O_8 Cluster in the ε Phase of Solid Oxygen

The investigation of the molecular dissociation and metallization of molecular solids has been a long-term problem in solid-state physics and earth and planetary sciences. The investigation of the pressure-induced metallization and molecular dissociation processes of the simplest diatomic molecules, such as H_2, N_2, O_2, F_2, Cl_2, Br_2, and I_2, has, for a long time, attracted much attention. It is known that oxygen solidifies into a state called the β-phase at room temperature and 6 GPa, and with further increase of pressure, the β-phase undergoes phase transitions to the δ-phase at 9 GPa and the ε-phase at 10 GPa (Fig. 1). Because of the enhancement of in molecular interactions, the pink color of the β-phase changes orange (δ-phase) and red (ε-phase), and further to black with increasing pressure. Akahama *et al*. found that a ζ-phase appears at 96 GPa when ε-phase oxygen is further pressured (Fig. 1) [1]. The ε-phase, which has a metallic luster, is known to exhibit superconductivity at low temperature [2]. Oxygen molecules are one of the very few molecules having magnetic moments, and have attracted attention from the viewpoint of the relationship between the molecular magnetization and crystal structures, electronic structures, and superconductivity. Until now, as possible models of the ε-phase structure, the O_4 model of a pair of O_2 molecules (estimated from optical measurements) and the chain model, in which the O_2 molecules are one-dimensionally connected (theoretical prediction) have been proposed. However, the diffraction patterns calculated from these models are not consistent with the experimental one, and thus these models have been in doubt. We have attempted powder X-ray diffraction experiments and structural analyses of the ε-phase [3].

The oxygen ε-phase was prepared as follows. First, oxygen gas and a diamond-anvil high-pressure cell (DAC) were cooled with liquid nitrogen, and thus the oxygen was liquidized. The liquid oxygen was enclosed in the sample chamber of the DAC (60 μm in diameter and 30 μm in thickness), and pressurized to solidify it. The solidified oxygen can maintain the solid state under continued applied pressure even at room temperature. Then, X-ray diffraction patterns of the solidified oxygen powder were obtained using beamline **BL10XU**.

The analytical procedure for determining the structure from the powder diffraction patterns was as follows. First, we assumed that the crystal structure of the oxygen ε-phase belongs to the lowest symmetry space group, *P1*, and constructed an initial model by the simulated annealing method. Secondly,

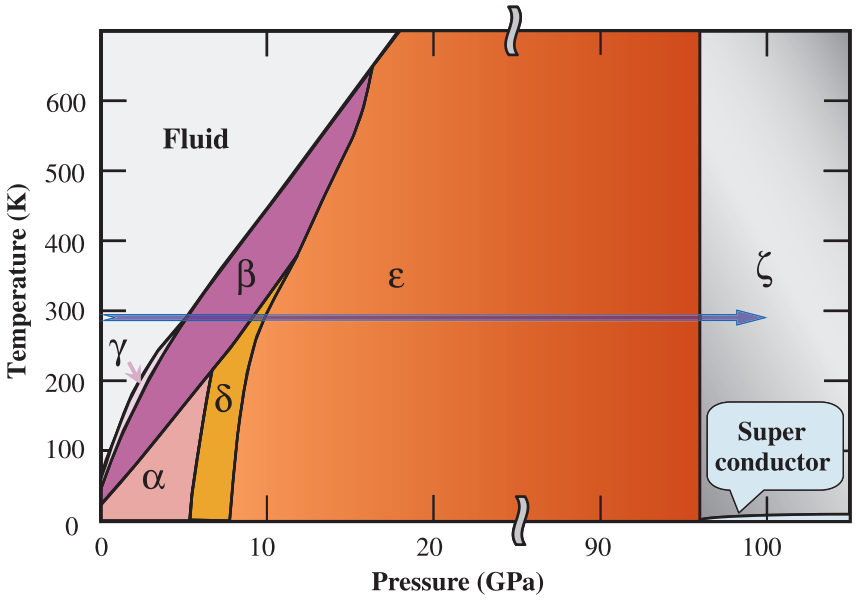

Fig.1. Pressure-temperature phase diagram of oxygen.

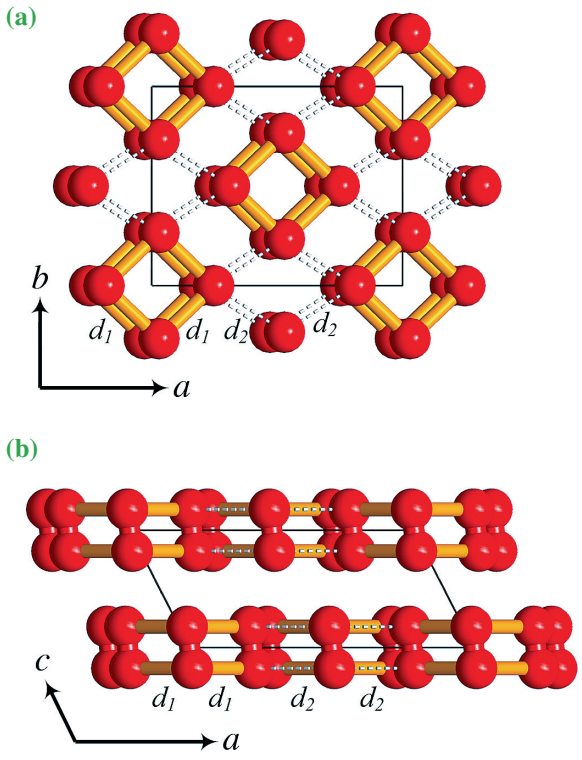

Fig. 2. Crystal structure of oxygen ε-phase formed at 11 GPa. **(a)** Projected figure to the *ab* plane, **(b)** Projected figure to the *ac* plane. The intramolecular bond length of the oxygen molecule was fixed at 1.20 Å. The intracluster bond length of the O_8 cluster (orange bar line d_1) is 2.34 Å, and the intercluster distance (dotted line d_2) is 2.66 Å.

considering the features of the structure, the symmetry was gradually raised from *P1* to $P\bar{1}$, *C2*, and *C2/m*. Lastly, after making the structure more precise using the Rietveld analysis, the structure obtained showed an O_8 cluster in which four oxygen molecules take a boxlike arrangement (Fig. 2). Thus, we have found that the structure of the ε-phase is based on an O_8 cluster, but is different from the O_4 model estimated from optical measurements or from the chain model predicted theoretically. Furthermore, we have confirmed that this structure is formed under pressure up to 96 GPa.

The boxlike cluster is a unique conformation that was first discovered for oxygen (Fig. 3), and has never been reported experimentally or theoretically for any other diatomic molecules. The formation mechanism of the O_8 cluster found in this work is not yet clear, and we hypothesize that the charge transfer between oxygen molecules or the magnetic moment of oxygen molecules plays a significant role in the formation. Hereafter, based on the structure of the ε-phase, we plan to determine the structure of the oxygen ζ-phase formed under pressures above 96 GPa, which exhibits metallization and superconductivity. If successful, the results will provide significant information for the clarification of the mechanisms of metallization and superconductivity of oxygen. Also, because of the discovery of the new diatomic-molecule conformation in our work, we expect that structural analyses of hydrogen and other elements will be accelerated.

Two weeks after the publication of our study [3], a British group reported the crystal structure of the ε-phase determined by single crystal X-ray diffraction [4]. This independent study revealed the same O_8 structure and was immediately reviewed [5].

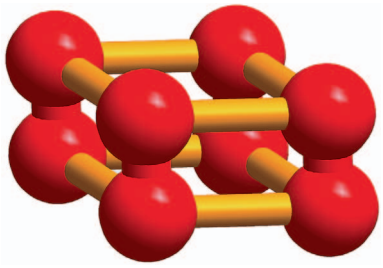

Fig. 3. Structure of the O_8 cluster found in the solid oxygen ε-phase.

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References

[1] Y. Akahama *et al.*: Phys. Rev. Lett. **74** (1995) 4690.
[2] K. Shimizu *et al.*: Nature **393** (1998) 767.
[3] *H. Fujihisa, Y. Akahama, H. Kawamura, Y. Ohishi, O. Shimomura, H. Yamawaki, M. Sakashita, Y. Gotoh, S. Takeya and K. Honda: Phys. Rev. Lett.* ***97*** *(2006) 085503.*
[4] L.F. Lundegaard *et al.*: Nature **443** (2006) 201.
[5] B. Militzer and R.J. Hemley: Nature **443** (2006) 150.