

# New insights on the possible crystalline structure of the metallic $\zeta$ phase of solid oxygen

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Solid oxygen has been shown, unlike nitrogen and hydrogen, to undergo a transition to a metallic state at a room temperature at 96 GPa [1,2]. The electronic transition to the metallic phase ( $\zeta$ -O<sub>2</sub>) is accompanied by a structural transition [3]. Weck *et al.* [4] have shown, by X-ray diffraction of single crystals, the displacive nature of planes of O<sub>2</sub> molecules initiated as the  $\varepsilon$ - $\zeta$ -O<sub>2</sub> transition takes place. Goncharov *et al.* [5] have reported a discontinuity of the Raman-active O<sub>2</sub> stretching vibration wavenumber, beyond the  $\varepsilon$ -O<sub>2</sub>/ $\zeta$ -O<sub>2</sub> phase boundary starting at 103 GPa, as an evidence that the  $\zeta$ -O<sub>2</sub> phase, although clearly molecular, is not isostructural to the  $\varepsilon$ -O<sub>2</sub> as speculated from earlier powder X-ray diffraction results [3]. To further elucidate the nature of the  $\zeta$ -O<sub>2</sub> phase, we have undertaken a study of dense solid oxygen under the best hydrostatic pressure conditions. In this presentation, we report recent results of X-ray diffraction and Raman spectroscopy experiments performed on single crystals of oxygen imbedded and oriented differently in solid helium, studied across the  $\varepsilon$ -O<sub>2</sub> to  $\zeta$ -O<sub>2</sub> phase line and beyond, to pressures close to 140 GPa. The successful growth of individual single crystals of oxygen in helium was based on the very low miscibility of liquid O<sub>2</sub> in liquid He at 450K and 22.5 GPa at a concentration of 2.5 mol % of O<sub>2</sub>. Under those conditions and upon cooling or pressure increase, the phase segregated liquid oxygen transformed into the pure solid  $\varepsilon$ -O<sub>2</sub> phase, resulting in good quality single crystals. Pressures were calculated using the calibrated spectral shift of the ruby luminescence R-lines, well resolved at all pressures. X-ray diffraction images recorded from single crystals in the  $\zeta$ -O<sub>2</sub> phase, in different orientations, indicate most likely a crystalline structure different from that of the  $\varepsilon$ -O<sub>2</sub> phase. The  $\zeta$ -O<sub>2</sub> phase is characterized by the occurrence of a significant lattice plane stacking fault arrangement resulting in large Bragg peak shifts. Furthermore, our Raman spectroscopic results indicate, in agreement with those published [5], a significant decrease of the O<sub>2</sub> stretching vibration wavenumber at 103 GPa with respect of that extrapolated from the  $\varepsilon$ -O<sub>2</sub> phase and, in addition, the appearance of a second Raman-active line at a wavenumber slightly above the former. The increase of pressure induced a gradual splitting between the stretching vibration wavenumbers in the  $\zeta$ -O<sub>2</sub> phase.

## References

- [1] - S. Desgreniers, Y. K. Vohra, and A. L. Ruoff, J. Phys. Chem. 1990, **94**, 1117-1122.
- [2] - K. Shimizu *et al.*, Nature, 1998, **393**, 767-769.
- [3] - Y. Akahama *et al.*, Phys. Rev. Lett., 1995, **74**, 4690-4.
- [4] - G. Weck, P. Loubeyre, and R. Le Toullec. Phys. Rev. Lett., 2002, **88**, 035504/1-4.
- [5] - A. F. Goncharov, E. Gregoryanz, R. J. Hemley, and H-k. Mao. Phys. Rev. B., 2003, **68**, 100102/1-3.