ESRF

ESRF	**Experiment title**: Solid Oxygen at High Temperature and High Pressure: a Study of a New Crystalline Phase near the Melting Line by Single-Crystal X-ray Diffraction	**Experiment number**: HS2294
Beamline:	**Date of experiment**: from: November 22, 2004 to: November 25, 2004	**Date of report**:
Shifts:	**Local contact(s)**: Dr. Micheal Hanfland	*Received at ESRF:*

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Report:

Introduction

The magnetic moment of the O_2 molecule (S=1) and the resulting affinity to pairing, have been advanced to explain the rich phase diagram of solid oxygen under pressure and below 300 K in comparison to those of other solid molecular systems (e.g., H_2, N_2). Phases of solid oxygen at low temperature (T < 640K) and high pressures (P < 15 GPa) are well documented. In particular at 10 GPa and 300 K, solid oxygen transforms into a red-brown crystal with a monoclinic structure (space group: A2/m, Z=8): the ε-O_2 phase. Recently, the nature of the magnetic interaction and ordering has been demonstrated from neutron diffraction experiments [1]. Furthermore, the nature of chemical changes induced by pressure, the density effect with the formation of O_4 molecules [2] or collective effects with the formation of extended herringbone type chains [3], is still subject to discussion. At higher pressure, dense solid oxygen has been shown to undergo a semiconductor-to-metal transition [4] accompanied by a structural phase transition at 96 GPa [5, 6].

Recently, using Raman spectroscopy, we have identified a new phase of dense solid oxygen at high temperature and high pressure [7]. Although close to the ε-O_2 phase (Fig. 1), the new phase is distinct, as indicated by its light orange colour and by a discontinuity of the O-O stretching vibration frequency at the phase boundary. The primary goal of the HS-2294 experiment was to record X-ray diffraction images necessary to confirm the existence of the new phase of solid oxygen along the melting line and to solve its crystalline structure. The experiment was judged very challenging as it required the growth of excellent quality single crystals of oxygen in the proposed new phase, near the melting line at 750K and 22 GPa.

In order to (1) confirm the existence of the new phase of dense solid oxygen at high temperature, (2) determine its crystalline structure, (3) give insights on its relationship with neighbouring phases in the phase diagram near the melting line, (4) provide a determination of the volume discontinuity at the new phase and the ε-O_2 phase (5) provide a better understanding of molecular crystal growth habit at high temperature and high pressure, we had proposed to carry out X-ray diffraction using monochromatic synchrotron radiation on dense single crystals of oxygen maintained at high temperature and high pressure in diamond anvil cells. And, to maintain at high temperature and pressure the good crystallinity needed to carry out angle-dispersive X-ray diffraction using monochormatic synchrotron radiation, we had planned to slowly grow single crystals of oxygen from high temperature at high pressure across the melting line.

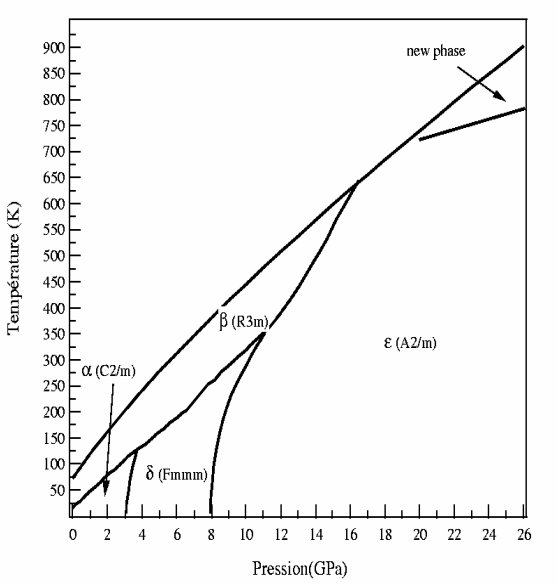

Fig. 1. The oxygen phase diagram. A new phase has been observed above 20 GPa and 750 K.

Experimental Method

Two membrane diamond anvil cells with high X-ray aperture ($2\theta_{max}$ = +/- 37 °, φ = 360°) and equipped with a Re resistance for internal heating were loaded at low temperature and ambient pressure in our laboratory with pure oxygen. To circumvent any possible reaction between the restraining gasket material (Re) and the hot and dense oxygen, the internal wall of the compression chamber was protected by a thin layer of gold. Because the sought-after phase is stable only at high temperature and high pressure, it was impossible to grow crystals prior to coming to the ESRF ID9 beamline. Hence, the crystal growth had to be carried out *in-situ* at the ID9 beamlime. Visual observations as well as angle dispersive X-ray diffraction at the ID9 beamline were used to assess the progress of the crystal growth in the appropiate phase. Pressure and temperature were measured by the temperature-corrected shift of the R-luminescence of ruby and by a thermocouple located close to the compression chamber, respectively. We performed angle dispersive X-ray diffraction with a focussed monochromatic beam at E = 33 keV. The X-ray diffraction images were collected with an on-line image plate detector (MAR 3450).

Results and Conclusion

Crystalline growth of O_2 single crystals was initiated in-situ at the ID9 beamline by decreasing T from ~ 800 K up to the melting line at 20 GPa. Angle dispersive X-ray diffraction was used to monitore the liquid-to-solid phase transition and the actual crystal growth at high temperature and high pressure. Unfortunately, our attempts with two different diamond anvil cells to achieve the growth of single crystals in the new phase at 750K and 22 GPa failed. The diffusion of hot oxygen in the diamond anvils resulting in the decrease of pressure and/or the possible reaction of oxygen with diamond or gold at the pressure-temperature conditions prevailing can be invoked as probable mechanisms for failure. We must emphasize the fact that the experiment was technically challenging. The use of the ID 9 beamline was essential to monitor the progress of the crystal growth and would had been imperative if single crystals of the new phase of oxygen had be obtained. The use of the ID 9 beamline was also very instrumental in assessing what should be done next to succeed. In that respect, we plan to pursue and complete our study of the new dense phases of solid oxygen.

References

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