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Theoretical calculations for solid oxygen under high pressure

Kazuki Nozawa, Nobuyuki Shima and Kenji Makoshi

Graduate School of Material Science, University of Hyogo, 3-2-1, Kouto, Kamigohri, Hyogo 678-1297, Japan

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Abstract

The crystal structure of solid oxygen at low temperatures and at pressures up to 7 GPa is studied by theoretical calculations. In the calculations, the adiabatic potential of the crystal is approximated by a superposition of pair-potentials between oxygen molecules calculated by an *ab initio* method. The monoclinic α structure is stable up to 6 GPa and calculated lattice parameters agree well with experiments. The origin of a distortion and that of an anisotropic lattice compressibility of the basal plane of α -O₂ are clearly demonstrated. In the pressure range from 6 to 7 GPa, two kinds of structures are proposed by x-ray diffraction experiments: the α and orthorhombic δ structures. It is found that the energy difference between these structures becomes very small in this pressure range. The relation between this trend and the incompatible results of x-ray diffraction experiments is discussed.

1. Introduction

At low temperatures or under pressures, molecular oxygen is solidified by weak intermolecular interactions. At zero pressure, oxygen transforms to monoclinic α -O₂ through γ - and β -O₂ by cooling. In the α phase, oxygen molecules condense with their molecular axis perpendicular to the basal plane of the monoclinic lattice. As shown in figure 1(a), experiments demonstrated that the unit cell includes two oxygen molecules and the structure belongs to the $C2/m$ space group [1]. The ground electronic state of the oxygen molecule is the spin triplet state. The molecular spins, which are perpendicular to the molecular axis, order antiferromagnetically on the basal plane of α -O₂ with the easy axis parallel to the b -axis. The basal plane is illustrated in figure 1(b). Arrows in the figure show the directions of magnetic moments. The crystal structures of solid oxygen might be correlated with the magnetic moments even at high pressures.

A Raman experiment reported a phase transition from α -O₂ to another monoclinic or orthorhombic structures below 3 GPa [2]. However, x-ray diffraction experiments using a high-brilliance synchrotron radiation source reported different phase diagrams. Akahama *et al* reported α -O₂ transforms to ϵ -O₂ directly at 7.2 GPa at 19 K [4]. Although they also found an anomaly in the lattice constants just before the transition to ϵ -O₂, it was not considered as a sign of a transition to other phases. Gorelli *et al* also reported the stability of α -O₂ up

to about 5.3 GPa, and they found orthorhombic δ -O₂ (space group: $Fmmm$) above 5.3 GPa at 65 K [5]. Although the monoclinic α structure is ascertained to be stable up to about 5 GPa at low temperatures in both experiments, the stable structure at pressures between 5 and 7 GPa is considered to be open to question. For higher pressures, recent x-ray diffraction experiments have revealed that ϵ -O₂ consists of O₈ clusters [6, 7]. The ϵ phase transforms to the metallic ζ phase at higher pressure (~ 100 GPa) and finally to a superconducting state [8–10]. The mechanism of the transition from or to the ϵ phase and the structure of the ζ phase are still unknown.

Regarding theoretical studies, Eters *et al* obtained the structure of α -O₂ using semi-empirical pair-potentials including magnetic interactions between O₂ pairs and predicted a phase transition from the α to an orthorhombic phase at 2.3 GPa [3]. We performed theoretical calculations using *ab initio* pair-potentials and reported that the monoclinic α structure is stable up to 6 GPa [11]. A part of these results will be presented in this paper. First-principles investigations based on density functional theory (DFT) [12] were performed especially for higher pressure phases ϵ and ζ [13–18]. The predicted structure for insulating ϵ -O₂ is however not consistent with the experimental one. This is caused by a failure of the local density approximation (LDA) to describe the magnetic interaction between oxygen molecules [19]. Because the failure does not influence the metallic state calculations, the structural relaxation based on DFT with an appropriate starting structure can predict the

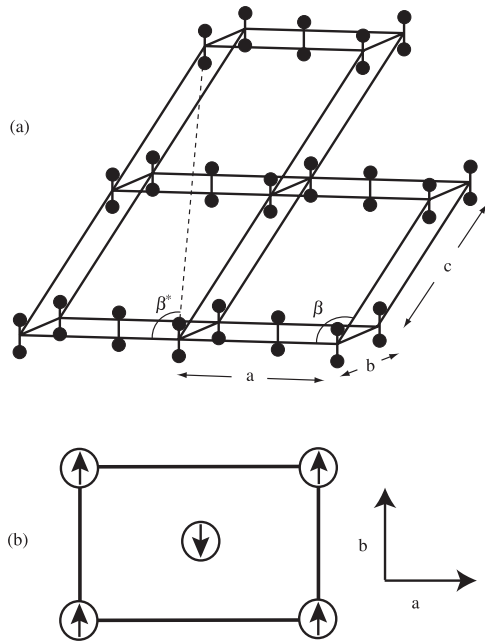


Figure 1. (a) Monoclinic unit cell of α -O₂. The unit cell includes two oxygen molecules. At $\beta^* = 90^\circ$, the unit cell becomes an orthorhombic $Fmmm$ structure. (b) The basal plane of α -O₂. Oxygen molecules are denoted by circles and molecular axes are perpendicular to the ab plane. Arrows represent magnetic moment directions.

structure of the ζ phase. A recent first-principles study reported a plausible structure for the metallic ζ phase [18]. In this paper, we study the insulating α and δ phases. The total energy is evaluated as a superposition of the pair-potentials obtained by quantum chemistry calculations including configuration interactions.

2. Theory and calculation

Under low pressures, solid oxygen consists of weakly bound oxygen molecules. Therefore, the interactions between molecules need to be reproduced exactly in order to calculate the structure. The total energy calculation based on DFT is often used to investigate structures of various crystals. Unfortunately, DFT calculations within the LDA (or with gradient corrections) do not give the correct intermolecular interactions for magnetic oxygen molecules. It is related to the symmetries of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), and the well-known bandgap-underestimation problem of the LDA [19]. Both of the HOMO and LUMO of the interacting oxygen molecules are originated in the π_g (gerade) orbital of O₂. Thus the underestimation of the HOMO–LUMO gap causes a serious overestimation of the exchange energy. We actually confirm DFT calculations do not reproduce the α structure at zero pressure. In many cases, quantum chemistry calculations including the configuration interactions reproduce intermolecular interactions correctly. In this paper, we evaluate the total energy as a superposition of intermolecular

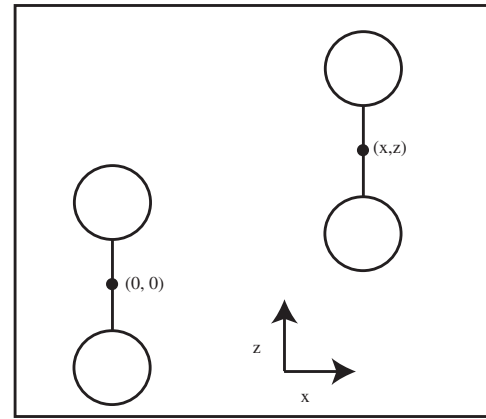


Figure 2. A schematic view of coordinates for pair-potentials. The vector (x, z) is the relative position of the molecules.

potentials (pair-potentials) calculated by an *ab initio* method with configuration interactions.

In order to reduce the degrees of freedom of the O₄ system, we introduce the following assumptions into the calculations.

- (i) Antiferromagnetic ordering in the ab (basal) plane.
- (ii) $C2/m$ lattice symmetry.
- (iii) A molecular axis perpendicular to the ab plane.

These assumptions are consistent with the known properties of the structure of α -O₂, and we can treat the orthorhombic δ structure as a special case with the monoclinic angle $\beta^* = 90^\circ$.

In the orthorhombic structure, two types of magnetic ordering along the c -axis are allowed: ferromagnetic or antiferromagnetic ordering. In the α phase, the magnetic ordering along the c -axis is obviously ferromagnetic because of the periodicity along c -direction. Although a recent neutron diffraction experiment reported antiferromagnetic ordering along the c -axis in the δ phase [20], we assume ferromagnetic ordering along the c -axis because it simplify the treatment of the transition from the α to δ phase. We have, however, confirmed that the difference in the total energy between the two kinds of ordering on the same lattice is very small. It is ascribed to the weak magnetic interaction between molecules in different c -layers.

Following assumption 1, there are two kinds of pairs of oxygen molecules. One is the pair in which magnetic moments are parallel (ferromagnetic pair, F). The other is the pair in which magnetic moments are antiparallel (antiferromagnetic, AF). Assumptions 2 and 3 restrict the geometric configuration of molecules. In addition to these assumptions, we fix the interatomic distance in O₂. With these constraints, the degrees of freedom of the O₄ system, in other words the number of geometric parameters of pair-potentials, are reduced from twelve to two. The remaining degrees of freedom are the relative position of molecules. The relative position of oxygen molecules (x, z) is defined as given in figure 2. Consequently, the total energy is written as

$$U_{\text{total}} = \sum_{l,m,n} [U^{\text{F}}(x_{lmn}^{\text{F}}, z_n) + U^{\text{AF}}(x_{lmn}^{\text{AF}}, z_n)]. \quad (1)$$

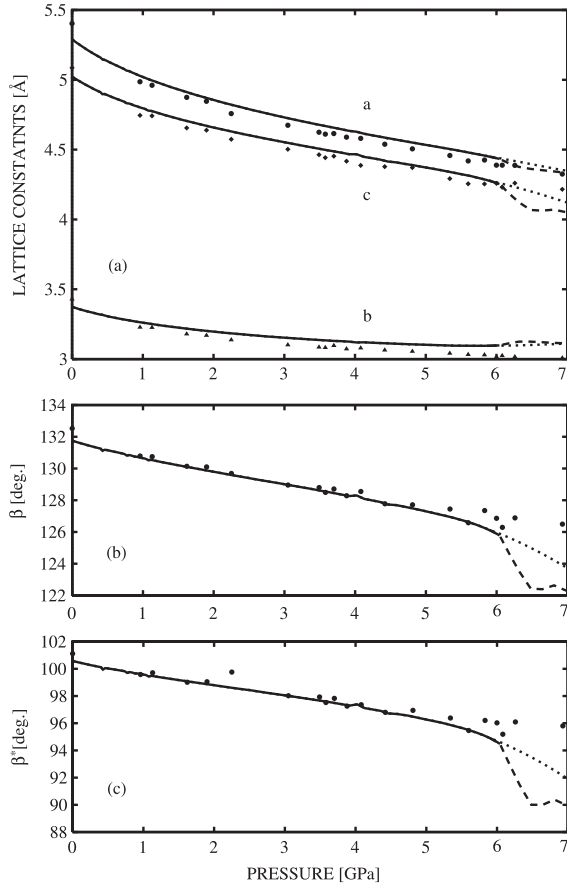


Figure 3. Pressure dependences of (a) lattice constants and monoclinic angles (b) β and (c) β^* up to 7 GPa. Calculated values are denoted by solid lines and experimental values are represented by closed circles, triangles and diamonds. See the text regarding the dashed and dotted lines.

In the equation, pair-potentials U^F and U^{AF} denote interactions of the F and AF pairs, respectively. l , m and n are indices of lattice vectors and coordinates x_{lmn}^F , x_{lmn}^{AF} and z_n are given as

$$x_{lmn}^F = \sqrt{(la - nc \cos \beta)^2 + (mb)^2}, \quad (2)$$

$$x_{lmn}^{AF} = \sqrt{\left(\left(l + \frac{1}{2}\right)a - nc \cos \beta\right)^2 + \left(\left(m + \frac{1}{2}\right)b\right)^2}, \quad (3)$$

$$z_n = |nc \sin \beta|. \quad (4)$$

Here, a , b , c and β are the lattice constants and the monoclinic angle, respectively. Pair-potentials U^F and U^{AF} are calculated by the complete active space self-consistent field (CASSCF) method [21]. The CASSCF calculation is performed with the GAMESS program [22] using the 3s2p1d atomic natural orbital basis set [23]. Details of the calculations and the pair-potentials obtained have been given in our previous brief report [11].

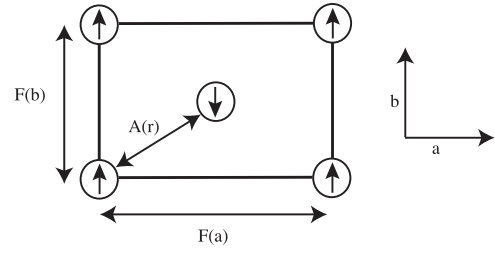


Figure 4. A model of the ab plane. Circles denote oxygen molecules, and arrows represent magnetic moment directions. The unit cell includes four AF pairs and six F pairs. Two F pairs in which the intermolecular distances are $2r$ are not taken into account in the discussion.

3. Results and discussions

3.1. Structures up to 6 GPa and their origin

A Raman experiment reported α -O₂ transforms to another monoclinic structure or orthorhombic structure under 3 GPa [2]. X-ray diffraction experiments by Akahama *et al* and Gorelli *et al*, however, showed the α structure is stable up to higher pressure. In this section, we present a result of the theoretical calculations showing that the α structure is stable up to 6 GPa.

The calculated pressure dependences of lattice parameters up to 6 GPa are shown in figures 3(a)–(c). The results of higher pressure, which is also shown in the figures, will be discussed later. In the figures, solid lines represent calculated lattice parameters, and closed circles, triangles and diamonds are experimental results [1, 4]. The values of pressure are evaluated by the numerical differentiation of the total energy with respect to the volume ($P = -\partial E/\partial V$).

As previously mentioned, Raman and theoretical studies reported phase transitions in this pressure range [2, 3]. The structural transition predicted by the theoretical calculation was accompanied by abrupt changes of the lattice parameters at 2.3 GPa. As shown in figure 3, the present results decrease continuously with increasing pressure and there is no sign of the structural transition to the δ structure up to 6 GPa.

As shown in figure 3(a), the crystal is less compressible along the b -axis than the a -axis. The relation of the anisotropic lattice compressibility and the AF ordering in the ab plane is discussed by Akahama *et al* [4]. The b/a ratio is 0.638 at zero pressure, increasing with pressure to reach 0.691 at 6 GPa. The experimental value is 0.635 at zero pressure [1], reaching 0.687 at 6 GPa [4]. The agreement between the calculation and experiments is very satisfactory. As previously reported, the crystal structure of α -O₂ is considered as the result of magnetic interactions between oxygen molecules [3]. In order to clarify how the magnetic interactions affect the crystal structure, we consider a simple model of the ab plane as shown in figure 4. This figure shows the top view of the ab plane. The molecular axes are perpendicular to the figure, and arrows represent the magnetic moment directions of O₂ molecules. The unit cell contains ten pairs of oxygen molecules: four AF pairs at a distance $r = \sqrt{a^2 + b^2}/2$ and three kinds of F pairs at distances a , b and $2r$. For simplicity, we neglect interactions

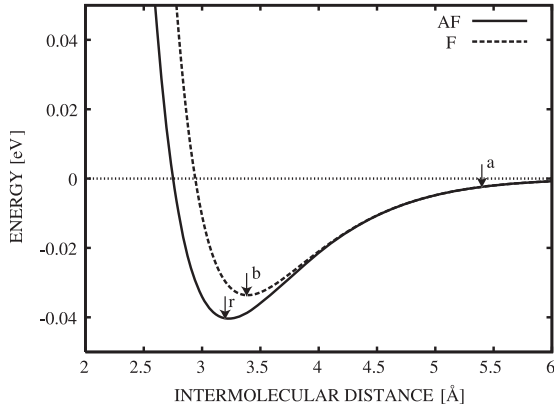


Figure 5. The optimized values of (a, b, r) and the pair-potentials. These pair-potentials correspond to $U^F(x, 0)$ and $U^{AF}(x, 0)$, which are defined in the previous section. Arrows denote the optimal values of (a, b, r) . Note that the values of b and r are almost at the minimum of the pair-potentials.

between molecules in which intermolecular distances are $2r$. Consequently the (total) energy of this system is written as

$$E(r, b) = 4A(r) + 2\left[F(\sqrt{4r^2 - b^2}) + F(b)\right], \quad (5)$$

where $A(x)$ and $F(x)$ denote interactions (pair-potentials) of the AF and F pairs at a distance x . Calculated intermolecular potentials $A(x)$ and $F(x)$, which correspond to $U^{AF}(x, 0)$ and $U^F(x, 0)$ in (1), are shown in figure 5. The optimal energy of (5) is obtained at $(a, b, r) = (5.42, 3.41, 3.20)$, and these are indicated by arrows in the figure. The obtained values are very close to the experimental values at zero pressure (5.40, 3.43, 3.20) [1].

Evidently (5) is dominated by the first term because of its coefficient and the fact that $A(x)$ has a deeper minimum than $F(x)$. Thus we obtain the optimal value of r , $r_0 \equiv 3.2$ where $A(r)$ takes the lowest energy. Then the problem is simplified as $E(r_0, b) = 4A(r_0) + 2E_2(b)$, where $E_2(b) = F(a(b)) + F(b)$ and $a(b) = \sqrt{4r_0^2 - b^2}$. $E(r_0, b)$ takes a minimum on the condition $\frac{dE_2(b)}{db} = 0$, i.e.,

$$a(b) \frac{dF(b)}{db} = b \frac{dF(a)}{da}. \quad (6)$$

This condition is symmetric for b and a , then $a = b (= \sqrt{2}r_0)$ satisfies the condition. It gives, however, the highest energy because $\frac{d^2F}{db^2}$ is negative at $b = \sqrt{2}r_0 \sim 4.5$ as shown in figure 5. Another solution b_0 of (6) is located on the slightly larger side of the minimum of $F(x)$: at around 3.4. As a result, the optimal value of r and b , and the structure of the ab plane therefore, strongly depend on the position of the minimum of $A(x)$ and $F(x)$. The difference of $A(x)$ and $F(x)$ corresponds to the exchange energy. If there are no magnetic interactions between the molecules, $A(x)$ is equivalent to $F(x)$. In this case, following the above discussion, the optimal value of r is equal to b_0 and it gives the close-packed triangular lattice. Distortion is not introduced if there is only one kind of pair-potential. Namely the origin of the distorted triangular lattice

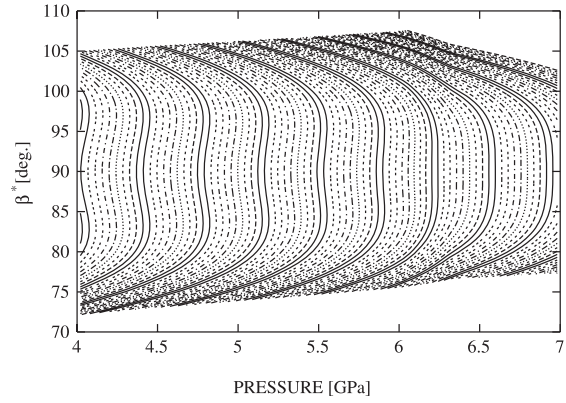


Figure 6. The contour plot of the total energy as a function of the pressure and β^* in the pressure range 4–7 GPa. The volume of the unit cell and lattice constants a and b are fixed at optimal values at each pressure, which are denoted by the solid and dashed lines in figure 3. The difference in the energy between the monoclinic α and orthorhombic δ structures is very small at around 6 GPa. Contours increase by 2 meV.

in the α phase is attributed to the existence of two kinds of pair-potentials, in other words, the magnetic interaction.

The anisotropic lattice compressibility of the ab plane, which was pointed out by Akahama *et al* [4], can be easily understood from figure 5. First we consider a situation where the lattice is compressed along the a -axis and the length along the b -axis is fixed. In this case r decreases following the relation $r = \sqrt{a^2 + b^2}$ and the first term of (5) increases due to the repulsive interaction. Some part of the increased energy is however canceled out by the term of $F(a)$ because it is in the attractive region. On the other hand, when the lattice is compressed along the b -axis and the a -direction is fixed, both of the terms $A(r)$ and $F(b)$ increase, and as a result the total energy E increases steeply compared with the previous case. This is the origin of the anisotropic lattice compressibility of the α phase.

3.2. Structures above 6 GPa

X-ray diffraction experiments by Akahama *et al* and Gorelli *et al* showed the monoclinic α structure is stable up to higher pressure than the previously proposed transition pressure. Around 6 GPa, however, they proposed different structures. Akahama *et al* reported a direct structural transformation from α - to ϵ -O₂ at 7.2 GPa. On the contrary, Gorelli *et al* found δ -O₂ between α - and ϵ -O₂. In this section, we discuss the stability of α - and δ -O₂.

In figure 3, dashed lines above 6 GPa show the lattice parameters of the optimal structure. The dotted lines present extrapolated values from the data below 6 GPa, namely those forming the monoclinic α structure. Although optimal values (dashed lines) show the orthorhombic structure is stable above 6 GPa, the energy of the orthorhombic structure is very close to that of the monoclinic (dotted lines) structure.

Since the δ -O₂ can be considered as a special case of α -O₂ ($\beta^* = 90^\circ$), we illustrate the total energy as a function of β^* and pressure. Figure 6 presents the pressure dependence

of the cross section of the total energy from 4 to 7 GPa. In the figure, the lattice constants a , b and the volume of the unit cell are fixed to the optimal values presented by the solid and dashed lines in figure 3(a). Therefore the only independent parameter is β^* at each pressure. In the low pressure range, the total energy takes minima at two values of β^* , which give equivalent monoclinic α structures, and the orthorhombic structure ($\beta^* = 90^\circ$) is unstable. With the adopted constraints on the crystal structure and geometric configurations of molecules, it can be derived analytically that the first derivative of the total energy with respect to β^* is zero at $\beta^* = 90^\circ$ (orthorhombic structure) at each pressure, i.e., the total energy takes a maximum or minimum value at the δ structure [19]. With increasing pressure, the δ structure becomes stable at around 6 GPa in place of the α structure, the energy difference between these structure is however less than 0.5 meV (~ 5 K) even at 7 GPa. Unfortunately, with the precision of the present calculations, the energy difference may be too small to decide which structure is stable. We obtained however an important result that the monoclinic-angle-dependence of the total energy is very small in this pressure range. Akahama *et al* and Gorelli *et al* proposed different structures in this pressure range. It is reasonable because the experiments were performed at temperatures higher than the energy difference we obtained. The very small energy difference in this pressure range implies that several structures which have various monoclinic angles can be allowed at finite temperature. Mita *et al* performed Raman scattering experiments and observed peaks above 5 GPa [24]. Although the origin of the peaks is unresolved, they indicated the existence of a complicated mixed phase at this pressure range. Further investigations are needed to determine the origin of the unknown peaks.

At high temperatures, many experiments demonstrated the stability of orthorhombic δ -O₂. The stability of δ -O₂ at high temperature is understood from figure 6. As shown in the figure, the energy surface forms a double-well or parabolic shape. In either case, they are symmetric with respect to β^* around $\beta^* = 90^\circ$ and the energy barrier separating the wells is very low. Therefore the expectation value of β^* becomes 90° even at low pressure because of the effect of thermal excitations.

Akahama *et al* reported abrupt changes of the lattice parameters at the phase boundary of the α and ϵ phases. In the present calculations, however, corresponding changes of lattice parameters are not obtained up to 12 GPa. This may be caused by the constraints on the crystal and/or magnetic structure in our calculations. A recent neutron diffraction experiment shows a disappearance of the magnetic long-range ordering in the ϵ phase, but it does not exclude the short-range order [25]. Intermolecular potentials adaptable to other magnetic configurations may be required to obtain the ϵ structure.

4. Summary

We investigated crystal structures of solid oxygen under pressure with *ab initio* pair-potentials taking account of the

different spin states. Under 6 GPa, the obtained structure is monoclinic α and the calculated lattice parameters agree well with the results of the x-ray diffraction experiment. The origin of the distortion of the basal plane and that of the anisotropic lattice compressibility of α -O₂ are clearly demonstrated as being caused by the existence of two kinds of intermolecular interaction, namely magnetic interactions. The crystal structure under the pressure range from 6 to 7 GPa is discussed using the total energy surface projected on the P - β^* space. Although orthorhombic δ -O₂ is obtained as the stable structure, the energy difference between α - and δ -O₂ is less than 5 K in this pressure range. This implies the possibility of a mixed phase including some structures which have various monoclinic angles. It seems to be consistent with recent x-ray diffraction and Raman experiments.

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