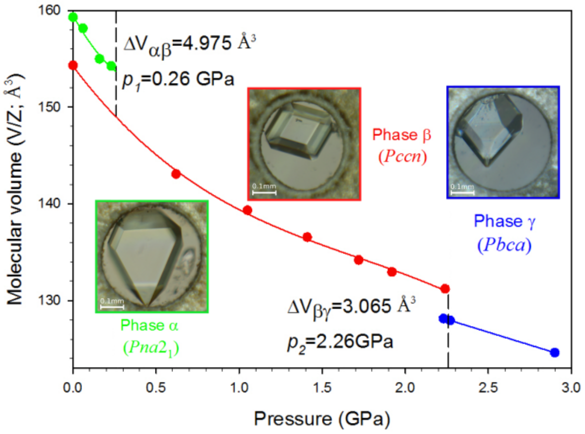


Figure 1: Pressure dependence of molecular volume (*V*/*Z*) in BzIm phases α, β and γ. The dashed lines indicate transition points p_1 and p_2 at 296 K observed in the compression runs. The insets show crystals *in-situ* grown in the DAC chamber (0.4 mm in diameter).

Acknowledgments

This study was supported by the TEAM 2009-4/6 grant of the Foundation for Polish Science.

References

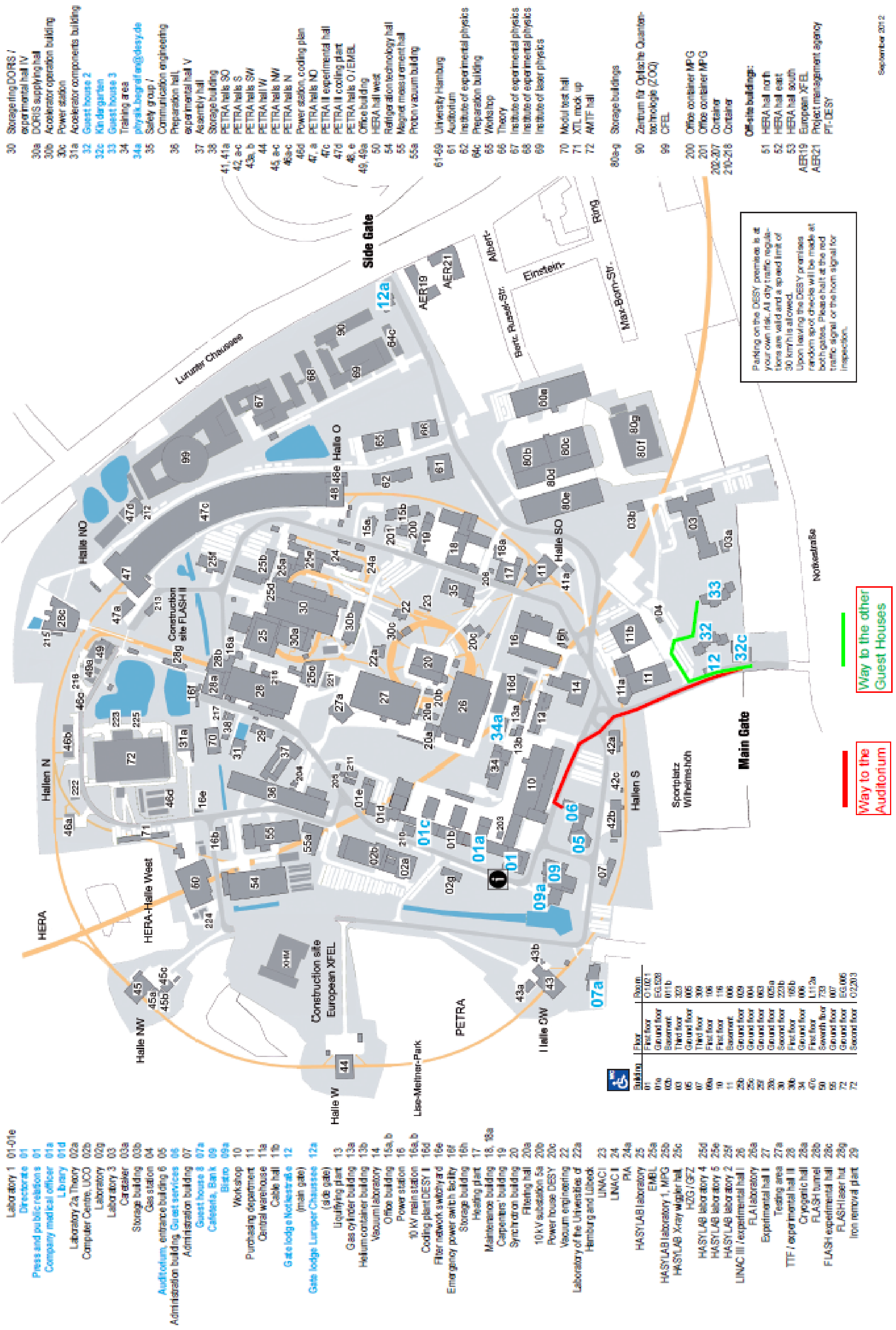
[1] M. Szafrański, A. Katrusiak, G. McIntyre, *Phys. Rev. Lett.*, **89**, 5507-5510 (2002).

[2] A. Katrusiak, M. Szafrański, *J. Am. Chem. Soc.*, **128**, 15775-15785 (2006).

* witar6@gmail.com

Notes

Map of DESY


Laboratory 1 01-01e
Directorate 01
Press and public relations 01
Company medical officer 01a
Library 01d
Laboratory 2a, Theory 02a
Computer Centre, UCO 02b
Laboratory 02g
Laboratory 3 03
Caretaker 03a
Storage building 03b
Gas station 04
Administration building 6 05
Auditorium, entrance building 06
Administration building, Guest services 06
Administration building 07
Guest house 8 07a
Cafeteria, Bank 09
Bistro 09a
Workshop 10
Purchasing department 11
Central warehouse 11a
Cable hall 11b
Gate lodge Notkestraße 12
(main gate)
Gate lodge Luruper Chaussee 12a
(side gate)
Liquifying plant 13
Gas cylinder building 13a
Helium container building 13b
Vacuum laboratory 14
Office building 15a,b
Power station 16
10 kV main station 16a,b
Cooling plant DESY II 16d
Filter network switchyard 16e
Emergency power switch facility 16f
Storage building 16h
Heating plant 17
Maintenance building 18, 18a
Carpenters' building 19
Synchrotron building 20
Filtering hall 20a
10 kV substation 5a 20b
Power house DESY 20c
Vacuum engineering 22
Laboratory of the Universities of Hamburg and Lübeck 22a
LINAC I 23
LINAC II 24
PIA 24a
HASYLAB laboratory 25
EMBL 25a
HASYLAB laboratory 1, MPG 25b
HASYLAB X-ray wiggler hall 25c
HZG / GFZ 25d
HASYLAB laboratory 4 25d
HASYLAB laboratory 5 25e
HASYLAB laboratory 2 25f
LINAC III / experimental hall 26
FLA laboratory 26a
Experimental hall II 27
Testing area 27a
TTF / experimental hall III 28
Cryogenic hall 28a
FLASH tunnel 28b
FLASH experimental hall 28c
FLASH laser hut 28g
Iron removal plant 29
30 Storage ring DORIS / experimental hall IV
30a DORIS supplying hall
30b Accelerator operation building
30c Power station
31a Accelerator components building
32 Guest house 2
32c Kindergarten
33 Guest house 3
34 Training area
34a physik.begreifen@desy.de
35 Safety group / Communication engineering
36 Preparation hall, experimental hall V
37 Assembly hall
38 Storage building
41, 41a PETRA halls SO
42 a-c PETRA halls S
43a, b PETRA halls SW
44 PETRA hall W
45 a-c PETRA halls NW
46a-c PETRA halls N
46d Power station, cooling plan
47, a PETRA halls NO
47c PETRA III experimental hall
47d PETRA III cooling plant
48, e PETRA halls O / EMBL
49, 49a Office building
50 HERA hall west
54 Refrigeration technology hall
55 Magnet measurement hall
55a Proton vacuum building
61-69 University Hamburg
61 Auditorium
62 Institute of experimental physics
64c Preparation building
65 Workshop
66 Theory
67 Institute of experimental physics
68 Institute of experimental physics
69 Institute of laser physics
70 Model test hall
71 XTL mock up
72 AMTF hall
80a-g Storage buildings
90 Zentrum für Optische Quantentechnologie (ZOQ)
99 CFEL
200 Office container MPG
201 Office container MPG
202-207 Container
210-218 Container
Off-site buildings:
51 HERA hall north
52 HERA hall east
53 HERA hall south
AER19 European XFEL
AER21 Project management agency PT-DESY
September 2012
Parking on the DESY premises is at your own risk. All city traffic regulations are valid and a speed limit of 30 km/h is allowed. Upon leaving the DESY premises random spot checks will be made at both gates. Please halt at the red traffic signal or the horn signal for inspection.
Way to the other Guest Houses
Way to the Auditorium
Luruper Chaussee
Side Gate
Main Gate
Notkestraße
Lise-Meitner-Park
Max-Born-Str.
Albert-Einstein-Ring
Bert.-Russell-Str.
Sportplatz Wilhelmshöh
Construction site European XFEL
Construction site FLASH II
HERA
PETRA
Halle N
Halle NO
Halle NW
Halle W
Halle OW
Halle O
Halle SO
Hallen S
HERA-Halle West
Building | Floor | Room

Further Information

Poster session:
The poster session will take place in the DESY canteen on Monday, 9th of September at 18.30 h.

Workshop Dinner:
The conference dinner will take place on the Alster River on Tuesday, 10th of September. There will be a shuttle from DESY to the harbor, starting at the DESY Auditorium (behind Bldg. 6) at 18.00 h.

W-Lan:
There is a special W-Lan for this workshop
Name/SSID: HIBEF
Key: AbciHunen8

Lunch:
Lunch will be provided in the tent in front of the Auditorium.

Cash machine:
There is a cash machine in Bldg. 9.

The following companies will exhibit at our conference

AdlOptica

Newport
Experience | Solutions

Sanchez Technologies
Thermodynamics & Core Analysis Laboratory Instruments

SYNTEK

Ocean Optics

Rigaku

STOE