Single-Crystal Structural Characterization of the Metallic Phase of Oxygen

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Angle dispersive x-ray diffraction measurements of oxygen single crystals in a helium pressure transmitting medium have been performed up to 133 GPa at room temperature. The crystalline structure of metallic ζ oxygen, above 96 GPa, is shown to be associated with a continuous displacive structural transformation taking place in the ab plane of the monoclinic $C2/m$ cell of the insulator ε phase. Although of first order, the change of crystalline structure to the metallic ζ phase from the ε phase is found to be isosymmetric, in agreement with recent calculations. Our Raman spectroscopy measurements on a single crystal of the ζ phase corroborate the present structure assignment. The interplay between metallization and structural changes is disclosed.

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The use of diamond anvil cells has made possible the search for pressure-induced metallization of very dense molecular systems. Many studies have already been published on the metallic forms of diatomic molecular solids since the discovery of the metallization of solid I_2 at 16 GPa [1]. For instance, metallic oxygen has been shown to occur above 96 GPa [2]. For other molecular systems, namely, solid H_2 and N_2, a dense metallic state has yet to be observed. Two questions motivate the study of metallization at high density. First, what are the physical properties of dense molecular metals? For example, the intriguing superconductivity of metallic oxygen, the only known molecular superconducting state, with a $T_c = 0.6$ K [3] is still not understood. Second, what is the mechanism underlying the metal-insulator phase transition? The case of I_2 has been elucidated only recently, with the existence of a transient incommensurate modulated structure, nested in between the insulating and dissociated metallic states [4]. The present experimental study is aimed at proposing a definite picture of the structural changes occurring in solid oxygen upon its pressure-induced metallization.

At 300 K and above 10 GPa, solid oxygen is stable in the ε phase. The full structural determination of the ε phase was carried out only recently by x-ray diffraction, using single crystals [5] and powder samples [6]. The structure of ε oxygen has a $C2/m$ symmetry with an association of four O_2 molecules to form O_8 units. ε oxygen remains stable up to at least 96 GPa, a pressure at which solid oxygen becomes metallic. The insulator-metal transition was first demonstrated by optical measurements, showing the closure of the electronic band gap with pressure, leading to a Drude-like reflectivity [2]. Subsequent electrical transport measurements confirmed a change in the static conductivity at 96 GPa [3]. The metallic state of oxygen is named the ζ phase.

The structural change from the ε to ζ phases has been a matter of continuous debate. A first powder x-ray study showed a continuity of the x-ray data through the transition, leading the authors to propose an isostructural transition with a small discontinuity in the lattice constants [7]. A subsequent single-crystal x-ray diffraction study indicated a continuous displacive phase transition, triggered by metallization and taking place from 96 GPa to 106 GPa above which a new structure, not isostructural to the ε phase, is stable [8]. Raman spectroscopy studies confirmed the structural change and the molecular nature of the ζ phase [9]. Various first-principle density-functional theory (DFT) calculations have been carried out to help resolve the structure of the ζ phase. An earlier work of Serra *et al.* proposed the $C2/m$ structure with four molecules per unit cell [10]. More recently, two competitive lowest enthalpy structures were proposed from calculations [11]: one of space group $C2/c$, containing four O_2 molecules per unit cell, arranged in a chainlike herringbone structure, and a second one, suggested as being the best candidate, isosymmetric to the ε phase, with chainlike connections between the O_8 units. However, the underestimation of the band gap in DFT calculations has made it difficult to resolve the link between metallization and structural changes. Two recent GW calculations, meant to improve the calculation of the band gap, have indicated that the insulator-metal (IM) transition occurs along with the structural transformation [12,13]. In all calculations, however, an unusually large disagreement between the calculated and the measured transition pressures remains. Also, the ε-O_8 structure has not the lowest enthalpy. In brief, while the molecular nature of metallic oxygen has appeared as a common outcome of experimental and theoretical studies, the structural determination of the metallic phase still has remained elusive. Using here the same x-ray single-crystal diffraction method that was used to solve the structure of the ε phase [5] and Raman spectroscopy, we conclude below that ζ oxygen has the $C2/m$ structure with eight O_2 molecules in the unit cell. Furthermore, combining with previous experimental measurements, we can propose a mechanism of the IM transition.

Angle dispersive x-ray diffraction measurements (ADXD) were performed on the ID27 beamline at the European Synchrotron Radiation Facility [14] on three different oxygen single crystals embedded in helium, used as a quasihydrostatic pressure transmitting medium up to 133 GPa at room temperature. When a crystal is embedded in helium, the nonhydrostatic stress has been quantified to be 0.3–0.5 GPa at 150 GPa [15]. The method for growing high quality single crystals of oxygen in helium has been described elsewhere [8]. Crystals of different orientations were selectively grown, based on the anisotropic optical properties of the dense oxygen phases, as illustrated in Fig. 1. The monochromatic beam, at about 33 keV, was focused down to below 10 μm, hence preventing diffraction from the surrounding Re gasket. Scattered photons were collected by a MAR345 area detector. The pressure was measured using the ruby luminescence gauge [16] with an uncertainty estimated to be smaller than ± 0.4 GPa at the maximum pressure.

The diffraction data obtained on the three different crystals were very similar. Consequently we report here the diffraction data from one crystal, named crystal B hereafter, given its most favorable and useful orientation. The orientation matrix of crystal B was refined in the ε phase at a starting pressure of about 22 GPa, by collecting angle resolved diffraction images, in ω steps of 1° over the entire cell aperture. This method being time-consuming, due to the relatively long readout time of the area detector, the evolution with pressure up to 95 GPa of the ε phase was thus obtained from diffraction images recorded while performing a complete ω rotation. At 95 GPa, a second ω-resolved collection of diffraction images was recorded in order to accurately determine the diffraction peak positions in reciprocal space and to assess the quality of the single crystal prior to the transition to the metallic ζ phase. Then for five pressure steps, between 97 GPa and 125 GPa, only complete ω-rotation images were collected. Finally, we performed a last ω-resolved image collection at 133 GPa, a pressure far above the ε-ζ transition pressure and well into the metallic regime. At 22 GPa, up to 60 reflections, with 25 unique, have been observed down to a resolution of 0.8 Å; all reflections have been well indexed using a $C2/m$ monoclinic unit cell (with $a = 7.573$ Å, $b = 5.382$ Å, $c = 3.614$ Å, and $\beta = 116°$). Upon pressure increase, crystal twinning was reproducibly observed in all three crystals. An inspection of the rocking curve for the various observed reflections indicated that the mosaicity of the crystal remained nevertheless remarkably very small ($<1°$) at 95 GPa, owing to the quasihydrostatic conditions provided by He. The evolution of the diffraction peaks is consistent with those previously reported from a single-crystal energy dispersive x-ray diffraction (EDXD) experiment [8]. Finally an unconstrained fit of the measured d-spacings at each pressure step indicates that the monoclinic $C2/m$ unit cell is indeed valid up to 96 GPa.

The IM transition at 96 GPa is accompanied by a significant change of the diffraction images. Oxygen diffraction spots suddenly broaden and spread azimuthally. Further-

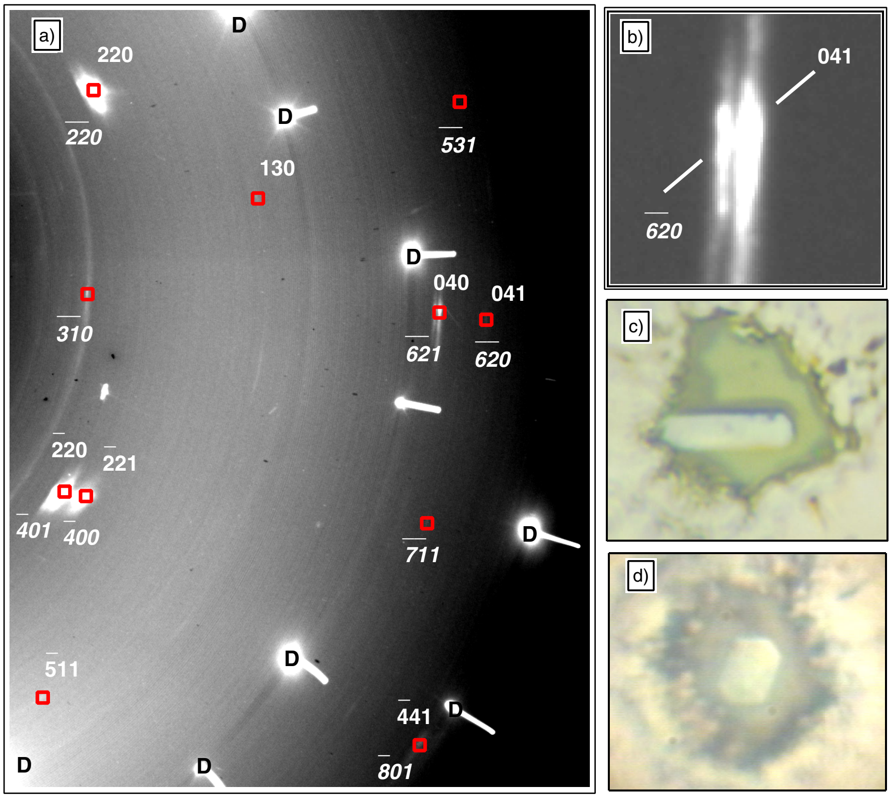

FIG. 1 (color online). (a) Details of the diffraction image of crystal B of solid oxygen at 133 GPa, overlaid with the indexing of reflections arising from identified twins, indicated by normal and italic indexing, respectively. (b) A magnification of Fig. 1(a), illustrating two different reflections belonging to the twins. (c) and (d) Photomicrograph of two oxygen single crystals, surrounded by He in Re gaskets at 125 GPa, with the c axis perpendicular and parallel to the image, respectively. The field of view for both images is approximately 75×75 μm^2.

more, the rocking curves, while still presenting well defined maxima, extend over several degrees in ω, indicating a deterioration of the single crystal. At the transition, a significant decrease in intensity or even disappearance of some of the diffraction peaks is observed, indicating unambiguously the important structural changes at the ϵ-ζ transition. The displacive nature of the transition is confirmed by the "sliding" of diffraction peaks during the transition. The structural transition to the ζ phase is complete above 106 GPa. Details of the diffraction image of the ζ phase, recorded at 133 GPa, is given in Fig. 1. The ω-resolved scans carried out at 133 GPa and their comparison with the scans performed in the ε phase below 96 GPa allow the explanation of the presence of doublets on the image as stemming from the merging of two different reflections belonging to twin crystals, as illustrated in Fig. 1.

Above 110 GPa, reflections observed remaining in the ζ phase could be indexed either using a monoclinic unit cell of space group $C2/m$ or $C2/c$. A study of the diffraction intensity does not permit the unmistakable selection of a space group over another. Although we believe we have obtained the very best oxygen crystals in the ζ phase so far, their quality was still inadequate to make possible a full refinement of the structure as it was done for the ε phase. A careful analysis of d-spacings, however, enables the elimination of the $C2/c$ monoclinic unit cell, proposed as a possible candidate for the ζ phase. This is illustrated with the integrated pattern of four selected diffraction lines, as shown in Fig. 2. The first three reflections are attributed to the first twin. They are indexed as the $(\bar{7}\ \bar{1}\ 1)$, $(7\ 1\ \bar{1})$, and $(\bar{5}\ \bar{3}\ 1)$ reflections in the $C2/m$ space group. A fourth reflection, indexed as $(5\ 3\ \bar{1})$ within the $C2/m$ representation, is found to belong to the second twin. If the $C2/c$ cell representation were correct, the four reflections should belong to the same hkl class (021) and should thus be centered on the same 2θ value. Symmetric reflections and the same reflections belonging to different twins have exactly the same d-spacing indicating that the difference between the $(7\ 1\ \bar{1})$ and $(5\ 3\ \bar{1})$ classes is real and not due to crystal strain or to the displacement of the crystal with respect to the incident x-ray beam during the ω scan. Our analysis leads to the conclusion that the $C2/c$ monoclinic cell is not valid. Finally, the space group and unit cell assignment are further confirmed by a careful examination of the Raman spectroscopy measurements carried out on the same single crystal at 118 GPa. This is shown in Fig. 2. Indeed, the $C2/c$ unit cell with the oxygen atoms in the $8f$ Wyckoff positions (four molecules) allows for six Raman active modes $(3A_g + 3B_g)$, while 12 Raman active bands $(7A_g + 5B_g)$ are expected for the $C2/m$ unit cell, with the oxygen atoms of eight molecules in the $8j$ and $4i$ Wyckoff positions. As the number of Raman active bands observed at low wave numbers, nine in total, already exceeds that predicted by the group theoretical analysis for the $C2/c$ unit cell, our spectroscopic results corroborate the conclusion drawn from our x-ray diffraction results. It should be

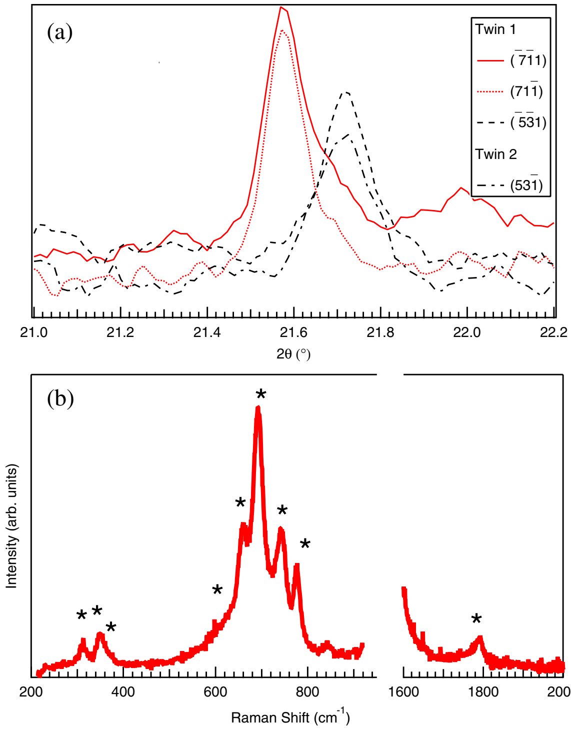

FIG. 2 (color online). (a) Integrated x-ray diffraction pattern of four selected reflections at 133 GPa. (b) Raman spectrum of crystal B of solid oxygen in helium at 118 GPa at 300 K. The stars indicate the positions of the observed Raman active bands. No Raman signal from oxygen is observed between 900 and 1600 cm^{-1}.

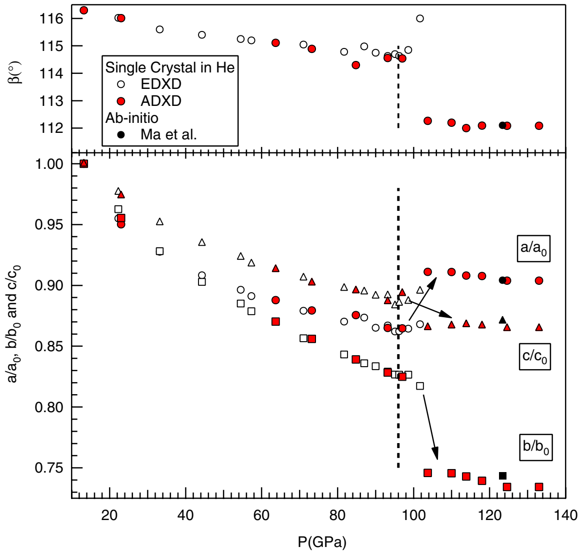

FIG. 3 (color online). Pressure dependence of the lattice constants a (●), b (■), c (▲) and angle β of the $C2/m$ monoclinic cell: $a_0 = 7.970$ Å, $b_0 = 5.633$ Å, $c_0 = 3.711$ Å, and $\beta = 116.3°$ at 13.2 GPa [5]. The present data are the filled gray (red) symbols. Data plotted with open symbols are taken from Ref. [8]. The solid black symbols are the calculation of Ma, Oganov, and Glass [11]. The vertical dashed line indicates the metallic transition pressure.

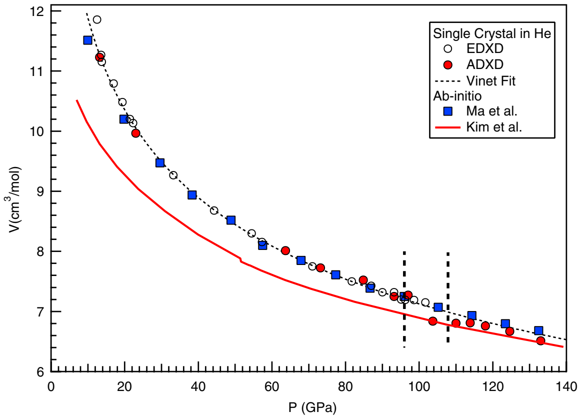

FIG. 4 (color online). Equations of state of solid oxygen, in the ε and ζ phases with a comparison between experiment (EDXD data are taken from Ref. [8]) and calculations of Ma, Oganov, and Glass [11] and Kim *et al.* [12]. The vertical dashed lines indicate the pressure range of the displacive transition.

emphasized that a similar Raman spectrum for the ζ phase was previously reported [9], but its interpretation was ambiguous given that it was collected under nonhydrostatic conditions and, most likely, arose from a sample presenting mixed phases.

The evolution of the lattice parameters with pressure is presented in Fig. 3. Lattice parameters are plotted along with the results of the previous EDXD single-crystal measurements. The abrupt change of lattice parameters in between 96 GPa and 106 GPa demonstrates clearly the onset of a first-order phase transition. Interestingly, the unit cell presents a large contraction (of about 10%) in the *b* direction, while the *a* lattice parameter shows only a slight increase.

The ε-ζ transition can be viewed as being mostly an ''intraplane'' transformation. The atomistic transformation associated to this isostructural transition can be better extracted from the results of *ab initio* calculations [11,12], since a full refinement of the atomic position from the x-ray data was not possible. The O_8 units connect along the *b* direction so that the intra-O_8 distance and inter-O_8 distance become equal, resulting in a shortening of the *b* axis, an increase of *a* axis, and a slight decrease of *c* axis. The present x-ray diffraction data nevertheless reproducibly demonstrate that this transition is not only of first order but proceeds gradually with pressure. The transition actually takes place between 96 GPa and 106 GPa. At 96 GPa, the closure of the indirect band gap in the ε phase induces at first a small displacive transition along the *b* direction which is completed at 106 GPa and is accompanied by a discontinuous transition to the new molecular arrangement in the *ab* plane through the connection of the O_8 units.

As shown recently, measured equations of state are considered a reliable test of DFT calculations [17]. The respective equations of state of solid oxygen in the ε and ζ phases are shown in Fig. 4. The experimental data are compared to the results of two DFT calculations [11,12] using the same DFT–generalized-gradient-approximation exchange correlation. It was questioned whether this DFT–generalized-gradient-approximation exchange correlation used in the calculations was adequate, given the large underestimation of the IM transition pressure. While the first *ab initio* equation of state reproduces well the experimental data [11], the second [12] largely underestimates pressures by approximately 15 GPa (using the most recent calibration of the ruby pressure scale [17] would not significantly change this comparison). However, it is worth noting that a detailed discussion of this theoretical discrepancy as applied to the case of dense solid oxygen is beyond the scope of this Letter.

In conclusion, the present single-crystal x-ray diffraction data have demonstrated the isosymmetric nature of the ε-ζ phase transition in solid oxygen. The combination of first-principle calculations with the present diffraction data gives a convincing view of the atomic displacements leading to the new structure. One can draw a similarity between the structural changes induced by metallization in solid I_2 and solid O_2. In both cases, metallization by the closure of the band gap causes an instability of the lattice that evolves, through a displacive phase transition, into the denser structure along with the dissociation of molecular entities, I_2 and O_8, respectively. A further transformation of metallic O_2 into an atomic metal is predicted at much higher pressure, namely, above 250 GPa [11]. Single-crystal x-ray diffraction in this pressure range represents at this point a formidable challenge.

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