L-33 **Saturday, 18.06., 9^{40} - 10^{20}**

Extended Abstract

Crystallography at high pressure using synchrotron radiation

M. Hanfland[1]*

[1]*European Synchrotron Radiation Facility, 71, avenue des Martyrs, CS 40220, 38043 Grenoble, France*

Keywords: high pressure, crystallography

*e-mail: hanfland@esrf.fr

ID09A was a state of the art high pressure diffraction beamline at the ESRF, carrying out monochromatic diffraction experiments with large area detectors. Powder and single crystal diffraction experiments could be performed at high pressures in diamond anvil cells, permitting accurate determination of crystallographic properties of the investigated samples. After more than 20 years of successful operation, ID09A has been closed in November 2015. It will be replaced by a new and improved beamline, ID15B.

X-ray source for ID15B will be the U20 in vacuum undulator from ID09A. The monochromator will be a horizontally diffracting nitrogen cooled Si (111) single bounce Bragg monochromator. ID15B will operate at a fixed angle with an energy of 30 keV. Experience with ID09A has shown, that 30 keV is well matched for high pressure diffraction experiments in DACs. Two transfocators with 200 μm diameter linear (1-D) beryllium compound refractive lenses for vertical and horizontal focussing, respectively, will provide a highly variable and very clean beam with an expected minimum spot size on the sample of less than 5 x 5 μm^2. The expected flux will be comparable to ID09A. The experimental setup, build mostly from components already in use on ID09A, will be located on an extremely stable granite table. Data will be collected with a MAR555 flat panel detector.

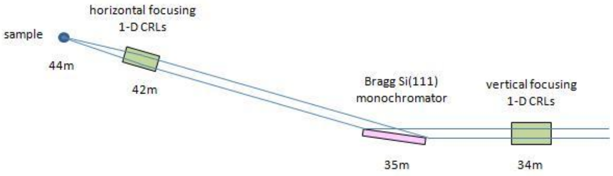

Figure 1. Optical layout of ID15B.

Recent technical advances have significantly added to the utility of single crystal X-ray diffraction experiments at high pressures [1]. New ways of supporting diamond anvils, like Boehler Almax anvils [2], have considerably increased the volume of accessible reciprocal space. Use of Helium or Neon as pressure transmitting medium extends substantially the practicable pressure range. Flat panel detectors have noticeably decreased the data collection time and increased the accuracy. Data can be collected at low and high temperatures. Even single crystal diffraction experiments with laser heating have become possible [3].

One system extensively studied with single crystal diffraction is arsenolite (As_4O_6) and its interaction with Helium. During a first experiment [4] we discovered that Helium can enter the molecular arsonolite crystal forming an intercalation compound with the stoichiometry As_4O_6 + 2He. The same type of reaction was observed independently in powder diffraction experiments [5]. To better understand the transformation more diffraction experiments on single crystals with ~25 μm diameter were performed. He penetration starts between 3 and 4 GPa and is complete after 2 days. Split reflections and changing intensity ratios indicate, that He is slowly infiltrating the crystal from the outside. During pressure release He leaves the arsenolite crystal at 3 GPa. The He discharge is fast.

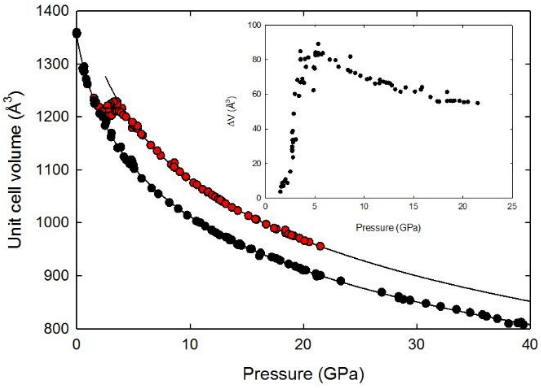

Figure 2. Volume of As_4O_6 (black dots) and As_4O_6 + 2He (red dots) as function of pressure. The insert shows the volume difference, decreasing from 80 $Å^3$ after complete intercalation at 5 GPa to 60 $Å^3$ at 20 GPa.

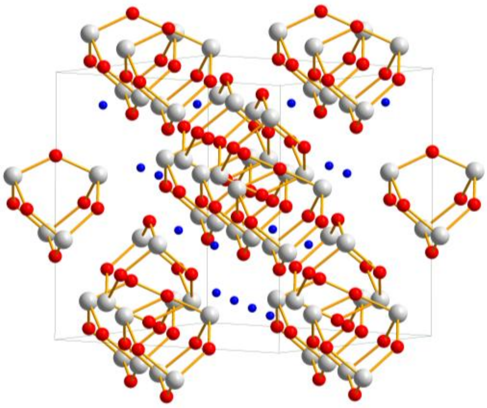

Figure 3. Structure of As_4O_6 + 2He at 11.6 GPa. The Helium atoms (blue) are in the 16c positions (origin choice 1, centre of the As_4O_6-molecules in the 8*b* positions).

The structure of the He intercalated arsenolite was determined from the single crystal data. He intercalated As_4O_6 remains cubic (S.G.: *Fd*-3*m*). Difference Fourier maps show, that the He atoms are located in the 16c positions. Refinement indicates, that the 16c positions are probably fully occupied confirming the As_4O_6 + 2He stoichiometry.

No penetration is observed with Neon as pressure transmitting medium. He infiltration can also be avoided by increasing the pressure rapidly to over 10 GPa permitting us to study the structural properties of arsenolite under quasi hydrostatic conditions to very high compressions. No structural transitions or signs of amorphisation were observed for pressures approaching 40 GPa.

Other systems extensively studied are superconducting radical cation salts derived from the donor molecule bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF, or ET for short) [6]. They constitute an important class of materials in the burgeoning field of molecular organic conductors. ET and iodine form a plethora of polymorphic phases, denoted by small Greek letters, the electrical conductivities of which range from semiconducting to metallic to superconducting.

One polymorphic phase is α-$(ET)_2I_3$, a prototypical organic metal, known to undergo a metal-insulator transition at 135 K. The transition can be suppressed by pressure. At ambient temperature we discovered a structural phase transition at ~13 GPa. The structure of the high pressure phase was determined from the single crystal data. During the transition α-ET_2I_3 remains triclinic (S.G.: R-1). The unit cell volume doubles. A small discontinuity indicates a first order phase transition. The most remarkable change is in the configuration of the triiodide molecules. Before the transition both I – I distances are equal and the molecule is straight. After the transition both I – I distances are considerably larger, they are no longer equal and the molecule is at an angle. No additional transitions or signs of amorphisation were found for pressures approaching 30 GPa.

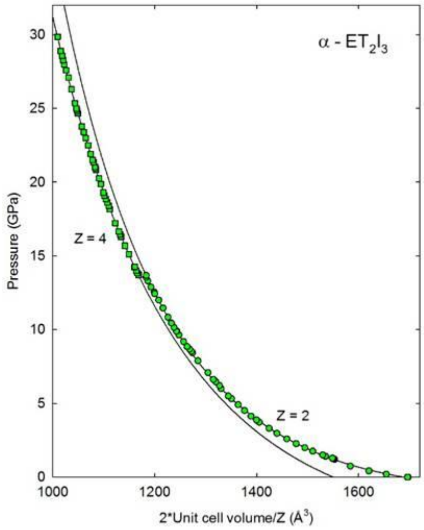

Figure 4. Equation of state of α-ET_2I_3. α-ET_2I_3 undergoes a structural phase transition at ~13 GPa with a doubling of the unit cell volume.

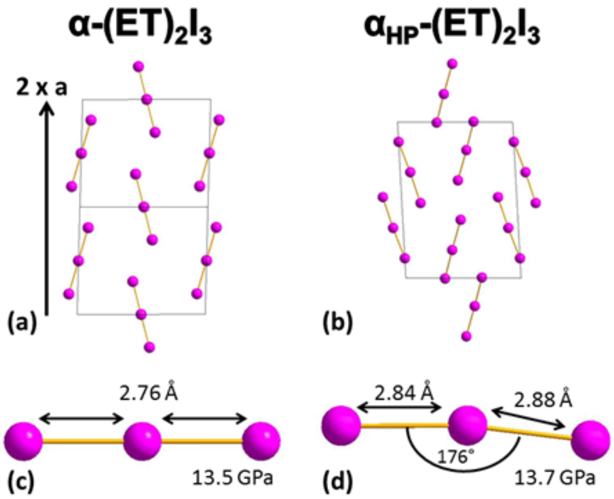

Figure 5. I_3 molecule before and after the phase transition. In the high pressure phase I – I bond lengths increase and the molecule is no longer symmetric.

Single crystal diffraction permits an exhaustive characterization of the structural changes under pressure. Molecules in certain molecular solids compressed with a quasihydrostatic pressure transmitting medium as shown here for As_4O_6 and bis(ethylenedithio)-tetrathiafulvalene can be surprisingly stable up to exceptionally high compressions.

Acknowledgments: Work done in collaboration with S. Brun and H. Müller. Arsenolite single crystals from P.A. Gunka.

---

[1] M. Merlini, M. Hanfland, *High Pressure Research* **33** (2013) 511.
[2] R. Boehler, K. DeHantsetters, *High Pressure Research* **24** (2004) 391.
[3] I. Kupenko, *et al, Review of Scientific Instruments* **83** (2012) 124501.
[4] P.A. Gunka, *et al., Crystal Growth & Design* **15** (2015) 3740.
[5] J.A. Sans, *et al.*, Physical Review B **93**, (2016) 054102.
[6] S. Brun - Études structurales des conducteurs organiques bidimensionnels à haute pression, PhD-thesis, Grenoble (2013).