O_8 Cluster Structure of the Epsilon Phase of Solid Oxygen

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Despite many experimental and theoretical studies, the crystal structure of the ε phase of solid oxygen has not been determined. We performed powder x-ray diffraction experiments and the Rietveld analyses in this study to show that a new arrangement of the monoclinic space group $C2/m$ could fit the diffraction patterns of the ε phase and obtained a structure that consisted of an O_8 cluster with 4 molecules. The dependence of the lattice parameters, the molar volume, and the intermolecular distances on the pressure was investigated.

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Studies on molecular dissociation and metallization of simple dimolecules such as H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2 have been an important subject in high pressure science. Oxygen is the first light element in which metallization was confirmed experimentally. Solid oxygen shows successive phase transitions from β [1], to δ at 9.6 GPa [2,3], and to the ε phase at 9.9 GPa [2,4] at room temperature exhibiting colors of pink, orange, and red, respectively. The change of color corresponds to an increase in the interaction between molecules. The red color of the ε phase becomes darker with increasing pressure. The near-ir reflectivity increased at around 100 GPa suggesting metallization [5]. Akahama *et al.* discovered a structural phase transition from the ε to the ζ phase at 96 GPa [6,7]. Further superconductivity above 100 GPa has been observed [8], and the metallization of solid oxygen was confirmed. The molecular character is still present in the ζ phase [9].

Many experiments on the magnetism of various phases of solid oxygen have been performed, and their theories have been studied [10–19]. A magnetic frustration in the ε phase was predicted by the density-functional theory by assuming a triangular configuration in the *ab* plane [20]. On the other hand, Raman [21] and neutron [22] experiments claim a collapse of the magnetic moment at the $\delta-\varepsilon$ transition. Magnetic properties of the ε phase remain unclear since its structure has not been solved. A recent review explained the importance for solving this structure [23].

Some powder diffraction studies have been carried out for solid oxygen [24–26]. A monoclinic $C2/m$ structure with 8 molecules in the cell has been proposed for the ε phase [6,7,27]. Johnson *et al.* analyzed the atomic coordinates and the molecular configuration of this structure [27]; however, their result was not consistent with the results of optical experiments [28–31] and theoretical reports [32]. Successful results have not been obtained even for structure analyses with single crystals [33–35]. Thus, the purpose of this study is to determine the crystal structure of the ε phase of oxygen by an angle-dispersive powder x-ray experiment.

The powder x-ray diffraction experiments were carried out using a monochromatic synchrotron radiation source on the BL10XU station at SPring-8, in Hyogo, Japan. Powder diffraction patterns of the oxygen samples were collected by an angle-dispersive method with a diamond anvil cell (DAC) and an imaging plate detector (IP). Liquid oxygen was loaded into a hole in a metal gasket set in the DAC at a low temperature of 77 K and used as a sample after an oxygen gas with 99.999% purity was liquefied in a cryostat. More than 10 experimental runs were performed to check the reproducibility of the diffraction pattern. Diamond anvils with a 400-μm culet and a tungsten carbide backing plate with a conical aperture were used in

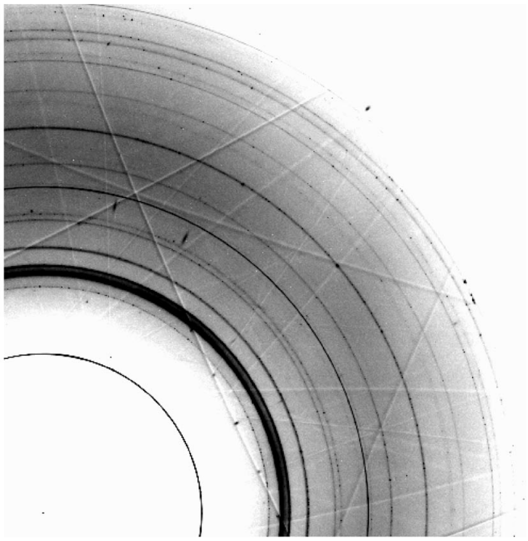

FIG. 1. Powder diffraction image of ε-O_2 at 11.4 GPa recorded on an imaging plate detector.

runs up to 20 GPa to obtain the full Debye-Scherrer rings. On the other hand, diamond anvils with a 250-μm culet and a tungsten carbide backing plate with a slit aperture were used in runs up to 100 GPa. The pressures were determined by the ruby scale under a quasihydrostatic condition [36]. The x-ray beams were collimated by a pinhole with a 10 μm diameter. The typical exposure time was 20 minutes. All the runs produced consistent results. As previously reported, the β phase successively transformed to the δ phase at 9.5 GPa, to the ε phase at 10.0 GPa, and to the ζ phase at 96 GPa. Figure 1 shows a part of the diffraction image of the ε phase that was obtained at 11.4 GPa. An x-ray wavelength for this run was 0.4964 Å. A one-dimensional powder pattern was obtained by averaging the diffraction intensity along the ring [37]. Small spots on the image that arose from large grains were omitted from the averaging. The Rietveld analysis program RIETAN2000 [38] was used for structure refinements.

The powder pattern at 11.4 GPa was indexed and its lattice was determined to be C-centered monoclinic with $a = 8.145$ Å, $b = 5.744$ Å, $c = 3.771$ Å, and $\beta = 117.0°$. As previously reported [6,27,33], this lattice corresponds to the doubled a and doubled b axes of a monoclinic α phase (space group $C2/m$) which exists at low temperature and contains two oxygen molecules. Therefore, the monoclinic cell for the ε phase must contain 8 molecules. Some references denote the space group of the ε phase as $A2/m$, not as $C2/m$ of the α phase; however, they are identical. The Rietveld analysis was performed on a space group $C2/m$, which was used in a previous model [6,27,33] and produced the following atomic coordinates: O1 (0.288, 0.250, 0.179), O2 (0.003, 0, 0.162), O3 (0.565, 0, 0.162). O1, O2, and O3 atoms each formed molecular pairs of O1-O1, O2-O2, and O3-O3, respectively. Their intramolecular distances were fixed at 1.20 Å. This model could not fit the diffraction intensity well (Rwp = 3.4%) as shown by the arrows in the top pattern and in the inset in Fig. 2. Since the centers of the molecules were fixed to special positions, i.e., at the origin of the lattice, the molecules only have the degrees of freedom for tilt.

However, we were able to provide the degrees of freedom for both the tilt and the translation to an oxygen molecule with the same space group of $C2/m$ by introducing a new arrangement in which the centers of the molecules were not fixed to the special positions. As shown in the bottom pattern in Fig. 2, this arrangement gave a much better Rietveld fit (Rwp = 2.3%) than that of the previous model. The intramolecular distances were fixed to 1.20 Å again. The lattice parameters and the unit cell volume were refined to be $a = 8.141 \pm 0.002$ Å, $b = 5.747 \pm 0.001$ Å,

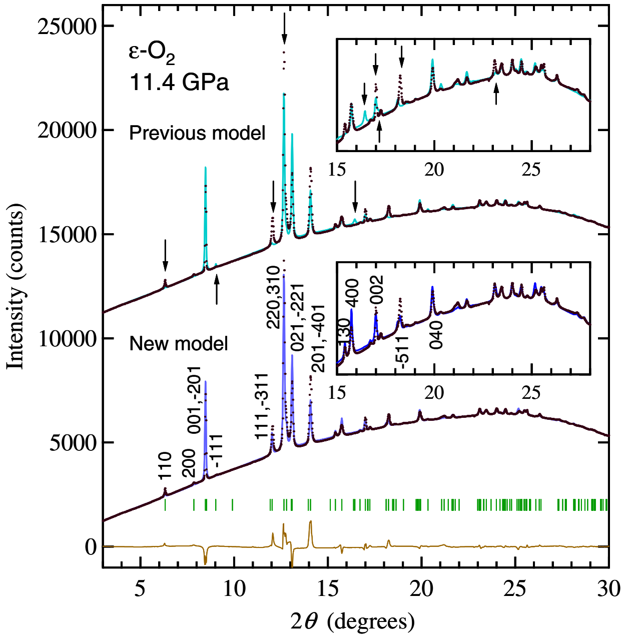

FIG. 2 (color online). Observed diffraction pattern of ε-O_2 at 11.4 GPa (dots) and the calculated profile (curve) after the Rietveld refinement with the previous (top) and the new (bottom) models. The insets show enlarged views of the high angle part of the patterns. Misfits in the previous model shown with arrows were improved in the new model. Corrections in the preferred orientation were not made.

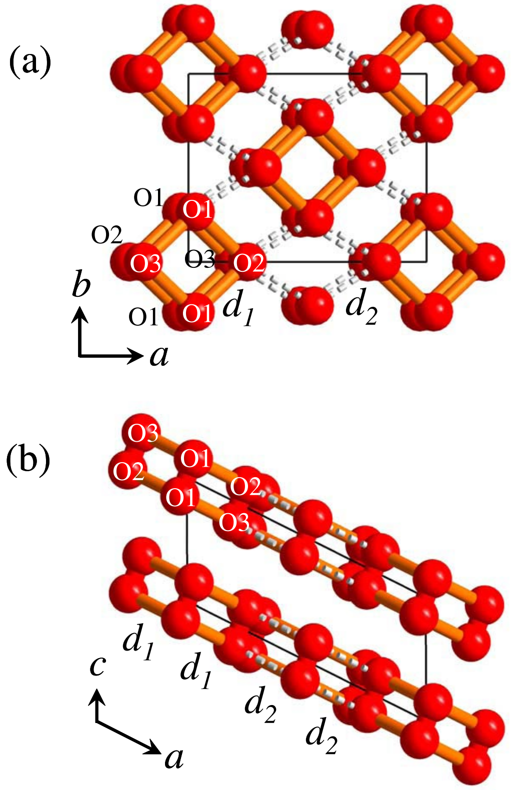

FIG. 3 (color online). Proposed structural model of ε-O_2 at 11.4 GPa viewed along (a) the c and (b) the b axes. Labels d_1 and d_2 show intra- and intercluster distances. There are two O_8 clusters in the unit cell. One is located at the origin of the lattice and the other is at the center of the ab plane.

$c = 3.773 \pm 0.001$ Å, $\beta = 117.07 \pm 0.01°$, and $V = 157.18 \pm 0.04$ Å^3. The atomic coordinates were obtained as follows: O1 $(0.029 \pm 0.001, 0.266 \pm 0.001, 0.177 \pm 0.001)$, O2 $(0.247 \pm 0.001, 0, 0.177 \pm 0.001)$, O3 $(0.190 \pm 0.001, 0, -0.177 \pm 0.001)$. The O1 atoms formed a molecular pair of O1 − O1$[-x, y, -z]$ and could move along the b axis. The O2 and O3 atoms formed molecular pairs as O2-O3 and could move along the a and c axes. Since the translation along the c axis worsened the Rietveld fitting, the center of the O2-O3 molecule was fixed to $z = 0$.

Figure 3(a) shows the ab plane of the refined structure of the new arrangement where the centers of the molecules are not on the special positions. A box made up of 4 molecules appears by connecting the nearest intermolecular distance d_1 (2.34 Å) and is shown with solid bars. This distance is significantly shorter than the interbox distance d_2 (2.66 Å) as shown with the dashed bars. Therefore, the box of 4 molecules could be interpreted as an O_8 cluster. The reason for doubling the a and b axes from the α to the ε phase originates from the appearance of this cluster. Figure 3(b) shows the ac plane. The molecular axis and the crystallographic ab plane are perpendicular in the α, β, and δ phases; however, the molecular axis shows a 7° tilt from the ab plane in the ε phase. This is caused by the formation of the box shaped cluster. The previous $C2/m$ model [27], the O_4 unit model by optical experiments [29–31], and the theoretically proposed herringbone chain model [32] have not been consistent with each other. However, the above mentioned O_8 cluster can be used to explain the results of the optical experiments including the O_4 unit, and the shape of the O_8 cluster was found to resemble a part of a herringbone chain having right-angled edges. Thus, the O_8 cluster model is consistent with both the optical and theoretical studies.

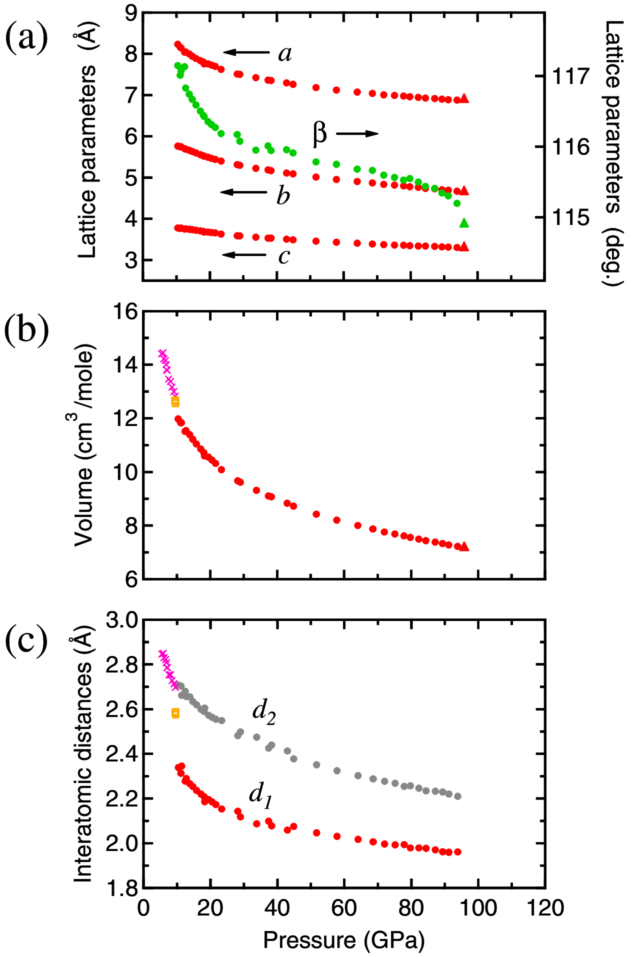

FIG. 4 (color online). Pressure dependence of the structural parameters of ε-O_2 for (a) the lattice parameters a, b, c, and β, (b) the molar volume, and (c) the intermolecular distances d_1 and d_2 shown in Fig. 3. Triangles at 96 GPa in (a) and (b) are data obtained from a single crystal work [34]. Cross marks and open squares in (b) and (c) represent the data for β-O_2 and δ-O_2.

The dependence of the lattice parameters of the ε phase on the pressure are indicated by the circles in Fig. 4(a). a, b, and c all decrease monotonically. The triangles on the figure are obtained from a single crystal study at 96 GPa [34] and agree with our data. The β decreases gradually above 25 GPa, but begins to decrease rapidly above 80 GPa and is a precursor for the transition to the ζ phase at 96 GPa. The dependence of the molar volume on the pressure is indicated by the circles in Fig. 4(b). The volume decreased to 61% from 11 GPa to 95 GPa. The triangle at 96 GPa from the single crystal study [34] also agrees with our data. Cross and open square symbols are the data for the β and δ phases at room temperature. The volume gaps with the first order transitions of β-δ and δ-ε are 1.6% and 5.4%, respectively. The dependence of the intermolecular distances, which are labeled as d_1 and d_2 in Fig. 3, on the pressure is shown in Fig. 4(c). Both distances decreased monotonically with pressure. The crosses and open squares indicate the intermolecular distances for the β and δ phases at room temperature calculated from their lattice parameters. The d_1 and d_2 become degenerate in the β and δ phases. The d_1 in the ε phase is significantly shorter than the distances in the β and δ phases. This corresponds directly to the large volume reduction of 5.4% at the δ-ε transition and suggests the appearance of the O_8 cluster in the ε phase. The d_2 decreases to 2.2 Å at 95 GPa. This value is comparable to the d_1 at 15 GPa and is short enough for the electron orbitals to overlap. The transition to the ζ phase may occur by the connection of O_8 clusters. Localized electrons in the O_8 cluster would spread in the ab plane and result in a two-dimensional metallic state. The structure analysis of the ζ phase is now in progress.

According to Raman experiments, the vibron wave number decreases in the δ-ε transition [2,39]. Further vibrons which are in principle ir inactive for homonuclear dimolecules become active, and a strong absorption band appears [40,41]. This result suggests the existence of an O_2-O_2 interaction. The O_4 model [29–31] is a good model to explain this; however, it only has two vibrons of symmetric and antisymmetric stretching modes. This is inconsistent with the optical experiment where the ε phase shows a total of 4 vibron peaks around 1500 cm^{-1} to 1600 cm^{-1} in Raman and ir spectra [7]. On the other hand, the O_8 cluster has 4 vibron modes and can explain the optical experiment [7] better than the O_4 model. A magnetic frustration in the ε phase was predicted by assuming a triangular configuration in the *ab* plane [20]. However, the molecules are actually located on the square rather than on the triangle, so a calculation with the new structure would result in a different type of state. Since the neutron experiment [22] has reported that there is no long-range magnetic ordering in the ε phase, a local magnetic structure, such as a vortex in 4 molecules, would remain. A charge transfer between molecules such as O_2^+-O_2^- was predicted [42]. Thus, a theoretical study based on the new structure is very important for clarifying the magnetic structure and the charge transfer in the ε phase.

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