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## Structural studies of $\beta$ -O<sub>2</sub> under pressure

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### Abstract

The structure and lattice compression of the  $\beta$ -O<sub>2</sub> phase have been studied by synchrotron x-ray diffraction experiments at 277 and 300 K. The pressure dependence of the lattice constants,  $a$  and  $c$ , obtained from a powder indicated anisotropic compressibility.  $a$  is almost three times as compressible as  $c$ . This large linear compressibility of  $a$  may be attributed to the antiferromagnetic interaction in the basal plane. Single-crystal analyses at 6.1 GPa and 300 K suggested that the oxygen atom is disordered with a threefold axis of symmetry.

### 1. Introduction

The  $\beta$ -O<sub>2</sub> phase occurs at low temperature between 24 and 55 K under ambient pressure as well as under high pressure between 5.5 and 9.4 GPa at room temperature [1] (see figure 1). Its crystal structure has a rhombohedral lattice (space group:  $R3m$ ) and at low temperature, the magnetic moment of O<sub>2</sub> molecules shows antiferromagnetic order: the so-called frustrated spin triangle lattice in the basal plane [2–4]. Magnetic interactions will play an important role not only as regards the molecular arrangement but also in the compressibility of the crystalline solid. Up to now, x-ray structural studies of this phase have been rare and only one powder x-ray diffraction experiment under pressure has been reported [5]. Two single-crystal analyses have been reported below 6.8 GPa [2, 3]. However, there has been no report of precise compression data for  $\beta$ -O<sub>2</sub>.

In this report, we present the pressure dependence of the lattice constants and the result of a single-crystal analysis for  $\beta$ -O<sub>2</sub> and discuss the observed anisotropic and anomalous compressibility.

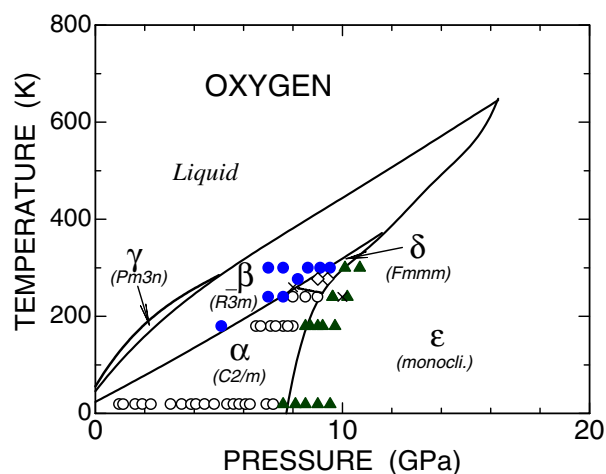


Figure 1. The phase diagram of solid oxygen [1].

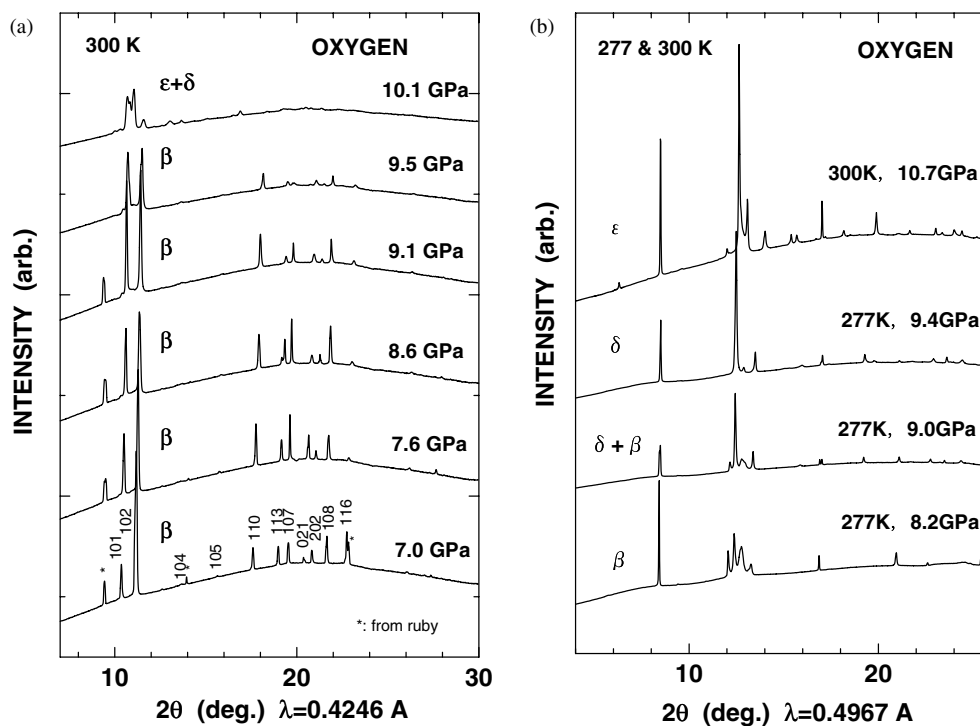
## 2. Experimental details

X-ray powder diffraction experiments at 300 and 277 K were carried out by an angle-dispersive method with an IP and a monochromatic SR source of  $\lambda = 0.4246 \text{ \AA}$  (ID30 at ESRF) and  $0.4967 \text{ \AA}$  (BL10XU at SPring-8), respectively. It was difficult to get powder x-ray patterns below 6.8 GPa due to recrystallization. Single-crystal analyses of  $\beta$ -O<sub>2</sub> in a Merrill–Bassett cell were performed at 6.1 GPa with two monochromatic SR x-ray sources of  $\lambda = 0.2483$  and  $0.41365 \text{ \AA}$ , on BL02B1 at SPring-8. Details of the beamline used for the single-crystal analysis have been described elsewhere [6].

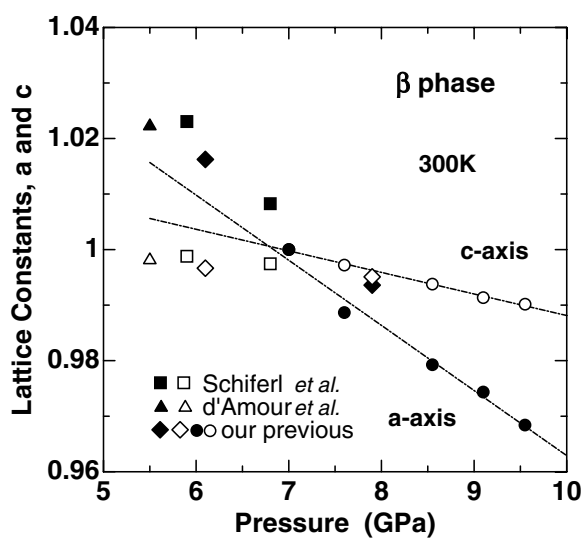
## 3. Powder x-ray diffraction

Figures 2(a) and (b) show the pressure dependences of the x-ray powder patterns at 300 and 277 K, respectively. The  $\beta$ -phase, during isothermal compression at 300 K, is stable up to 9.5 GPa and transformed into a mixture of  $\delta$ - and  $\epsilon$ -phases at 10.1 GPa. The  $\epsilon$ -phase, during isothermal decompression at 277 K, is transformed into the orthorhombic  $\delta$ -phase at 9.4 GPa. The  $\delta$ -phase coexists with the  $\beta$ -phase at 9.0 GPa. The pattern at 8.4 GPa is explained as the  $\beta$ -phase with a stacking fault along the  $c$ -axis [1]. These phase relations, which are added in the phase diagram shown in figure 1, are consistent with our previous results [1]. It should be noted that powder samples recrystallized at 6.8 GPa as the pressure was decreased from 10 GPa. Therefore, it was difficult to obtain reliable powder patterns below 6.8 GPa.

The pressure dependences of the lattice constants,  $a$  and  $c$ , are illustrated in figure 3, together with our data obtained from the single-crystal analysis and previous data [2, 3]. The lattice constants are normalized with the values of  $a = 2.785(1)$  and  $c = 10.244(7) \text{ \AA}$  at 7.0 GPa. Two prominent features are found in this figure. One is the anisotropic compressibility:  $a$  is almost three times as compressible as  $c$ . This large linear compressibility of  $a$  may be attributed to the antiferromagnetic interaction in the basal plane although the magnetic order is short range [4, 7]. The other is the anomaly in the pressure dependence around 6.8 GPa.  $a$  seems to contract discontinuously by about 1% while  $c$  elongates by 0.3%. Figure 4 shows the pressure dependence of the molecular volume of solid oxygen at room temperature. The values of the molecular volume for the  $\epsilon$ -phase agree with our previous data [8].



**Figure 2.** (a) X-ray diffraction patterns of solid oxygen at 300 K. (b) X-ray patterns of solid oxygen at 277 and 300 K.



**Figure 3.** Pressure dependences of the lattice constants of  $\beta$ -O<sub>2</sub>.

The dependence did not indicate any anomaly at 6.8 GPa. From the results, the volume reductions,  $-\Delta V/V$ , of the  $\beta$ - $\delta$  and  $\delta$ - $\epsilon$  phase transitions at the transition pressures are estimated to be 2.0 and 2.1%, respectively.

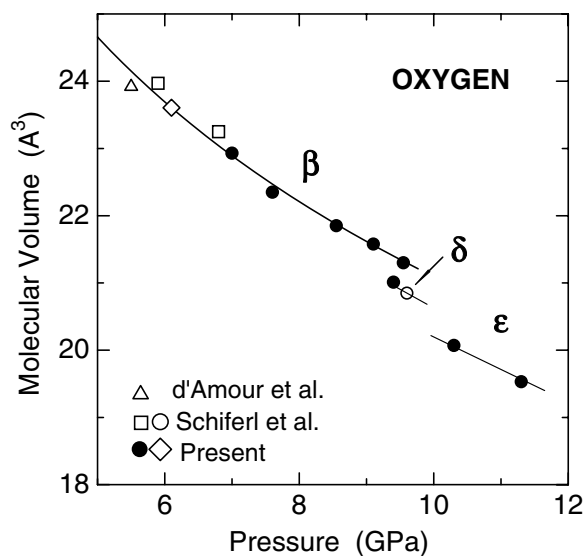


Figure 4. The pressure dependence of the molecular volume of solid oxygen.

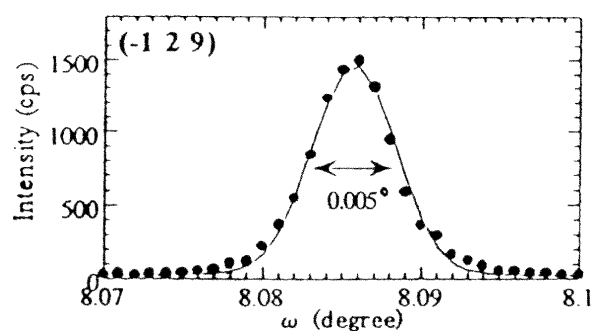
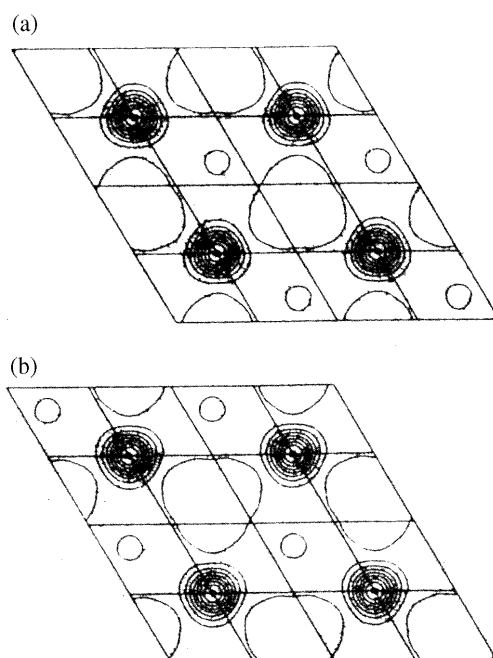


Figure 5. The profile of the  $(\bar{1}29)$  Bragg reflection of  $\beta$ -O<sub>2</sub> at 6.1 GPa.

#### 4. Single-crystal analysis

The single-crystal structure analysis of  $\beta$ -O<sub>2</sub> was carried out at 6.1 GPa and room temperature. Figure 5 shows the profile of the  $(\bar{1}29)$  Bragg reflection. The sample quality was very good and the full width at half-maximum was about 0.005°. Two domains in which the  $c^*$ -axis has opposite directions coexist in this sample. The data collection was carried out by several methods at each wavelength. RADIEL was used for the final analyses, and we show the result of the final analysis in table 1. For the structure analysis, we used independent reflections, and the 62 and 67 points at 0.2483 and 0.413 64 Å, respectively. The errors in the atomic positional parameter and the thermal parameters are equal to or better than those given by Schiferl *et al* [3] and  $R_f$  and  $R_w$  are better than those given by them. The lattice constants obtained,  $a$  and  $c$ , are consistent with previous data [2, 3] and support the presence of the anomaly at 6.8 GPa. The most remarkable thing is that the extinction effect is zero in the structure analysis performed with the higher-energy x-rays (49.93 keV, 0.2483 Å). It is found that the thermal parameter in the basal plane,  $\beta_{11}$ , is considerable.



**Figure 6.** Fourier maps for  $\beta$ -O<sub>2</sub> in the basal plane at  $z = 0.058$  (a) and  $z = -0.058$  (b).

**Table 1.** Results of single-crystal analyses for  $\beta$ -O<sub>2</sub> at 6.1 GPa.

	This study		Previous <sup>a</sup>
Wavelength (Å)	0.2483	0.413 65	Mo K $\alpha$
Pressure (GPa)	6.1(1)	6.1(1)	5.5(1)
Number of reflections	62	67	46
Lattice constant $a$ (Å)	2.826(20)	2.830(4)	2.8467(2)
Lattice constant $c$ (Å)	10.160(77)	10.210(9)	10.2249(8)
Volume $V$ (Å <sup>3</sup> )	70.58(49)	70.75(9)	71.76(1)
Positional parameter $z$	0.057 88(9)	0.057 95(7)	0.0577(2)
Thermal parameters			
$\beta_{11} = \beta_{22} = 2\beta_{12}$	0.1454(5)	0.1457(5)	0.1647(7)
$\beta_{33}$ ( $\beta_{13} = \beta_{23} = 0$ )	0.0049(1)	0.0074(1)	0.0055(3)
Extinction effect	0.0(0)	1.5(1)	
$R$ -factor $R_f$	0.0405	0.0320	0.0345
$R$ -factor $R_w$	0.0182	0.0337	0.050

<sup>a</sup> From Schiferl *et al* [3].

Figure 6 shows the Fourier maps of  $\beta$ -O<sub>2</sub> in the basal plane at  $z = 0.058$  (a) and at  $z = -0.058$  (b) given by the structure analysis for the wavelength 0.41365 Å. This result suggests that the oxygen atom is disordered with a threefold axis of symmetry. Therefore, the anomaly in the pressure dependence of the lattice constants at 6.8 GPa may result from vibrational ordering of the molecular axis due to a certain change in the intermolecular interaction.

## 5. Conclusions

In the present x-ray powder diffraction study and the single-crystal analysis, precise compression data for  $\beta$ -O<sub>2</sub> were obtained and anisotropy of the compressibility was revealed. The pressure dependence of the lattice constants obtained exhibited an anomaly at 6.8 GPa. These results were discussed from the viewpoint of the magnetic interaction between oxygen molecules. The phase transitions from the  $\beta$ -phase to the  $\delta$ -phase and further to the  $\varepsilon$ -phase at 277 and 300 K were also confirmed.

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## References

- [1] Akahama Y, Kawamura H and Shimomura O 2001 *Phys. Rev. B* **64**
- [2] d'Amour H, Holzapfel W B and Nicol M 1981 *J. Phys. Chem.* **85** 130
- [3] Schiferl D, Cromer D T, Schwalbe L A and Mills R L 1981 *Acta Crystallogr. B* **37** 1329
- [4] Meier R J and Helmholdt R B 1984 *Phys. Rev. B* **29** 1387
- [5] Olinger B, Mills R L and Roof R B Jr 1984 *J. Chem. Phys.* **81** 5068
- [6] Noda Y *et al* 1998 *J. Synchrotron Radiat.* **5** 485
- [7] Uyeda C, Sugiyama K and Date M 1985 *J. Phys. Soc. Japan* **54** 1107
- [8] Akahama Y, Kawamura H, Häusermann D, Hanfland M and Shimomura O 1995 *Phys. Rev. Lett.* **74** 4690