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On the Nature of Solid Oxygen Beyond the ε–ζ Phase Transition

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Summary

Solid oxygen has been shown, unlike nitrogen and hydrogen, to undergo a transition to a metallic state at room temperature at 96 GPa. The understanding of the mechanism of this insulator-metal phase transition is still controversial. The electronic transition to the metallic phase (ζ-O_2) was first shown to be accompanied by an iso-structural transition. Weck *et al. (2002)* have then shown, by single crystal X-ray diffraction, that the transition is not isostructural but of a displacive nature within the molecular plane of the ε-O_2 phase; the single crystal is even re-constructed above 110 GPa. However the structure of the (ζ-O_2) phase could not be refined. Yet, it has been shown that the x-ray data were not compatible with the various theoretical predictions. Furthermore, it was shown that metal oxygen is molecular but the magnitude of the wavenumber discontinuity of the vibron at the ε-ζ transition differs between the two Raman spectroscopy studies.

To further elucidate the nature of the ζ-O_2 phase, we have undertaken a study of dense solid oxygen under the best hydrostatic pressure conditions. In this communication, we report recent results of Raman spectroscopy experiments carried out on single crystals of oxygen imbedded and oriented differently in solid helium, across the ε-O_2 to ζ-O_2 phase transition and beyond, to pressures close to 140 GPa. Our results indicate, in agreement with those published [5], a significant decrease of the O_2 stretching vibration wavenumber at 103 GPa with respect of that extrapolated from the ε-O_2 phase and, in contrast, the appearance of a second Raman-active line at a wavenumber slightly above the former. The increase of pressure induces a gradual splitting between the vibron wavenumbers. We tentatively associate our observation with the displacive structural transition observed by X-ray diffraction. Finally, we report recent single crystal X-ray diffraction data, obtained at the ESRF.

Introduction

Desgreniers *et al.* (1990) first indicated a transition above 96 GPa from a semiconducting to a metallic state in solid oxygen based on the changes of its optical properties measured to 132 GPa. Shimizu *et al.* (1998) provided, from electrical transport measurements, a definite proof that indeed the ε-O_2 phase underwent a transition to a metallic state, which was also shown to be superconducting. Akahama and co-workers (1995) infered from X-ray diffraction of polycrystalline samples the onset of an isostructural transition at 96 GPa from the ε-O_2 phase to the new ζ phase. For the lack of well resolved X-ray diffraction patterns, mostly due to non-hydrostatic conditions on polycrystalline oxygen samples, no definite crystalline structure was proposed for the ζ phase. Successful growth of single crystals of oxygen imbedded in helium for compression under the best hydrostatic conditions to pressures above 100 GPa gave the opportunity to Weck *et al.* (2002) to carry out energy dispersive X-ray diffraction. Clear changes were detected across the ε-ζ phase transition; the authors concluded that the metallization is associated with a continuous displacive structural transformation taking place for pressures in excess of 96 GPa.

The evolution with increasing pressure of the molecular stretching vibration (vibron) provides an indication of the persistent molecular nature of the ε-O_2 phase. It has been shown in earlier studies (Akahama 1996, Weck 2002) that the raise of pressure induces a steady increase of the vibron energy in the semiconducting ε-O_2 phase, known to be stable to 96 GPa from X-ray diffraction studies, as previously noted. Goncharov *et al.* (2003) recently showed that the steady increase of the oxygen molecular stretching energy in the ε-O_2 phase, was followed by a discontinuous change in the vibron wavenumber in the pressure range between 96 and 120 GPa. Changes in the lattice modes of vibration were also observed with the occurrence of additional Raman-active lines corresponding to the ζ phase. It was thus concluded that the transition from the ε to the ζ phase is not isostructural and in fact must be of first order.

To further elucidate the transition from the ε to the ζ phases and the nature of the latter phase, we undertook a study of dense solid oxygen under the hydrostatic pressure conditions. We have focused on Raman spectroscopy and X-ray diffraction of oriented single crystals of oxygen imbedded in helium, to achieve indeed the best hydrostatic conditions to pressures in excess of 100 GPa.

Experimental Method

Single crystals of oxygen were grown in helium using membrane diamond anvil cells equipped with low fluorescing natural diamonds (culet diameter of 300 μm beveled by 7° to 100 μm flat) and Re gaskets. The successful growth of individual single crystals of oxygen in helium was based on the very low miscibility of liquid O_2 in liquid He at 450K and 22.5 GPa with a concentration of 2.5 mol % of O_2 (Weck 2001). Under those conditions and upon cooling or compression, the phase segregated liquid oxygen transformed into a single crystal in the pure ε-O_2 phase. As a function of pressure, below, across, and above the metallic (ε–ζ phase) transition, we have studied three different single crystals, oriented differently with respect to the diamond anvil culets. Two crystals (crystals 2 and 3) presented an orthogonal direction with respect to the third one (crystal 1). Raman spectra were recorded with increasing and decreasing pressures using a Dilor XY triple subtractive spectrograph equipped with a cooled CCD detector in a near-back scattering geometry. Most Raman spectra were recorded with an excitation from the Kr^+ laser tuned to 647.1 nm. Additional spectra were also obtained with the 514.5 nm Ar^+ laser line and at 532.1 nm from a frequency-doubled diode pumped Nd:YAG laser. No heating resulting for laser illumination was recorded, as verified by the absence of additional Raman shifts as a function of laser power. We estimated the spectral resolution (instrumental) to be within 1 cm^{-1}. At all pressures, we recorded well resolved R-lines of $Al_2O_3:Cr^{3+}$, used as the pressure gauge using the quasi-hydrostatic calibration at 300K (Mao 1986). Figure 1 illustrates an example of $Al_2O_3:Cr^{3+}$ luminescence recorded, in this case, at 119 GPa. Given the very good quality of the luminescence spectra recorded from the optical pressure gauge, the uncertainty in

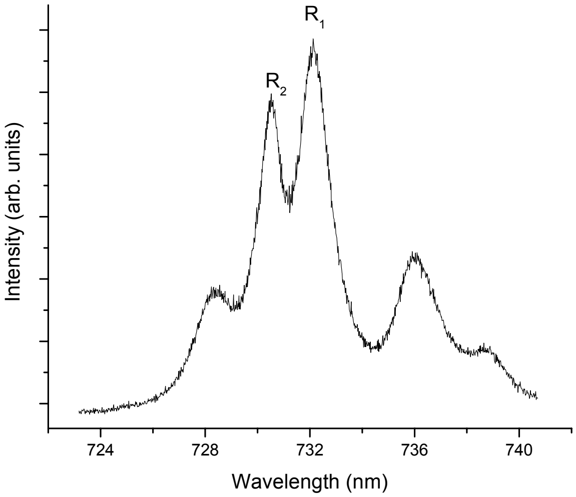

Fig. 1. Photoluminescence of a 7 μm sphere of $Al_2O_3:Cr^{3+}$ in solid helium, recorded at high pressure, namely, 119 GPa. The luminescence is excited at λ_{laser} = 647.1 nm. The pressure is estimated at 300K using the hydrostatic pressure calibration (Datchi 1997). The R_1 and R_2 lines of $Al_2O_3:Cr^{3+}$ were well resolved at all pressures in this study. Other lines are also from $Al_2O_3:Cr^{3+}$.

pressure was mainly related to the R-line shift calibration with pressure rather than the spectral determination of the R_1 wavelength.

X-ray diffraction on the single crystals grown for Raman spectroscopy was also carried out. X-ray diffraction images were recorded at ESRF ID30 and ID09 beam lines using focused X-ray beams at λ = 0.3738 Å and a MAR3450 imaging plate detector. X-ray diffraction images were processed with FIT2D (ESRF).

Results and Discussion

The anisotropic optical properties of solid oxygen in the δ- and ε-phase, arising from planes of aligned molecules, are well known (Desgreniers 1990). Among the three single crystals grown for the present study, one sample (crystal 1) was oriented approximately orthogonal to the other two crystals (2 and 3), as judged by their absorption of visible light at pressure around 15 GPa. Consequently, we were able to record as a function of pressure the Raman spectra from orthogonal crystalline faces and hence to characterize any possible arising differences. It must be emphasized that all single crystals were grown in He starting with the same O_2 concentration and using the same procedure.

Although the level of Raman light signal with respect to the background degraded as a function of pressure, due to the photoluminescence arising from the diamond anvils and the higher sample reflectivity both significantly increased with pressure, we could nevertheless measure Raman shifts corresponding to the molecular vibration up to 140 GPa. Figure 2 illustrates the change of vibron energies (wavenumbers) below and across the ε–ζ phase line for the three different crystals. The data were recorded with decreasing pressures from 140 GPa for crystal 1 whereas, for crystals 2 and 3, data were obtained for increasing pressures. From the present results, it is first noted that over the field of stability of the ε-phase, the linear change of Raman shift with pressure recorded from our three single crystals, is in agreement with previous reports (Akahama 1996, Weck 2002, Goncharov, 2003). We have observed, however, marked differences between the two crystalline orientations, in the metallic ζ phase beyond the transition pressure of 96 GPa. Upon pressure decrease from 140 GPa to 90 GPa, for crystal 1, the Raman signal was observed as a single line which followed, within the uncertainty of our data points, the pressure dependence of that recorded for the ε phase. As such, solid oxygen probed in this given orientation did not present any discontinuity in the Raman active vibron across the ε–ζ phase transition.

For crystals 2 and 3, upon pressure increase from the ε phase, we observed a splitting of the vibron wavenumber, as shown in Fig. 2. The splitting was clearly noticeable for pressures above 105 GPa, i.e. beyond the pressure corresponding to the ε–ζ phase transition. It is not ruled out that the occurrence of two Raman lines started from 96 GPa, i.e., at the accepted ε–ζ phase transition pressure; the present data do not have the necessary resolution to confirm it. The two observed Raman lines departed from the single vibron peak obtained from crystal 1 to the lower and higher wavenumber sides. At the highest pressure reached on crystal 2, i.e., 119 GPa, the two Raman-active lines were separated by approximately 24 cm^{-1} (~ 1.3%). Goncharov *et al.* (2003) reported a gradual change in the vibron wavenumber across the ε–ζ phase transition in a polycrystalline oxygen sample leading to lower values as compared to those extrapolated from the ε phase, as shown in Fig. 2. The change of the vibron wavenumber was accompanied with the occurrence of new lower wavenumber vibrational modes associated with the ζ phase for pressures above 105 GPa and coexisting with those corresponding to the ε phase up to about 130 GPa (Goncharov 2003). It was thus concluded that the ε–ζ phase transition that takes place between 90 and 120 GPa is structural and first order, the ε and ζ phases coexist from 96 to 130 GPa perhaps due to pressure gradients. Our Raman spectroscopic results obtained under hydrostatic conditions did not show an obvious discontinuous change in the vibron wavenumber at 96 GPa, i.e at the semiconductor-metal transition pressure (note: a clear change in the single crystal reflectivity was observed at 96 GPa as a definite indication of the onset of the metallic state, as reported in all previous studies). The vibron wavenumber continued its progression upon pressure increase beyond 96 GPa. At around 105 GPa, we did observe a Raman line broadening followed by a further splitting of the vibron upon pressure increase. We are led to advance the possibility that oxygen transits from a semiconductor state, the ε-O_2 phase, to a metallic state and further undergoes a structural phase transition, the ζ-O_2 phase, with a different crystalline structure. As reported by Weck *et al.* (2002), the ζ-O_2 phase could result from a displacement of lattice planes and lead to a situation of non-equivalent molecular sites that gives rise to the splitting of the molecular stretching energies. It stands to reason to further conclude that ζ phase corresponds to a different crystalline structure with, however, still a definite molecular character as compared to the ε-O_2 phase.

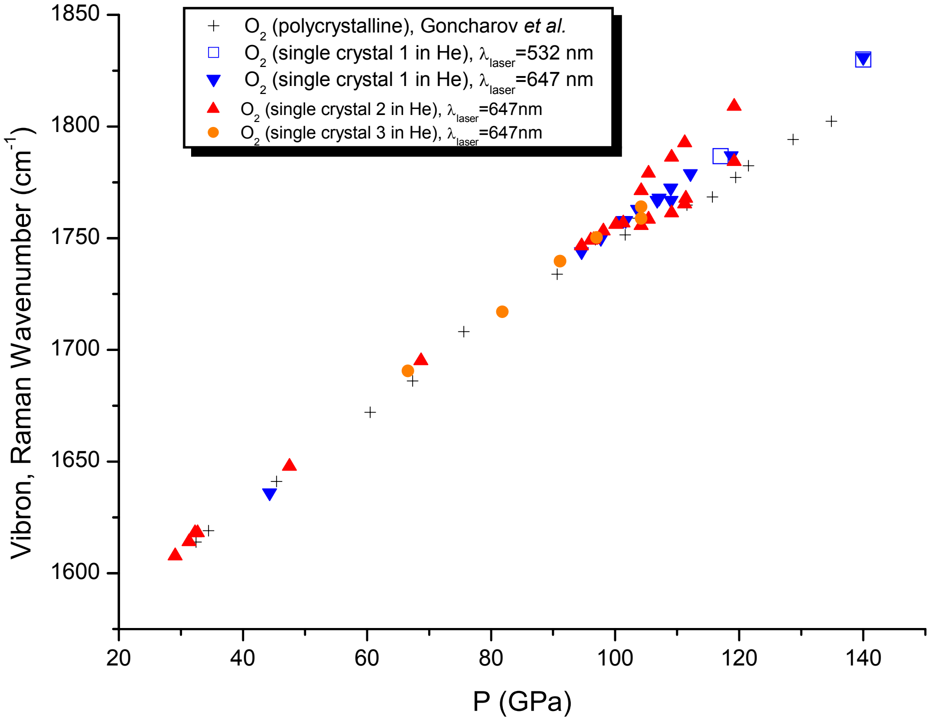

Fig. 2 Raman wavenumber shifts of oxygen stretching mode(s) as a function of pressure at room temperature. Results plotted for three different crystals (solid symbols) are presented along with similar data reported by Goncharov *et al.* (2003) (+). Open symbols are data points obtained with λ_{laser} = 532.1 nm for single crystal 1.

To further characterize the nature of the ζ phase, especially its crystalline structure, we have carried out X-ray diffraction on the same single crystals grown for the Raman spectroscopy experiments. Given the fixed single crystal orientations and the limited reciprocal space accessible through the diamond anvil cells used to attain pressures above 100 GPa, we have yet to converge to a definite crystalline structure for the ζ-O_2 phase. Nevertheless, our results have confirmed the occurrence of a different crystalline structure for pressures above the stability field of the ε-O_2 phase. Further experiments are planned with different single crystal orientations with respect to the diamond anvil cell geometry to achieve more complete X-ray diffraction data sets.

Conclusion

Given the important fact that our Raman spectroscopic data were obtained from single crystals under the best hydrostatic conditions, we offer the following conclusions: (1) we have observed no noticeable discontinuity of the vibron wavenumber at the semiconductor-metal transition that takes place at 96 GPa; (2) the splitting of the vibron wavenumber which starts at around 105 GPa could correspond to a structural phase transition across the ε–ζ phase line (3) the ε–ζ phase transition is not isostructural and the fact that we have observed a splitting of the molecular stretching vibration as a function of pressure substantiates the displacive nature of the ε–ζ phase transition as reported by Weck (2002) (4) the molecular character is preserved in the ζ phase. Finally, X-ray diffraction experiments on single crystals of oxygen in He submitted to pressures above 100 GPa are underway to elucidate the structure of ζ-O_2 .

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