



Beamline: ID-27	Experiment title: Molecular-to-Atomic Transition in Solid Oxygen	Experiment number: HC-5076
	Date of experiment: from: December 1, 2022 to: December 5, 2022	Date of report: February 22, 2023
	Shifts: 12	Local contact(s): Mohamed Mezouar and Bjorn Wehinger
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Report

Introduction

As pressure increases, solid oxygen shows a wide range of physical properties [1]. In its ϵ -phase, which is stable from 9 to 96 GPa, oxygen molecules associate to form O_8 units. The $C2/m$ structure of O_8 oxygen was unveiled by single-crystal X-ray diffraction (XRD) [2]. Computational studies have found another chainlike structure to be energetically slightly more favourable than the O_8 -cluster structure [3]. At pressure above 96 GPa at room temperature, solid oxygen further transforms from the semiconducting ϵ -phase to the ζ -phase, still a molecular solid. The transition marks the closing of the semiconductor band gap [4]. The structural characterization of the metallic ζ -phase and the mechanism of the ϵ - to ζ -phase transition have been studied by single-crystal XRD [5], although they are not fully understood. And *ab initio* calculations predict the metallization at lower pressure than the structural changes. Calculations also suggest the possibility of two competitive lowest-enthalpy structures for the ζ -phase: one arranged in a chainlike herringbone structure and a second one with chainlike connections between O_8 units [3]. A complete structural determination is required to elucidate the nature of the ζ -phase. Addressing how interatomic bonding is affected and how crystalline phases develop upon further compression are bound to result in unexpected discoveries.

The objectives of this research proposal regarding dense solid oxygen were as follows: re-examine the structure of ϵ - O_2 and attempt to determine the structure of the ζ -phase, prevailing above 96 GPa. We also aimed at addressing other relevant questions: is the metallic phase of oxygen stable upon further densification? How does molecular bonding evolve and lead to yet unknown denser crystalline phases? Can the application of pressure lead to a molecular dissociation? We worked to resolve these research objectives by taking advantage of the upgraded capabilities of the ID27 High Pressure Beamline, by carrying out powder and single crystal X-ray microdiffraction to elucidate crystalline structures at extreme pressure conditions.

Experimental Details

Three gasketed diamond anvil cells capable of reaching pressures in excess of 100 GPa were loaded with mixtures consisting of an inert gas (Ne or He) and oxygen, with a maximum concentration of 20% oxygen. The intent was to obtain both polycrystalline (with Ne) as well as a single crystal sample (with He) of oxygen at high pressure following the reported procedure [5,6]. Micrograins of gold were used as the X-ray pressure calibrant using the accepted equation of state [7]. To improve the X-ray diffraction patterns recorded

upon compression, the samples were thermally annealed using the in situ near-IR laser heating system available at the beamline. X-ray diffraction patterns were recorded during heating to monitor any possible changes. After heating, taking advantage of the small beam (about $1 \times 1 \mu\text{m}^2$, with $\lambda = 0.3738 \text{ \AA}$) available at the ID-27 beamline, X-ray diffraction images were recorded mostly from single crystals, but also from polycrystalline samples, at different locations on a given sample according to a fine grid. XRD data were processed using several analysis X-ray diffraction software tools, including Dioptas [8], CrysAlisPro [9], VESTA [10], and Olex-2 [11].

Summary of Results

Oxygen mixed with Ne to produce fine polycrystalline samples, although laser heated at high pressure, did not yield XRD data suitable for atomic position refinement as anticipated. For this report, we thus concentrate on results achieved from a single crystal grown under pressure in He. From the X-ray diffraction images, the very good quality of the single crystal led to the confirmation of the crystalline structure of the ϵ -phase having a monoclinic unit cell (space group: $C2/m$) with eight oxygen molecules. Furthermore, the clustering of four molecules to form “ O_8 supramolecular units” was validated [2]. A refinement of the structure parameters in the ϵ -phase, carried out at each pressure up to 100 GPa, indicate a substantial decrease of the intermolecular distance in the O_8 units (d_1) as well a more pronounced change in the mean distance between the units (d_2). This latter observation indicates a tendency for an enhanced interaction between molecules nested in neighbour units. Our preliminary results show a slight but measurable decrease of the O-O distance ($d(\text{O-O})$) as the pressure approaches that of the transition to the ζ metallic phase. A larger uncertainty is likely on the highest-pressure data point and an estimate of $d(\text{O-O})$ is bound to be less accurate close to the transition pressure (100 GPa) given the deterioration of the X-ray diffraction recorded. Figure 1 summarizes our results. Beyond 100 GPa, pressures at which oxygen single crystals show the definite optical properties of a metallic state [4] (Fig. 2), we observed a significant degradation of the single crystals resulting from the displacive transition to the ζ -phase.

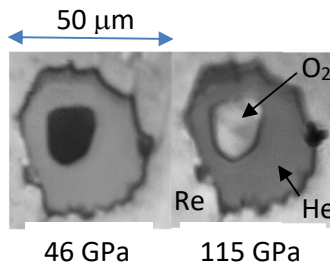


Fig. 2. Microphotographs of a single crystal of oxygen grown in He in a diamond anvil cell, shown at two different pressures, in the semiconducting ϵ -phase (46 GPa) and the metallic ζ -phase (115 GPa).

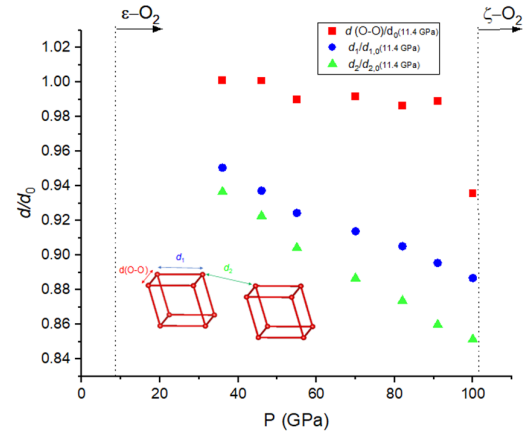


Fig. 1. Pressure-induced changes of the relative interatomic and intermolecular distances in the ϵ -phase of oxygen presenting “ O_8 supramolecular units”.

In fact, Bragg reflections, although sharp and well defined in the ϵ -phase, were more diffuse and smeared as recorded above 100 GPa, an indication of the increase of the crystal mosaicity and possibly residual strain. Annealing of the sample to improve the crystalline quality at elevated temperatures using laser heating above 100 GPa was not conclusive, at least with the use of minimal laser power incident on the crystal to avoid any further damage. Attempts to refine the crystalline structure of the ζ -phase to improve on the reported results [4] have proved not conclusive thus far. With the meaningful XRD results obtained close to the ϵ - ζ phase transition in oxygen reported here, however, we are confident that with our techniques to grow single crystals at high pressures, a major achievement by itself, the adjustment to our experimental protocol, and the use of the ID 27 extreme

conditions diffraction capabilities will soon lead to a definite crystalline structure solution of the ζ -phase of oxygen. Additional work on this project is underway.

References

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