Bonding in the $\varepsilon$-Phase of High Pressure Oxygen

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Abstract. The electronic basis of the formation of (O$_2$)$_4$ clusters in the newly discovered structure in the $\varepsilon$ phase of solid O$_2$ is elucidated through the analysis of the electron topology from first-principles calculations using the Bader atoms-in-molecules method. It is shown that the intra-cluster O$_2$ interaction is consistent with a donation-acceptor bond rather than the spin-pairing of two open-shell molecules. Distortion of the (O$_2$)$_4$ cluster with increasing pressure is also investigated. It is shown that these structural changes eventually lead to a structural transition at 96 GPa, as observed experimentally.

1. Introduction
Solid oxygen has a complex phase diagram consisting of high-pressure phases with unusual physical properties [1]. When cooled at ambient pressure, three phases ($\alpha$, $\beta$, and $\gamma$) of solid oxygen have been identified. Under compression at room temperature a sequence of structural transformations leads to four distinct phases, namely, $\beta$-, $\delta$-, $\varepsilon$-, and $\zeta$-O$_2$. At 300K, the rhombohedral $\beta$ phase transforms first to $\delta$-O$_2$ at 5.4 GPa [1]. The $\delta$ phase has an orthorhombic structure with a long-range antiferromagnetic order [2]. At 9.6 GPa, $\delta$-O$_2$ transforms to the $\varepsilon$ phase [3]. The monoclinic $\varepsilon$ phase [4] is stable up to 96 GPa where it transforms into metallic $\zeta$ phase [5, 6]. The $\zeta$ phase shows superconductivity with a critical temperature of 0.5K at 105 GPa [7] but its structure still remains elusive [6]. Despite intense efforts over decades [1], the crystal structure of the $\varepsilon$ phase was only recently resolved by x-ray diffraction [8, 9]. The $\varepsilon$ phase reveals a remarkable monoclinic structure consisting of (O$_2$)$_4$ clusters. At 17.5 GPa the intermolecular distance within the cluster of 2.20 Å is significantly longer than the intramolecular distance of 1.20 Å which is almost identical to that of the free molecule. The very long intermolecular distance, however, raises important questions on the nature of the bonding between O$_2$ in the cluster [10]. A recent molecular orbital study investigated the stability of an isolated (O$_2$)$_4$ cluster as compared to S$_8$, but the nature of intermolecular and inter-cluster bonding was not discussed [11].

This paper presents results on the nature of chemical bonding in $\varepsilon$-oxygen through a topological analysis of charge density using the Bader atoms-in-molecules (AIM) method [12, 13]. The basic idea
of AIM analysis is to extract bonding information from the electron density \( \rho(r) \). The analysis of its electron density gradient \( \nabla \rho(r) \) helps to define an atom within a molecule or solid through the “zero-flux surface” condition. The analysis of the electron density extrema, i.e., at critical points, located at \( r_{cp} \) for which \( \nabla \rho(r_{cp}) = 0 \), allows the characterization of the nature of bonding. Once critical points are located and their curvatures are analyzed, (i.e., the second derivative- Laplacian, \( \nabla^2 \rho(r_{cp}) \)), they can be further classified according to the eigenvalues (\( \lambda_i \)) of the Hessian matrix. Other properties derived from the topological analysis of the charge density, such as the local energy, \( H(r_{cp}) \) [14, 15], have been used to characterize the interactions. It has been shown that the charge density topology is not sensitive to small changes in the electron density [16]. AIM has been applied with great success for the characterization of a variety of chemical bonds [17]. A recent review on the application to solids has been given by Gatti [13].

2. Computational Methods

The results reported here were obtained from the pseudopotential plane wave electronic codes VASP [18]. The projected augmented wave (PAW) potential [19] of oxygen atoms from the pseudopotential library was used. The Bader atoms-in-molecules (AIM) analysis was performed with the program InteGrity [20]. The total charge density was calculated using the latest version of VASP code where both the atomic core and pseudo-valence charge densities were explicitly included. The convergence of the calculated results has been carefully checked against the mesh size used to generate the charge densities. A 120\( \times \)120\( \times \)120 mesh was found to be adequate. In addition to VASP, calculations on the isolated \( (O_2)_4 \) were also performed with the localized basis set code Gaussian03 [21] employing a 6-311G(d,p) basis set for oxygen.

Even though \( \varepsilon \)-oxygen was found to be non-magnetic from neutron scattering experiments, weak itinerant magnetism cannot be ruled out [4]. To investigate this assumption spin-unrestricted calculations were performed on the known \( C2/m \) structure at 17 GPa [8,9] with an initial density matrix constructed with all spin-up 2\( p \) electrons. The wave function and geometry were found to converge to the spin-restricted solution. Thus the spin restricted method was used in ensuing calculations. Structural parameters of the \( C2/m \) phase at selected pressures from 9 to 110 GPa were fully optimized. The results obtained are similar to those reported recently using the same theoretical approach [22]. The calculated equation of state over the entire pressure range apparently is in good agreement with experiment [9]. However, at pressures over 60 GPa, the calculated unit cell parameters, although still reproduce the experimental trend, a sudden reduction in the monoclinic angle (\( \beta \)) than observed (80 GPa) was found [22]. The discrepancy can be traced to a deficiency of the GGA approach which underestimated the band gap energy and predicted, prematurely, metallization in the \( C2/m \) structure at 50 GPa. As reported elsewhere [23] a quasiparticle theory is needed to provide a correct description of the electronic structure. In this study, discussions on the chemical bonding in \( \varepsilon \)-oxygen will focus on the low pressure regime.

3. Results and Discussions

A comparison of the structure of the \( (O_2)_4 \) cluster in \( \varepsilon \)-oxygen with an isolated \( (O_2)_4 \) reveals some unique features of the bonding in the solid state. Geometry optimization of an isolated cluster led to a square prism structure (\( D_{4h} \) point group symmetry) with calculated intramolecular O-O bond lengths of 1.201 Å from Gaussian03 (1.216 Å, from VASP) and intermolecular \( O_2...O_2 \) distances of 2.120 (2.141) Å. Although, the intramolecular \( O_2 \) bond length is apparently in good agreement with experiment, the intermolecular \( O_2...O_2 \) distance of the isolated cluster, however, is significantly shorter than the observed separation of 2.34 Å at 10 GPa in the solid state. A much shorter \( O_2...O_2 \) distance predicted for the isolated cluster in the absence of external compression is surprising. Furthermore, at 10 GPa, the minimum contact distance between \( (O_2)_4 \) clusters in the solid state structure is 2.71 Å. Therefore, any significant inter-cluster interactions can be ruled out. In the free cluster, as has been characterized previously [1], the \( O_2...O_2 \) bond is derived from the paring of two electrons each from the \( \pi^* \) orbital of the participating \( O_2 \) molecule [11]. Thus, this can be described as
a true spin-coupled two-electron covalent bond. The fact that a much longer intermolecular distance was observed in $\varepsilon$-oxygen, leads to the inevitable conclusion that the nature of chemical bonding must be different from the isolated cluster.

We have attempted to analyze the charge density differences and electron localization function of the $(O_2)_4$ clusters in the $C2/m$ structure but failed to uncover obvious hints of covalent interactions between the $O_2$ forming the cluster. A detailed analysis of the charge density topology is necessary to characterize the intermolecular and intra-cluster interactions. For this purpose, accurate 3-D electron densities for $\varepsilon$-oxygen were generated from first principles calculations. The $(3,-1)$ bond critical points (BCP) derived from AIM analysis at 24 GPa are summarized in Table 1. As expected, the BCP’s of the $O_2$ molecules have the largest value of local density $\rho(r_{cp})$ (~0.55) and local energy $H(r_{cp})$ [12, 14, 15] (1.10 a.u.) and are indicative of genuine O-O covalent bonds. Significantly, intra-cluster BCP’s are found between $O_2$ molecules forming the $(O_2)_4$ cluster. The charge density at the critical point $\rho(r_{cp})$ ~0.06 with a positive Laplacian and a negative $H(r_{cp})$ (0.009 a.u.) are unambiguous signs of covalent interactions between $O_2$ molecules, being however much weaker than that expected for a normal covalent bond [17].

So what is the nature of the chemical bond in $\varepsilon$-oxygen? A positive Laplacian is perhaps surprising as it indicates “closed shell” interactions [12, 24] between the two O atoms of the adjacent $O_2$ molecules in the $(O_2)_4$ unit instead of the pairing of two “open-shell” spin-uncoupled orbitals forming a pair of two electron bonds. If the latter description were correct, the intermolecular distance would be close to that of a single $\sigma$-bond as predicted for the isolated cluster. The analysis, however, is consistent with the observed very long $O_2$...$O_2$ separation of about 2.34 Å at 10 GPa and 2.17 Å at 17 GPa. Results indicate that the $O_2$ molecules forming the rhomb-shaped clusters in the $\varepsilon$ phase are stabilized via donor-acceptor resonance structures, i.e. the donation of a paired $\pi^*$ electron from one $O_2$ into the empty $\pi^*$ orbital of the other. In this interpretation, the $O_2$ converted from a spin-uncoupled state of a free molecule into a spin-paired state (two electrons occupying one of the $\pi^*$ orbital) to facilitate interactions with the neighbouring $O_2$ forming the cluster. This description is consistent with the fact that the magnetic moment of solid $O_2$ has already decreased from 2 $\mu_B$ at the zero pressure structure to less than 0.5 $\mu_B$ to the $\delta$ phase preceding the $\delta$→$\epsilon$ transition [4]. Therefore, interactions between $O_2$ in the cluster cannot be due to simple spin pairing of electrons from the isolated molecules [4]. A crystallographic evidence supports this interpretation: the $O_2$ bond distance of 1.20 Å determined at 17.6 GPa [8] is longer than 1.180 Å found in $\beta$ $O_2$ at 5.5 GPa [25] and 1.175 Å in $\delta$ $O_2$ at 9.6 GPa and 297 K [1]. A longer O-O bond length observed at higher pressure suggests that two valence electrons occupy a single $\pi^*$ orbital thus reducing the bond order and increasing the length of the molecular bond. BCP’s are also identified between oxygen atoms of different clusters. As shown in Table 1, the electron density at these inter-cluster BCPs (0.028) are much smaller. Moreover, both the Laplacian and local energy density $H(r_{cp})$ are positive indicating closed shell van der Waals interaction between the clusters [15, 24]. Ring and cage CP’s were also identified but they are of minor significance and will not be discussed here.

When $\varepsilon$-oxygen is compressed, the intra-cluster $O_2$ distance ($d_1$) and inter-cluster distance ($d_2$) decrease rapidly [8, 9]. Although the theoretical calculations reproduce this trend, as commented above (vide supra), the agreement between theoretically predicted and experimentally observed lattice parameters is not as good at pressure higher than 60 GPa [22]. Nevertheless, the shape of the $(O_2)_4$ cluster is found to distort from a square prism to a diamond shape prism with increasing pressure. The $O_2$...$O_2$ bond angle decreases gradually from 88° at 20 GPa to 80° near the $\varepsilon$→$\zeta$ transition at 97 GPa [8, 9]. The distortion leads to changes in the structure and the electron density topology. Table 2 gives results of the AIM analysis on an over-pressurized $C2/m$ structure at 105 GPa. As indicated by $\rho(r_{cp})$ and $\nabla^2 \rho(r_{cp})$ the intra-cluster and inter-cluster interactions of 0.065 and 0.062, respectively, are now almost equivalent. The $(O_2)_4$ clusters in the $ab$ plane start to connect to each other. At this pressure, the calculated electronic band structure shows that the $C2/m$ is metallic. The linking of $(O_2)_4$ clusters may be the precursor for the $\varepsilon$→$\zeta$ phase transition.
4. Conclusion
The nature of the interactions between O\(_2\) molecules and the preference of the formation of (O\(_2\))\(_4\) clusters in the C\(_2/m\) structure of the \(\varepsilon\) phase have been elucidated from the analysis of the electron charge density using Bader atoms-in-molecules theory. It has been shown that overall interactions, particularly, weak non-bonding interactions between (O\(_2\))\(_4\) clusters help to stabilize the structure. Changes in the geometry of the (O\(_2\))\(_4\) cluster with pressure have been examined. It is shown that the lower pressure square prism cluster of \(\varepsilon\)-oxygen deforms into a diamond-shape prism at pressure close to the observed insulator-metal transition. It is shown that the enhanced interactions between the clusters lead to a calculated structural phase transition at 96 GPa.

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Table Captions

1. Bond critical point data (a.u.) located in the $C/2m$ structure of $(O_3)_4$ at 25 GPa.

2. Bond critical point data (a.u.) located in the $C/2m$ structure of $(O_2)_4$ at 105 GPa.
Table 1. Bond critical points for C2/m ε-oxygen at 24 GPa

| Bond            | Type          | \(\rho(r_{cp})\) | \(\nabla^2 \rho(r_{cp})\) | \(\lambda_1\) | \(\lambda_2\) | \(\lambda_3\) | \(H(r_{cp})\) |
|-----------------|---------------|-------------------|---------------------|---------------|---------------|---------------|---------------|
| O₃ – O₃         | Molecular     | 0.5501            | -0.536              | -1.555        | -1.527        | 2.546         | -1.109        |
| O₁ – O₂         | Molecular     | 0.5468            | -0.459              | -1.518        | -1.510        | 2.569         | -1.087        |
| O₃…O₂ (d₁)      | Intra-cluster | 0.0622            | 0.231               | -0.098        | -0.091        | 0.421         | -0.009        |
| O₃…O₁ (d₂)      | Intra-cluster | 0.0619            | 0.232               | -0.098        | -0.091        | 0.420         | -0.009        |
| O₃…O₂ (d₃)      | Inter-cluster | 0.0276            | 0.099               | -0.025        | -0.024        | 0.148         | 0.003         |
| O₃…O₂ (d₄)      | Inter-cluster | 0.0194            | 0.089               | -0.020        | -0.019        | 0.128         | 0.003         |
| O₃…O₂ (d₅)      | Inter-cluster | 0.0163            | 0.080               | -0.017        | -0.017        | 0.122         | 0.004         |

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Table 2. Bond critical points for an over-pressurized C2/m ε- oxygen at 105 GPa

| Bond                  | Type                | $\rho(r_{CP})$ | $\nabla^2 \rho(r_{CP})$ | $\lambda_1$ | $\lambda_2$ | $\lambda_3$ | $H(r_{CP})$ |
|-----------------------|---------------------|-----------------|--------------------------|-------------|-------------|-------------|-------------|
| O₃ – O₃               | Molecular           | 0.5882          | -0.737                   | -1.702      | -1.657      |             | -1.253      |
| O₁ – O₂               | Molecular           | 0.5866          | -0.663                   | -1.659      | -1.642      |             | -1.238      |
| O₃…O₃ (d5) Inter-cluster| 0.0652             | 0.291           | -0.100                   | -0.093      | 0.484       |             | -0.006      |
| O₃…O₂ (d1) Intra-cluster| 0.0619             | 0.280           | -0.094                   | -0.086      | 0.456       |             | -0.005      |
| O₃…O₁ (d2) Intra-cluster| 0.0619             | 0.282           | -0.093                   | -0.084      | 0.459       |             | -0.004      |
| O₃…O₂ (d3) Inter-cluster| 0.0484             | 0.219           | -0.066                   | -0.057      | 0.341       |             | -0.001      |
| O₃…O₂ (d4) Inter-cluster| 0.0449             | 0.204           | -0.058                   | -0.051      | 0.312       |             | 0.001       |