

Observation of Structural Transformations in Metal Oxygen

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X-ray diffraction and Raman measurements have been performed on solid oxygen up to, respectively, 115 and 120 GPa. Metallization at 96 GPa is shown to be associated with a continuous displacive structural transformation. At 110 GPa, a new structure is stabilized. The evolution of the vibron mode reflects also the sequence of phase transitions through the continuity of the vibron frequency at 96 GPa, then the broadening of the vibron peak into the background and finally the reappearance of a sharp vibron at 110 GPa with a -2.5% discontinuity in the frequency. The observation of the vibron peak demonstrates that metallic oxygen is molecular up to at least 120 GPa.

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The general trend of the evolution with pressure of simple molecular solids has been known since the 1930s: Electrons tend toward states of lower kinetic energy destabilizing intramolecular bonds and favoring metallic states. An understanding of this evolution under pressure is still incomplete and therefore this motivates a great current interest. Because of their simple electronic structures, homonuclear diatomic molecular solids of hydrogen, oxygen, and nitrogen are reference experimental systems and their pressure-induced metallization has been actively searched and studied. Neither the metallization of solid H_2 nor that of solid N_2 has been observed up to 350 GPa [1] and 250 GPa [2], respectively. On the other hand, the metallization of solid O_2 was first observed with the increase in the near infrared reflectivity of solid O_2 above 96 GPa that was attributed to the creation of nearly free electrons by pressure-induced band overlap [3]. Metallization was confirmed with electrical measurements that show a change of slope in the resistance-temperature curve at around 96 GPa [4]. Furthermore, superconductivity has been observed near 100 GPa with a transition temperature of 0.6 K. In this context, the understanding of the mechanism of the insulator-metal phase transition in solid O_2 is a central issue. In particular, two important questions remain: Is metallization associated with a first order structural transition? Is there a strong weakening or even a dissociation of the molecular bond at metallization? The aim of this Letter is to provide clear answers.

Many studies have already been devoted to the phase diagram of oxygen because it results from the interplay between magnetic order (the O_2 molecule is in a triplet state and remains magnetic at moderate pressure), efficient packing, and pressure-induced electronic changes. The oxygen molecules oriented perpendicular to planes are common to most phases of solid O_2 . Above 10 GPa at room temperature, solid O_2 transforms to the ϵ phase. From single-crystal analysis, the space group $A2/m$ with eight molecules in the unit cell has been proposed, but the exact atomic positions have still not been determined [5]. From angle dispersive powder x-ray diffraction (ADX), it

was proposed that the metallization of oxygen was associated with an isostructural transition from the monoclinic ϵ phase to a new ζ phase with a discontinuous change in lattice constants [6]. The vibron mode of O_2 has been measured up to 94 GPa by Raman scattering [7] and 92 GPa by infrared absorption [8]. No sign of the softening of the molecular bond could be inferred from the evolution of the vibron frequency with pressure. However, there has been no experimental evidence that the molecular bond remains in the metallic phase.

The present investigation of the insulator-metal phase transition in oxygen was made possible by exploiting the topology of the phase separation of O_2/He and O_2/Ne mixtures. The binary phase diagrams of O_2/He and O_2/Ne mixtures have been studied in detail and will be published elsewhere. The important point here is that above 10 GPa the miscibility of He or Ne in solid O_2 is very small (less than our limit of detection, 0.5 mol %). Also, we checked that we were measuring exactly the same properties in the ϵ phase for the oxygen solids embedded in rare gases (He or Ne) as with pure samples. Single crystals were slowly grown from a 2.6 mol % O_2 in the He sample at 450 K and 22.5 GPa, hence in the ϵ phase (corresponding to 30% volume O_2 oxygen in helium). On the other hand, O_2 and Ne are totally miscible in the fluid phase and completely phase separate in the solid above 7 GPa. Therefore, rapidly increasing pressure in an O_2/Ne mixture gives a fine mixed powder of O_2 crystals and Ne crystals, of about 1 μm size. Raman measurements in the Mbar range were performed in a 5.6 mol % O_2 mixture (corresponding to a 10 vol % O_2 in Ne). Experiments were performed in membrane diamond anvil cells [9], equipped with boron seats for the single-crystal x-ray diffraction measurements. In these experiments, beveled diamond anvils with 150 μm flats were used and that limits the present investigation to about 120 GPa. A high pressure loading technique (under 120 MPa) at room temperature was used. Pressure was measured using the $SrB_4O_7:Sm^{2+}$ and ruby luminescence gauges [10] with an error $< \pm 0.4$ GPa.

The technique to obtain accurate structural data on low- Z systems at Mbar pressure is based on a single-crystal energy dispersive x-ray diffraction technique employing the high brilliance of wiggler beams at the European Synchrotron Research Facility (ESRF), as previously reported on H_2 [11] and on H_2O [12]. The following features of this technique were seen to be essential to resolve the structural mechanism at the insulator-metal transition: (i) Only one reflection and its harmonics are obtained for a given orientation of the crystal, hence giving well resolved peaks; (ii) the position of the reflections in the reciprocal space are obtained through the orientation of the crystal in diffraction conditions. Therefore, sliding of planes can be observed and crossing of d spacings easily detected. Also, this complements the d spacings to constrain the structural refinement. (iii) Strains in the crystal can be finely detected through the variation of the d spacing of the reflections of a same class. Three single crystals grown in helium with different orientations were studied. Two experiments could be extended above 96 GPa. The helium cushion provides the best hydrostatic medium under pressure. Still, the single crystal deteriorates under pressure essentially up to 50 GPa (the width of the rocking curves increased from 0.1° to $\sim 1^\circ$) and then its quality remains constant. For each crystal, the reflections were related by the orientation matrix of the monoclinic unit cell and observed extinctions satisfy the $A2/m$ structure with $Z = 8$ [5]. In the first experiment, seven different diffraction lines and associated harmonics were followed within the x-ray aperture of the diamond anvil cell: $[(013), (0-3-1), (004), (2-22), (0-2-2), (-122), (02-2)]$. The orientation of the second crystal enabled the observation of the (100) reflection. Six diffraction lines were followed: $[(013), (22-2), (002), (100), (-122), (0-2-2)]$. At

each pressure, an unconstrained least squares fit gives the obtained monoclinic cell, as illustrated in Table I (upper panel) with the results at 96 GPa. No strain in the crystal was measured. The pressure-volume data obtained here are in good agreement with previous determinations. But fine effects are revealed. As seen in Fig. 1, at around 50 GPa, we observe the crossing of d_{0-2-2} with d_{013} and d_{0-3-1} with d_{004} . This crossing explains a slight different evolution of the lattice parameters of the ϵ phase than with ADX [6]. As reported in Fig. 2 the intraplanar compressibility (b and c axes) is seen to be greater than the interplanar one and above 30 GPa, the b axis becomes more compressible than the c axis.

Above 95 GPa, clear changes are detected in the diffraction data. The (013), (0-3-1), (002), (2-22), (22-2) reflections gradually disappear and are no more observable above 101 GPa. No discontinuity is observed for the d spacing at 96 GPa (see Fig. 1) and the monoclinic cell can be refined up to 101 GPa. But, as seen in Fig. 2, a change in the pressure evolution of the lattice parameters is observed. The change of the reflections in the reciprocal space was measured by the rocking curves. At 101 GPa, the (0-2-2), (-122) reflexions undergo strong variations of their d spacings and diffraction angles. On the other hand, the d_{100} shows only a slight change and keeps the same diffraction angles. The measurement of the rocking curve of the (0-2-2) in the transition region is presented in Fig. 3a. At 98 GPa, the rocking curve starts to spread continuously with pressure, indicating a change in the mosaicity of the crystal, but at 110 GPa the rocking curve is centered again around a new value indicating the reformation of the single crystal. At 110 GPa, a new structure is stabilized with discontinuous change in the d spacing, degeneracy lift (the d_{0-2-2} and d_{02-2} are split), and new position of the reflections in the

TABLE I. Single crystal diffraction data of oxygen solid. Upper panel: at 96 GPa in the first experiment, the unit cell refined is monoclinic ($Z = 8$) with the lattice constant $a = 3.297$ (± 0.013) \AA , $b = 4.654$ (± 0.008) \AA , $c = 6.886$ (± 0.012) \AA , $\beta = 114.9^\circ$ (± 0.14). The values in parentheses are calculated from the orientation matrix. Lower panel: at 110 GPa, a summary of the two runs [the diffraction angles for the peaks (100), (0-2-2), and (-122) of the second experiment have been recalculated to match the first experiment]. The uncertainty on ω and χ is about $\pm 1^\circ$ for (-122) and (022).

hkl	d (\AA)	ω ($^\circ$)	χ ($^\circ$)
002	3.123 (3.1243)	-11.3 (-11.3)	-142 (-142)
013	1.9014 (1.9011)	-0.74 (-0.81)	-120 (-120.14)
0-2-2	1.8654 (1.8659)	-11.4 (-11.9)	86.4 (86.34)
-122	1.7969 (1.7994)	-14.1 (-13.84)	-68.9 (-68.86)
0-3-1	1.5067 (1.5053)	-20 (-20.13)	108 (108.43)
2-22	1.0461 (1.04577)	15.5 (15.227)	174 (173.97)
hkl	d (\AA)	ω ($^\circ$)	χ ($^\circ$)
100	2.9858	38.63	-175.02
02-2	1.8444	19	-15.3
0-2-2	1.7819	-6.6	85.5
-122	1.6946	-14.8	-67.5

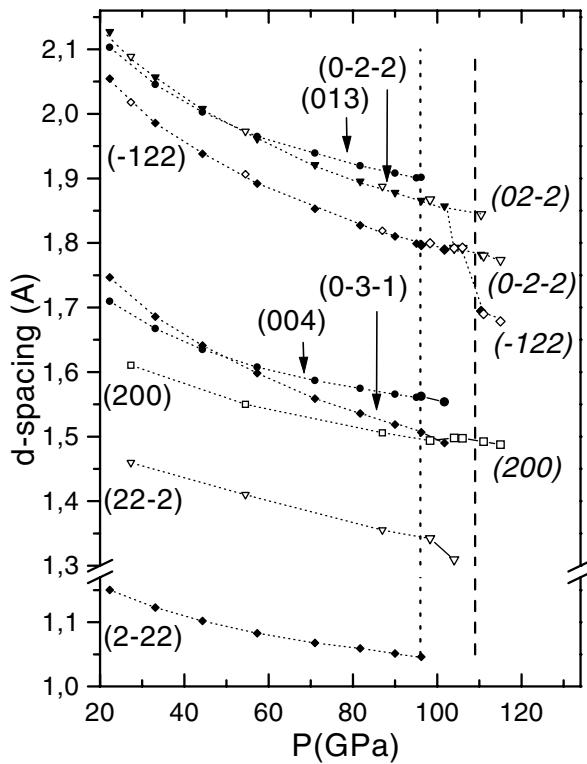


FIG. 1. Evolution with pressure of the d spacings. Full (empty) symbols correspond to the first (second) experiment. The two vertical lines (dotted and dashed lines) indicate the domain of transition (between 96 and 110 GPa).

reciprocal space. It is seen in Fig. 3b that the reflections are well resolved and strong. This clearly indicates a displacive transition, characterized by a modification and a sliding of the bc planes. This transition is taking place, partially due to kinetic effects, between 96 and 110 GPa. Table I (lower panel) summarizes the single crystal x-ray data at 110 GPa. At this pressure, the monoclinic cell cannot relate the x-ray data and in contrast to previous ADX study [6], this unambiguously shows that metal ζ -O₂ is not isostructural with ϵ -O₂. Unfortunately, there is not enough information to do a refinement of the new structure.

The molecular excitations of ϵ -oxygen have been studied previously by Raman and infrared spectroscopy [7,8]. But the intensity of the various spectra, particularly the vibron, strongly decrease under pressure and could not be followed in the metallic phase above 96 GPa. Although Raman measurements in the backscattering geometry have been reported on metals at Mbar pressures [14], the signal is generally very weak because it is a surface effect. We circumvent this problem by using the topology of the solid-solid phase separation of 10 vol % O₂ in Ne. Raman measurements of the vibron mode of O₂ were performed in transmission with 200 mW of a 488 nm Ar⁺ laser. We observed that the vibron intensity per molecule at a given pressure is strongly dependent of the volume fraction of O₂. The vibron intensity versus concentration shows a dramatic increase below 20 vol % of oxygen probably due

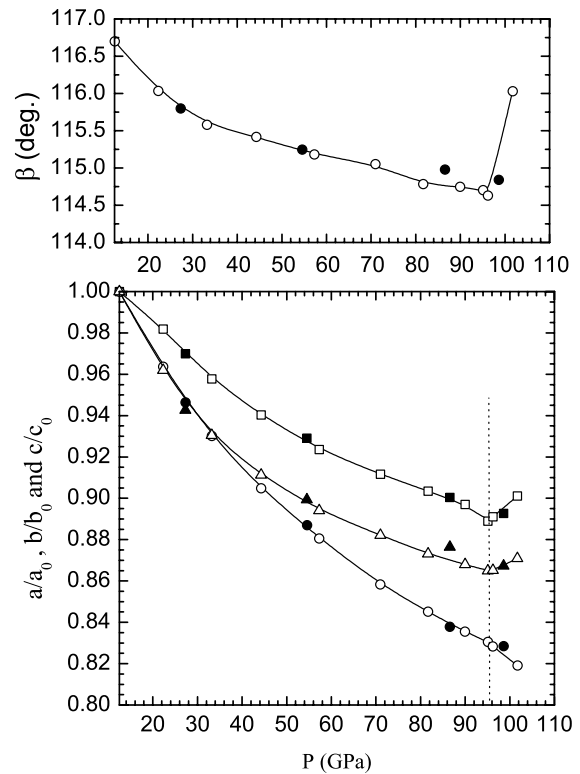


FIG. 2. Pressure dependence of the lattice constants a (■), b (●), c (▲), and angle β of the monoclinic cell of ϵ -O₂: $a_0 = 3.688$ Å, $b_0 = 5.621$ Å, $c_0 = 7.944$ Å [13]. The vertical dashed line represents the metallization at 96 GPa.

to a percolation-type effect. Moreover, the fine grained solid-solid mixture maximizes the surface/volume ratio of solid O₂, hence the Raman active part of the sample. Two experiments were performed above 110 GPa. As seen in Fig. 4, between 20 and 96 GPa, the vibron frequency in the ϵ phase increases linearly with pressure with a slope of 2.17 cm⁻¹/GPa, in good agreement with previous measurements [7]. At 96 GPa no discontinuity in the vibron frequency is observed. The vibron width also increases linearly with pressure and reaches 10 cm⁻¹ at 96 GPa.

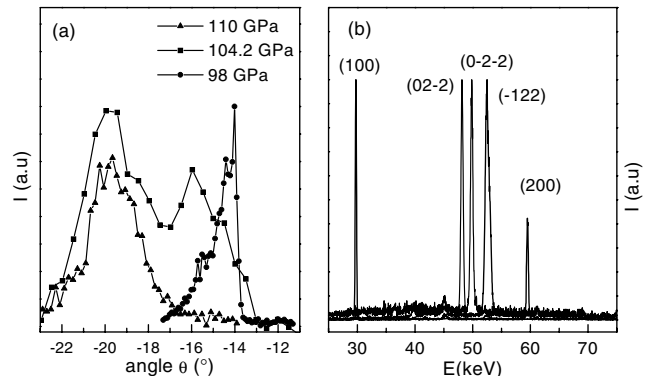


FIG. 3. (a) Evolution of the rocking curve with pressure observed in the second experiment for the peak (0-2-2). (b) X-ray spectra collected at 110 GPa: $E_d = 88.8$ keV.

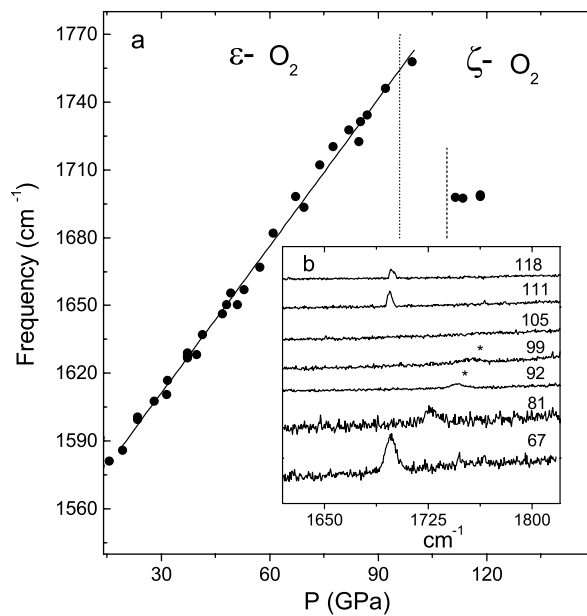


FIG. 4. (a) Pressure dependence of the vibron frequency. The circles are the data of two experiments. The line is a linear fit with a $2.17 \text{ cm}^{-1}/\text{GPa}$ slope. The two vertical lines (dotted and dashed lines) indicate the domain of transition (between 96 and 110 GPa). (b) Oxygen vibron spectra at several pressures above 60 GPa. The intensities have been normalized. The stars at 92 and 99 GPa indicate the position of the vibron peak.

But above 96 GPa, the vibron width increases dramatically merging the vibron into the background above 100 GPa. This large increase in width should be ascribed to the inhomogeneous broadening due to the displacive transition taking place above 96 GPa. At 110 GPa, when the new structure is stabilized, the vibron mode reappears but with a frequency jump of -2.5% compared to the vibron frequency extrapolated with the linear evolution in the ϵ phase. As seen in Fig. 4b, the vibron peak in the ζ phase is clearly defined with a width similar to the one observed at 60 GPa. This vibron is the signature of the O_2 molecule and therefore this demonstrates that oxygen remains molecular in the metallic ζ phase. The discontinuity in the vibron frequency could arise from the predicted change [15] of the intramolecular bonding due to the complete hybridization of the $\sigma\pi$, π , π^* bands in the metallic phase. It is interesting to note that between 110 and 120 GPa, the vibron frequency is almost independent of pressure. This means that the weakening of the intramolecular bond compensates the increase of the intermolecular interactions.

In summary, using both single-crystal x-ray diffraction and Raman measurements, it is shown that metallization

of oxygen is associated with the following sequence of phase transitions: (i) at 96 GPa, a continuous displacive phase transition triggered by metallization takes place up to 110 GPa. It is associated with interplanar sliding and intraplanar modifications of the bc planes. (ii) At 110 GPa, a new structure is stabilized. The ζ metal phase is not isostructural to the ϵ phase. Finally, it should be stressed that solid O_2 transforms continuously to its molecular metal similarly to what has been reported for iodine (and bromine at higher pressure [16]). This continuous transformation to the metallic phase might be quite universal in diatomic molecular systems and now remains to be observed in solid hydrogen.

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