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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:

https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Reports supporting requests for additional beam time

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** An X-Ray Diffraction Study on High Pressures 1D, Spin Driven Spatial Arrangements of O_2, Nano-Confined in a Zeolite.	**Experiment number**: **CH-5080**
Beamline: ID15B	**Date of experiment**: from: 03/05/2017 to: 06/05/2017	**Date of report**: 28/02/2018
Shifts: 9	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

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Report:

Scientific background :

Recently, we show that simple C bearing molecules can be packed in the nano-channels of pure SiO_2 zeolites at HP and polymerized under the sole effect of pressure and confinement [1-5], leading to novel nano-composites such as poly-(ethylene, acetylene and CO)/zeolite with potential remarkable physical properties. As host zeolites, we have used silicalite, with a 3D, interconnected channel system and TON which displays an entirely 1D channel system (pore diameter of 4.6Å×5.7Å) and led to form true 1D, unstrained, single embedded polymeric chains in the composites. We then moved to investigate HP 1D nano-phases of rare gases confined in TON [5,6]. In the case of Ne, Rietveld refinements of the crystal structure of TON indicate that 12 Ne atoms enter the unit cell of the zeolite completely filling the pores, in a disordered, liquid-like or glassy-like fashion. Also, the compressibility and structural distortions of the filled Ne TON at HP are considerably reduced as compared to the empty-pore TON zeolite. In addition, the crystalline form persists up to 20 GPa and is recovered after decompression. All these materials have been characterized by optical spectroscopy and synchrotron XRD. In particular, we always obtained very good Rietveld structural refinements of the zeolites, filled by low Z systems (Z=6, 8, 10), both in the recovered samples and at high pressures in diamond anvil cells (DACs), as reported in our many papers on this subject.

The principal aim of the present experiment was to investigate whether spin-spin (S=1) intermolecular interactions may lead to support 1D antiferromagnetic O_2 polymers or different 1D_arrangements of molecular clusters in dense oxygen, confined in TON, at pressures of 0.1-30 GPa. Our idea was based on the HP phase diagram of pure O_2 [7-9]. Solid O_2 displays layered antiferromagnetic phases up about 10 GPa at room T, the O_2 molecules being orthogonal to the layers. Above 7.5-10 GPa, depending on temperature, a low bandgap phase is formed, ε-O_2, with the molecules clustered into $(O_2)_4$ quartets [8,9]. Metallization then occurs at about 1 Mbar [7]. We have conducted several IR absorption and Raman spectroscopy measurements on a O_2/TON mixture, showing that indeed dense confined O_2 in TON mimics the very same behavior observed in bulk O_2 in this respect, above 10 GPa, i. e. it is observed clustering of the confined O_2 molecules

paralled by the quenching of the total spin of the cluster. The main goal of this synchrotron XRD experiment was to determine the resulting structure of 1D confined oxygen in TON, in combination with complementary information obtained from optical spectroscopy and spin dependent computer simulations. Of course, different spin-related spatial arrangements of confined O_2 may result over the entire pressure range of 0.1-30 GPa, which we want to investigate.

Experimental procedure:

Powder XRD has been performed in DACs on ID15B, with a monochromatic beam (λ=0.414132 Å) and a MAR555 flat panel detector. O_2 has been cryo-loaded in DACs together with TON powder, which has grain size of less than 1 μm. The average XRD pattern over a large number of grains has been measured, with a typical X-ray spot of 30 μm. Pressure has been measured using the ruby fluorescence method. We have used our own DACs along with ESRF-DACs. Pressure points have been obtained in O_2+TON at every 0.5 GPa from 0.1 to 20 GPa and then upon decreasing pressure, to check for pressure changes in the spin-spin driven 1D spatial arrangements of O_2 in TON. The diffraction patterns were analyzed and integrated using the FIT2D program. The Rietveld refinements were performed with the program Fullprof.

Preliminary Results:

In figure 1 we report a selection of XRD patterns on O_2+TON along a typical high pressure scan. The figure is zoomed on the most intense, low angle Bragg peaks of TON and the data shown are limited to below 10 GPa. XRD measurements are then available up to 20 GPa, while the quality of the diffraction pattern significantly decreases above 8-10 GPa, due to the spotty and overlapping Bragg peaks of bulk ε-O_2 along with this phase of bulk O_2, which also acts as the pressure transmitting medium (PTM), being highly not hydrostatic. Between 0.4 GPa and 1.0 GPa we observed the phase transition of the host TON framework from the *Cmc*2_1 to the *Pbn*2_1 structure with doubling of the primitive unit cell already found by us in TON with other PTMs [11]. Very high quality XRD pattern were obtained up to 6 GPa, above which pressure bulk O_2, the PTM, solidifies. In figure 2, we report a typical preliminary Rietveld refinements of the crystal structure of O_2 filled TON, at 3.0 GPa, indicating that 4 O_2 molecules enter the unit cell of TON completely filling the pores. Data analysis is still in progress. Monte Carlo modelling of the same O_2+TON system is also in progress within our group, which will constrain the experimental structural refinement as we already successfully tested on similar model mixtures such as Ne+TON and Ar+TON [5,6]. Even if structural refinements of the O_2+TON mixture above 10 GPa, where the O_2 clusters form, is expected to be very difficult, the full structural determinations at lower pressures will anyhow constrain the interpretation of spectroscopic data already available on the clusters.

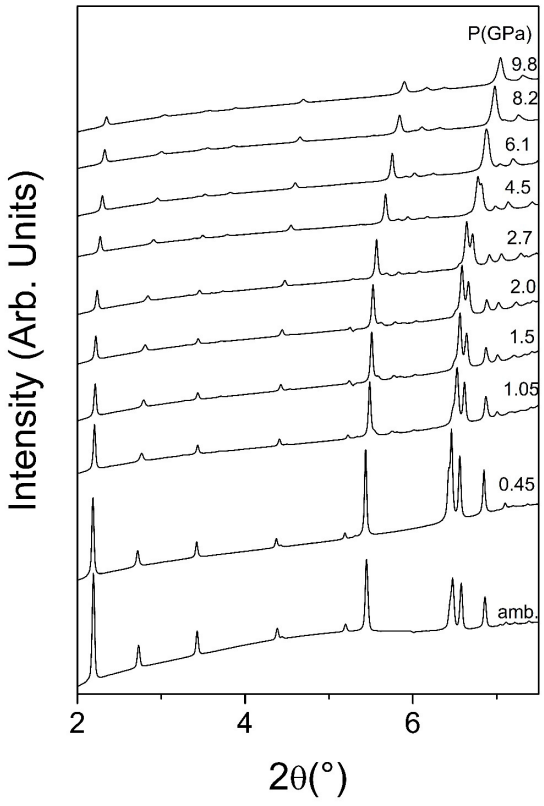

Fig. 1: selected XRD patterns of O_2+TON.

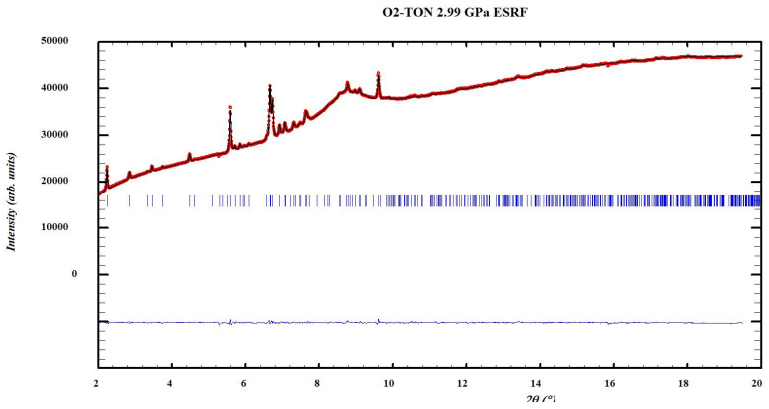

Fig. 2: Experimental, calculated and difference profiles from the Rietveld refinement of O_2+TON.

References

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