

New High-Pressure Structural Transition of Oxygen at 96 GPa Associated with Metallization in a Molecular Solid

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By using a high-energy and high-brilliance synchrotron radiation source in the European Synchrotron Radiation Facility and the Photon Factory, an angle-dispersive powder x-ray diffraction study of solid oxygen has been carried out up to 116 GPa at room temperature. A new high-pressure structural transition was observed at 96 GPa and explained as an isostructural transition with a discontinuous change in lattice constants in a monoclinic cell. Metallization of oxygen reported by Desgreniers, Vohra, and Ruoff [J. Phys. Chem. **94**, 1117 (1990)] is ascribed to the transition.

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Recently, pressure-induced metallization and molecular dissociation of homonuclear molecular solids of light elements, H₂, N₂, and O₂, have attracted special interest with a view to understanding the fundamental effect of chemical bonding. A report on metallization of hydrogen by Mao and Hemley [1] has stimulated numerous experimental studies on the properties of solid H₂ above 100 GPa. Whether or not solid H₂ is a molecular semimetallic above 150 GPa is still controversial [2–4]. On the other hand, for solid O₂ Drude-type metallic behavior has been observed in reflectivity spectra above 95 GPa by Desgreniers, Vohra, and Ruoff [5]. They have concluded that a transformation to a nearly free electron state takes place in solid oxygen.

Since the first observation of dramatic color changes at pressures on the order of 10 GPa in solid oxygen [6], many structural [7–12], optical [5,13–15], and magnetic [16] studies concerned with the high-pressure phases have been reported. The structures of three high-pressure phases at room temperature have been determined by single-crystal x-ray diffraction experiments to be $R\bar{3}m$ for β -O₂ at 5.5 GPa [7,8], $Fmmm$ for δ -O₂ at 9.6 GPa [8], and monoclinic for ε -O₂ at 19.7 GPa [9,10]. The stability of the ε -O₂ phase up to 61 GPa at room temperature has been observed in an energy-dispersive x-ray diffraction experiment [12]. Optical studies of absorption spectra [13] and infrared and Raman spectra [14,15] have suggested the presence of a strong intermolecular force (intermolecular charge transfer) between O₂ molecules in the ε -O₂ phase. It is well known that solid I₂, which is a typical molecular solid characterized by such an intermolecular charge-transfer interaction, transfers to a molecular semimetallic at about 18 GPa [17] and further to a monatomic metal phase at 21 GPa [18].

On the other hand, a systematic metallization and structural sequence of the phase transitions has been revealed in the group VIb elements S, Se, and Te, belonging to the same group as oxygen in the periodic table [19,20]. Metallization of these materials occurs in a monatomic phase. Whether or not such a systematic relationship applies to oxygen and which feature the metallic phase of solid oxygen displays, molecular or monatomic, are of interest to us.

The aim of this study is to research pressure-induced metallization and molecular dissociation of solid O₂ from a structural aspect. We have performed high-pressure powder x-ray diffraction experiments up to 116 GPa. An isostructural transition has been observed at 96 GPa. These are the first structural data collected from a light element at such pressures.

A diamond anvil cell (DAC), which has a tungsten carbide half cylinder seating with a rectangular-shaped slot to detect diffraction x rays, was used for high-pressure generation. The diamond anvils had a top surface diameter of 300 μm , a bevel angle of 7°, and a culet diameter of 400 μm . Liquid oxygen was loaded into a 150 μm diameter hole of a metal gasket (U-700) in the DAC at a low temperature of 77 K. Pressure was increased at room temperature and measured by the quasihydrostatic ruby scale [21].

X-ray diffraction experiments were carried out by an angle-dispersive method using an image-plate detector up to 116 GPa. High-brilliance synchrotron radiation (SR) from BL3 (undulator) in the European Synchrotron Radiation Facility (ESRF), which was monochromated to a wavelength of 0.4817 Å and focused using a Bragg-Fresnel lens, was used with remarkable success to obtain high-quality powder patterns of oxygen in the higher-

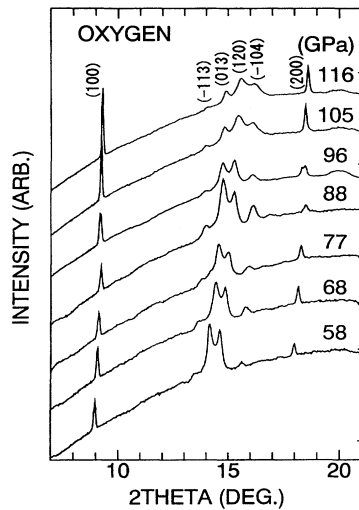


FIG. 1. Pressure variation in x-ray diffraction profiles for solid oxygen at room temperature up to 116 GPa. This was obtained with a monochromated beam of $\lambda = 0.4817 \text{ \AA}$ in ESRF. In order to collect diffraction x rays from more crystalline particles, the DAC was oscillated within $\pm 3^\circ$ during exposure. We find that a structural transition takes place at 96 GPa. The lines of the new high-pressure phase were assigned to the same unit cell as $\epsilon\text{-O}_2$. Background around $2\theta = 20^\circ$ is due to an imperfection of Pb shielding of high-energy x rays. We can see this shadow in the diffraction image in Fig. 2.

pressure region. X-ray diffraction data in a lower-pressure region were also obtained from a monochromatic beam of $\lambda = 0.6888 \text{ \AA}$ from BL6-B in the Photon Factory (PF), National Laboratory for High Energy Physics. Detailed descriptions of the SR experimental system and image integration software in ESRF [22] and PF [23] have been given elsewhere.

Figure 1 illustrates the pressure variation in the powder diffraction patterns of oxygen at room temperature. Patterns at pressures lower than 88 GPa, which come from the $\epsilon\text{-O}_2$ phase and have six reflections, exhibit a monotonic high-angle shift with increasing pressure up to 88 GPa. Though the diffraction images indicated a strong preferred orientation, the reflections were well assigned to the monoclinic lattice reported by Schiferl *et al.* [9,10].

A structural transition was observed around 96 GPa. A new reflection occurs at close quarters to the (200) reflection of the $\epsilon\text{-O}_2$ phase around $2\theta = 18.5^\circ$. The diffraction image at 96 GPa is shown in Fig. 2. We can see the new reflection just inside the (200) line as a doublet in a magnified image. An increase in linewidth of (100) reflection around $2\theta = 8.2^\circ$ was also observed. We can see from Fig. 1 that the relative intensity of the diffraction lines slightly changed after the transition. In Fig. 3, the pressure dependence of the d value for each line is shown up to 116 GPa. It is clear from the dependence that a structural phase transition occurs around 96 GPa. The

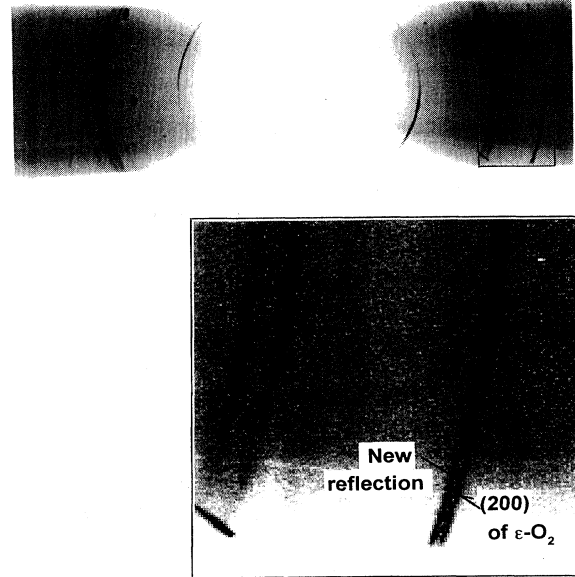


FIG. 2. Diffraction image of solid oxygen at 96 GPa. We can see the new reflection as a doublet with the (200) line of $\epsilon\text{-O}_2$ in the magnified image. Strong Bragg reflections come from the ruby chip.

number of observed diffraction lines in the new high-pressure phase is the same as those for $\epsilon\text{-O}_2$, and the change in the d value for each line at the transition is very slight. The results suggest that the structural transition may be explained by a modification of the monoclinic lattice of the $\epsilon\text{-O}_2$ phase such as elongation and contraction of its lattice constants.

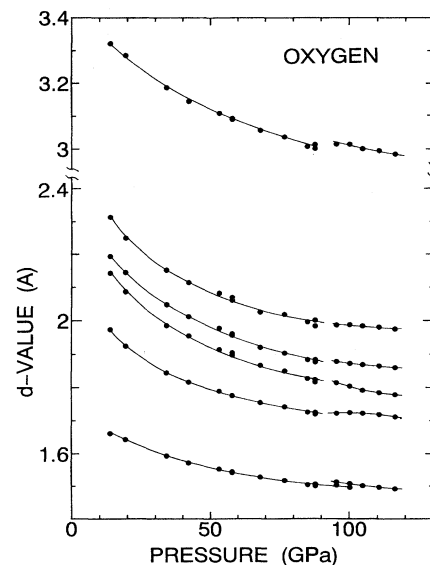


FIG. 3. Pressure dependence of d values for solid oxygen up to 116 GPa. This indicates a new structural phase transition at 96 GPa.

The observed six diffraction lines of the ε -O₂ phase were well interpreted by assuming the monoclinic unit cell as reported by Schiferl, Johnson, and Zinn [9], and the lattice constants were obtained at each pressure. The index of each line was also satisfied by the extinction rule for the base-centered lattice ($A2/m$) proposed by Johnson, Nicol, and Schiferl [10]. On the other hand, the lines could not be assigned to an orthorhombic unit cell proposed previously [11,12] within our experimental accuracy (typical value is ± 0.003 Å).

We also tried to assign six diffraction lines in the new high-pressure phase (ζ -O₂) to the same monoclinic lattice. The result at 116 GPa is shown in Table I. The calculated values are in good agreement with the experimental ones. The same results were obtained at 105 and 111 GPa, although the patterns at 96 and 101 GPa could not be assigned due to coexistence of the ε -O₂ and ζ -O₂ phases. An analysis by an indexing program did not provide any higher symmetric cell than monoclinic within experimental accuracy.

Figure 4 represents the pressure dependence of the lattice constants in the ε -O₂ and the ζ -O₂ phases normalized by the values ($a_0 = 3.699$, $b_0 = 5.617$, and $c_0 = 7.953$ Å) at 13.7 GPa. The lattice constants in the ε -O₂ phase exhibit monotonic pressure dependence, while the monoclinic angle β was almost constant at 116° within $\pm 0.5^\circ$. The dependence indicates a strong anisotropy of compressibility. The lattice constant b contracts twice as much as the lattice constant a . The anisotropy seems to arise from the proposed features [15] of the parallel alignment of all the O-O intramolecular bonds and the existence of O₂ molecular planes normal to the same O-O bond axis. Anisotropy in the width of the diffraction lines may also come from such a layerlike structure. Discontinuity of the lattice constants is found in Fig. 4 corresponding to the structural transition at 96 GPa. Lattice constants a and c elongate by about 0.7% of the values at 96 GPa and b contracts by about 1.4%.

Figure 5 shows the pressure dependence of the molar volume of oxygen. The molar volume was calculated by assuming that the monoclinic unit cell contains eight oxygen molecules. The volume reduction of the δ - ε phase transition was estimated to be 0.6–0.8 cm³/mole by ex-

TABLE I. Powder diffraction data for the new high-pressure phase (ζ -O₂) at 116 GPa. Lattice constants of the monoclinic cell are $a = 3.332$ Å, $b = 4.426$ Å, $c = 6.866$ Å, $\beta = 116.4^\circ$, $V = 90.72A^3$, and $Z = 8$.

No.	d_{obs}	$h k l$	d_{calc}	Error(%)
1	2.9852	1 0 0	2.9850	0.0054
2	1.9752	-1 1 3	1.9767	-0.0735
3	1.8601	0 1 3	1.8605	-0.0217
4	1.7782	1 2 0	1.7785	0.0198
5	1.7119	-1 0 4	1.7112	0.0411
6	1.4925	2 0 0	1.4925	-0.0013

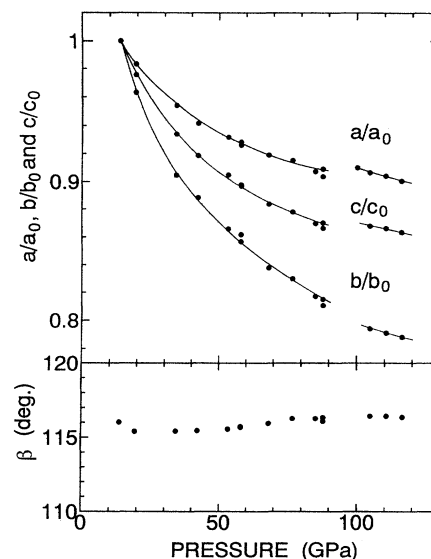


FIG. 4. Pressure dependence of lattice constants a , b , c , and β of a monoclinic unit cell for the ε - and ζ -O₂ phases. Values are normalized by those of ε -O₂ at 13.7 GPa.

trapolating the smooth fitted data to the phase boundary. The value corresponds to (5–6)% of the volume of the δ -O₂ phase just before the transition ($-\Delta V/V_B$). The volume reduction of the new high-pressure phase transition from ε - to ζ -O₂ was smaller than 0.1 cm³/mole ($-\Delta V/V_B < 1.4\%$) and was difficult to estimate by extrapolation. It seems that the volume reduction is too small compared with that expected in molecular dissociation. In the molecular dissociation of I₂, a $-\Delta V/V_B$ of about 6% has been observed [18]. The molar volume at the highest pressure of 116 GPa in this study was 6.83 cm³/mole, which corresponds to 0.47 of the 14.44 cm³/mole of the β -O₂ phase at 5.9 GPa [2].

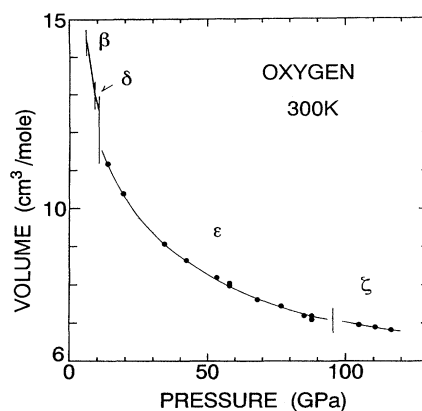


FIG. 5. Pressure dependence of the molar volume of solid oxygen at room temperature.

From visual observation under a metallurgical microscope, we saw that the appearance of the oxygen sample became as shiny as the metal gasket after the structural transition at 96 GPa. This behavior has also been observed by Desgreniers, Vohra, and Ruoff [5]. They have reported that at an approximate pressure of 95 GPa an increase in the near-infrared reflectivity is observed. This was attributed to the onset of creation of a nearly free electron by a pressure-induced band overlap. Because the metallization is accompanied by a structural transition, the band gap may close discontinuously. They have also pointed out from a linear extrapolation of the pressure dependence of the absorption edge that the absorption edge should approach zero at 110 GPa. This suggests that the metallization at 95 GPa occurred with an abrupt band gap closure. Our observation of the structural transition is consistent with this suggestion. In spite of the larger binding energy (5.21 eV) of O₂ than that (4.75 eV) of H₂, oxygen metallizes at a lower pressure than hydrogen. This fact may be explained by the strong intermolecular interaction of O₂.

The results obtained in this study suggest that in the newly observed high-pressure phase (ζ -O₂) oxygen molecules do not dissociate, that is, the phase is in a molecular (semi)metallic state. Such a state has been observed in solid iodine between 16 and 21 GPa. However, the process of metallization in solid oxygen differs from that in iodine. The case of oxygen is accompanied by a structural transition. In iodine no structural transition was observed [18].

The ζ -O₂ phase did not exhibit any analogy of structure with the high-pressure phases observed in other elements of the VIb group [19]. However, monatomic phases, which will be realized under high pressure, may show an analogy of structure with other elements of the VIb group because it is a common feature in such phases that *p* electrons play the main role in the electronic band structure.

In conclusion, powder x-ray diffraction experiments with oxygen were performed up to 116 GPa at room temperature, and a structural transition was observed at 96 GPa. The structure of the new high-pressure phase (ζ -O₂) was interpreted to be isostructural with a monoclinic unit cell of ϵ -O₂. The structural change was slight and not drastic as expected in molecular dissociation. Certain evidence of the molecular metal would be provided

by demonstration of the existence of the intramolecular stretching mode (vibron) in infrared or Raman spectra; an abrupt softening of this mode must then be observed at 96 GPa.

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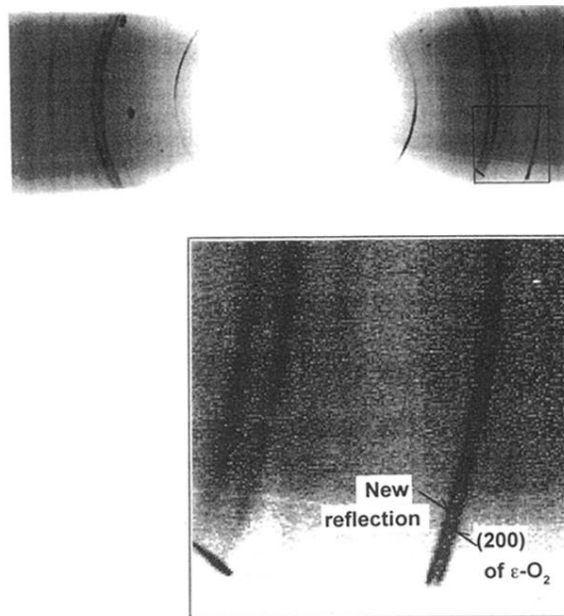


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