



	Experiment title: Structure of low temperature solid oxygen under pressure.	Experiment number: HS 1135
Beamline: ID 9	Date of experiment: from: MAY 3, 2000 to: MAY 8, 2000	Date of report: 29.8.2000
Shifts:	Local contact(s): Michael Hanfland	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

*Lorenzo Ulivi, IEQ-CNR, via Panciatichi 56/30, 50127 Firenze, Italy

*Federico A. Gorelli, Dipartimento di Fisica, Università di Firenze, Largo E. Fermi 2, 50125 Firenze, Italy

*Mario Santoro, LENS, Università di Firenze, Largo Enrico Fermi, 2 50125 Firenze, Italy

Report:

Low temperature X ray diffraction measurements on pure oxygen at high pressure have been performed for the first time. The angle dispersive method, with monochromatic radiation, at a wavelength of 0.4161 Å, and image-plate detection was used. Pressure was generated in a membrane DAC and measured with the ruby fluorescence method. Low temperature was reached by the use of a helium flux cryostat opportunely modified for the DAC. We performed three isothermal pressure scans at 298, 152 and 85 K, and one isobaric heating cycle at 5 GPa. The analysis of the diffraction patterns furnishes useful elements for the study of the low temperature part of the phase diagram of oxygen, which has not been completely characterized up to now, but does not provide answers to many open questions.

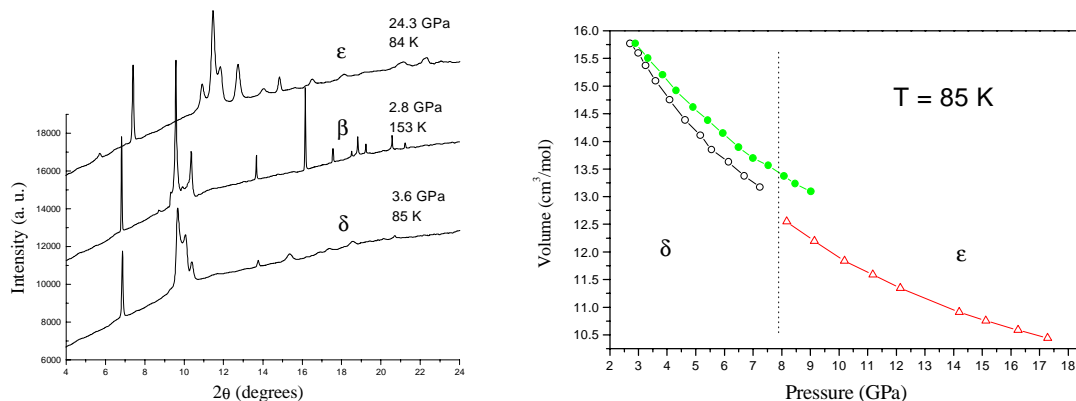


Figure 1a Diffraction patterns collected in the three phases studied. Spectra are shifted for clarity.

Figure 1b Equation of state at 85 K. Open and solid symbols represent measurements along decompression and compression runs respectively.

The cell was cryogenically loaded at ESRF with pure oxygen. Unfortunately the sample was never an ideal random powder in any of the solid phases studied. This strong preferred orientation and slightly non hydrostatic pressure condition did not allow a refinement of the data.

Three patterns, measured in the β , δ , and ϵ phases, are reported in figure 1a. The diffraction patterns relative to the ϵ phase can be indexed on the basis of a monoclinic cell with space group C2/m and eight molecules in the unit cell, accordingly with the proposed structure for this phase (Desgreniers et al., 1996). Similarly the data relative to the β phase indicate a rhombohedral structure with space group R-3m with three molecules in the unit cell in agreement with the previous studies at ambient pressure and low temperature (Donohue, 1974) as well as with the study at high pressure and ambient temperature (Schiferl et al., 1981).

On the contrary the diffraction patterns measured in the δ phase cannot be indexed with the proposed orthorhombic structure (Schiferl et al., 1983).

We have obtained a good agreement with a monoclinic structure C2/m with two molecules in the unit cell. This is the same structure as the one of the α phase, determined at lower pressures and temperatures. We think that the whole low temperature region of the phase diagram might be occupied by only one phase, the α phase. To establish this fact with certainty, new measurements at lower temperatures crossing the putative α - δ phase boundary (below 23 K) are needed.

The fact that the proposed structure for the δ phase is not correct may be due to the fact that previous measurements were done at room temperature where this phase exists only in a very small pressure range (about 0.5 GPa). Probably, three phases coexist at those pressure and temperature conditions.

The equation of state obtained at 85 and 152 K are reported in figures 1b and 2a. The values determined along decompression and compression runs are different, and are reported with open and full symbols respectively in figure 1b. This hysteresis may indicate the presence of non hydrostatic pressure conditions or of pressure gradients in the sample.

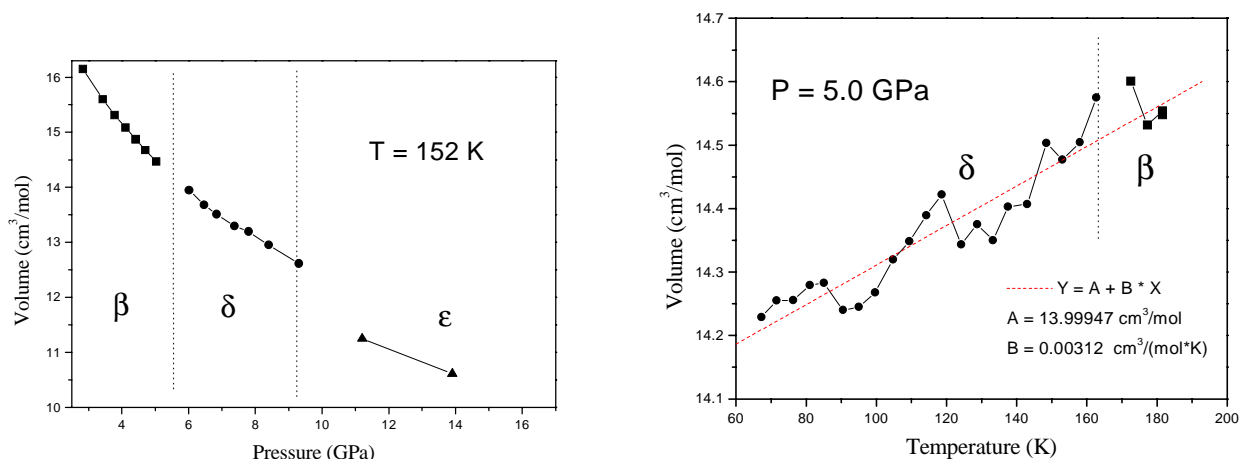


Figure 2a Equation of state at 152 K. Squares, circles and triangles represent the values of the volume in the β , δ and ϵ phases respectively.

Figure 2b Values of the molar volume obtained along the isobaric heating at 5.0 GPa.

In figure 2b the values of the volume obtained along the isobaric heating are reported. At this stage of the analysis the apparent thermal expansion may not be significant due to possible pressure instabilities and to uncertainty of the ruby scale as a function of temperature. In figures 2a and 2b no volume change can be measured at the β - δ phase transition, while a significant volume change is detected at the δ - ϵ phase transition (figures 1b and 2a).

S. Desgreniers, K. E. Brister, in *High Pressure Science and Technology*, ed. by .W.A. Trzeciakowski, p. 363, Word Scientific, Singapore (1996).

J. Donohue, *The Structures of the Elements*, New York, John Wiley (1974)

D. Schiferl, D. T. Cromer and R. L. Mills, *Acta Cryst.* **B37**, 1329 (1981)

D. Schiferl, D. T. Cromer, L. A. Schwalbe and R. L. Mills, *Acta Cryst.* **B39**, 153 (1983)