

Ab-initio structural search in solid oxygen at high pressure: from zero to finite temperature

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Abstract. The crystal structure of solid oxygen in the terapascal (TPa) regime has been investigated with Density Functional Theory and the Random Search algorithm at zero temperature. We also considered the effect of the entropy at finite temperatures using the Quasi-Harmonic Approximation, and we found that the regime of stability of solid oxygen differs strongly from the results predicted at zero temperature. Finally, we provide some insights of oxygen as a chalcogen element.

1. Introduction

Oxygen is a very interesting object of study: for instance, among common diatomic molecules (H₂, N₂, O₂, CO, F₂, etc.), oxygen is the only element that can carry a magnetic moment [1]. Aside from its abundance in the Universe, its importance for many fundamental biological functions, or its role in the absorption of solar radiation inside Earth's atmosphere, oxygen exhibits an unique combination of characteristics that make it a physical object of great interest for the scientific community. Nowadays, only molecular phases of solid oxygen have been found via experimental data, even at the highest pressures currently attainable in hydrostatic compression experiments. Up to this date, six solid phases of oxygen have been established unambiguously: half of them (α , β and γ) exist under equilibrium vapour pressure, and the other three (δ , ϵ and ζ) are obtained in the high pressure regime. Nevertheless, in the atmospheres of giant planets, inside and outside our solar system, non-molecular oxygen could be much more abundant than the molecular phases due to the extreme pressure and temperature conditions that are present. This hypothesis has motivated several theoretical and experimental studies aiming to get a better understanding of oxygen under those conditions, so that we can have a better comprehension of the processes that occur in planetary interiors.

Upon increasing pressure at low temperature, a first transformation takes place from α -oxygen to the anti-ferromagnetic δ -phase at approximately 6GPa [2, 3, 4, 5]. δ -phase is orthorhombic and it belongs to the space group Fmmm. In [5] another oxygen phase was described, which appeared at 10GPa and 300K and exhibited a visual change of the sample colour from light orange to dark red; this type of change is a particularity of solid oxygen. This new oxygen form was called ϵ -phase.

Several studies were carried out in order to define the structure of the ϵ -phase: optical [6, 7] and X-Ray powder diffraction studies [8, 9, 10] have demonstrated that the ϵ -phase retains a layered structure with parallel alignment of molecules that is typical for all known oxygen structures except for γ -oxygen. Gorelli *et al.* [11] suggested that ϵ -oxygen's most basic unit is not an O₂ molecule, but a cluster of molecules. This assumption was confirmed by X-Ray diffraction [12, 13]: ϵ -oxygen is an arrangement of groups of four O₂ molecules that form a monoclinic C2/m structure. The E-phase has been widely



studied using different DFT functionals and it has been demonstrated that for pressures above 30GPa, DFT methods are in very good agreement with experimental results [14]. A recent study [15] has proposed a new phase diagram for solid oxygen, where the single E-phase should be replaced with two phases $\epsilon_1 - O_2$ and $\epsilon_2 - O_2$: the first one is a local singlet spin 1 liquid, while the second one is a regular, Peierls band insulator separated by a first order phase transition near 20GPa.

A room temperature X-Ray study revealed that the E-phase remains stable up to 96GPa, when it suffers another transformation and becomes metallic in the ζ -phase [8]. This transition, from insulator to a metallic phase is unique, but to date remains unexplained. The lack of definitive experimental information on the atomic positions inside the unit cell in the ζ phase has made that the $\epsilon - \zeta$ phase transition is still a matter of discussion. But this phase is not only metallic: a theoretical study predicted that at 0.6K and 100GPa, the solid oxygen turns into a superconductor [16], and this result was later confirmed experimentally [17].

The scenario for even higher pressures is also intriguing, given the uncertainty regarding the question if the pressure applied to solid oxygen will lead to a molecular dissociation or further association: theoretical studies now suggest that even in the terapascal (TPa) regime oxygen remains molecular [18], in contrast with the fact that other diatomic molecules have suffered a molecular dissociation at much lower pressures [19-23].

In the present study we started by extrapolating the ζ -phase's equation of state to find a suitable density for solid oxygen around 350GPa in order to start increasing from there the external pressure that is applied on this system, up to 10TPa. At each pressure point, we performed a structural search looking for post- ζ -oxygen phases, in particular non-molecular ones. Our results agree with previous theoretical studies, which had already predicted non-molecular phases to appear only above 2000GPa (2TPa) [18], however, the range of pressures covered in our study offers more detail than previous studies and can still shed some new light about the nature of the molecular oxygen bonding at high pressures. In addition, we have performed calculations of a sizable contribution to the free energy of the system that comes from the entropy at finite temperatures, originated in the vibration degrees of freedom of the system. Our calculations at this level suggest that the regime of stability of the non-molecular forms, at temperatures of relevance for planetary sciences, differs strongly from the results predicted at zero temperature by [18].

2. Methodology

After deciding on an initial cell-volume to target a pressure in the range from 0.35 to 10TPa, triclinic structures of different sizes were randomly generated which had up to four atoms per unit cell. We started by generating randomly a set of cell parameters and then re-scaled them to fit the estimated volume at the target pressure [24]. Before re-scaling and in order to avoid needle-like or other very distorted shapes of the starting unit cell, the crystal lattices were generated by selecting three random numbers between 0.5 and 1.5 as the lengths of the cell-vectors and three random angles between 40° and 140° . Finally, we generated randomly up to four atomic positions inside the cell, filtering out cases with severe overlap between atoms. Following this recipe we generated a thousand samples for each pressure in this study.

Each sample was then relaxed until its atomic positions and cell parameters reached a nearby local minimum inside the free-energy landscape by following the gradient. It has been shown several times that by using this method, the set stable structures at different pressures, which are the ones with the lowest enthalpy, can be found and characterized in a reliable manner [18, 19, 25-31]. The force and energy calculations needed for the structural relaxations were done ab-initio, using the pw.x code from the Quantum ESPRESSO package [32]. We used the Perdew-Burke-Ernzerhof (PBE) generalized gradient (GGA) exchange- correlation functional [33], with ultra-soft pseudo-potentials and the Brillouin-Zone integrations were approximated with a converged $8 \times 8 \times 8$ k-points grid using the method of Monkhorst and Pack [34]. A plane-wave kinetic energy cutoff of 60Ry was selected, which is high but needed in order to calculate the stress on the cell accurately.

Given the unbiased nature of the structural search method being used, we often find ourselves starting from rather far-from-equilibrium configurations of the cell parameters and the atomic positions. Therefore, as a norm, we first ran a loosely converged calculation aimed to relax the system close enough to a nearby enthalpy minimum. Once we got this approximated structure, we performed a second more strict relaxation, using the k-point and cutoff parameters from the convergence tests that were mentioned before (in the tests, total energy differences had been converged to better than 5 meV per atom).

3. Results and discussion

3.1. Molecular solid oxygen

Every set of a thousand samples converged into a reduced number of local minima and, according to the high number of repetitions observed, we can say with confidence that there are no other energy minima available at each energy landscape studied. Since we are performing a structural search for pressures that are higher than zero, our comparison between structures was not done with the total energy, but with their enthalpies instead.

Once the global enthalpy was determined, we selected the best crystal structure, i.e. the one with the lowest enthalpy among all, at each studied pressure. Since we assume all our cells to be triclinic, the package FINDSYM [35] from the ISOTROPY Software Suite was used in order to find an equivalent conventional cell with higher symmetry that made further analysis easier. Over the entire range of pressures studied, we found three different symmetry groups for the unit cells with two oxygens: triclinic (P-1), monoclinic (C2/m) and orthorhombic (Cmcm); for the unit cells with four oxygens we found two kinds of orthorhombic structures (Cmma and Cmcm). At pressures above 0.55 TPa for the small cell and 1.5 TPa for the big one, the most stable structure was a dense zigzag-chains Cmcm phase. At 0.50 TPa, the bonds of the O₂ system are not completely symmetric to one another: we observed that from 0.40 TPa first neighbour distance increased significantly, while the second decreased. We found that when pressure was increased to 0.55 TPa, the two shortest interatomic distances became symmetrical and the oxygen coordination went from one to two (see Figure 1(a)), therefore, the first neighbour and the second neighbour distances converge at 0.55 TPa. A similar transition was found at 1.30 TPa for the O₄ unit-cell (see Figure 1(b)), in both cases much earlier than predicted by other studies [18].

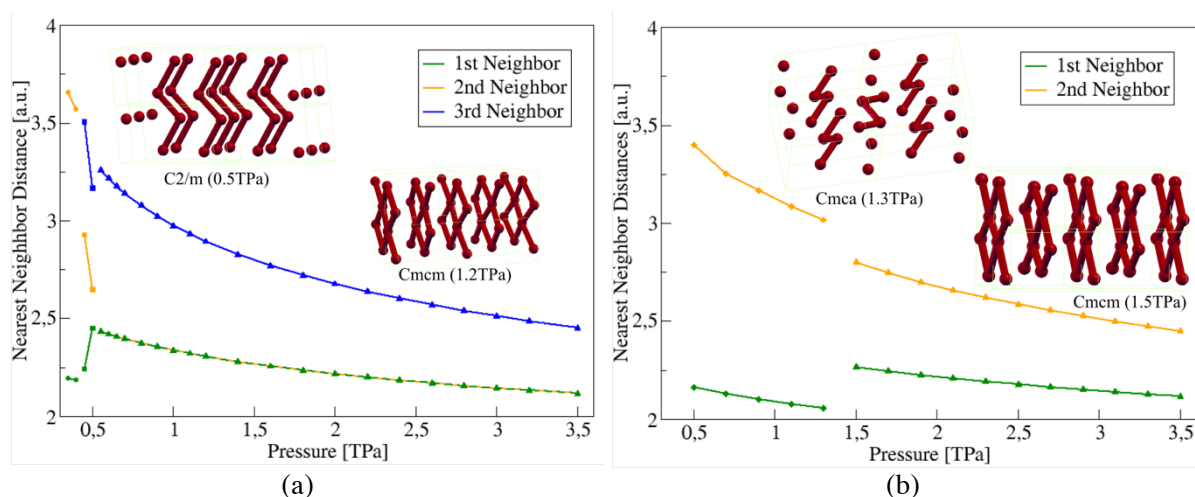


Figure 1. Evolution of the closest oxygen distances while pressure increases. (a) O₂ system structures: P-1 (circles), C2/m (squares) and Cmcm (triangles). (b) O₄ system structures: Cmma (diamonds) and Cmcm (triangles).

For both unit-cell sizes the stable structure at higher pressures is Cmcm, however for the O₄ unit-cell this symmetry group shows up at higher pressures than for the O₂ unit-cell. Due to the smaller amount

of degrees of freedom available to the O_2 system, the only arrangement that it can achieve at 0.55TPa is Cmcmm. The O_4 unit cell instead, having more atoms available to explore possible configurations, remains with the Cmcm structure, which seems to be more favourable energetically, until it reaches to 1.50TPa. By analysing the enthalpy per atom from 0.35 to 1.50TPa, the enthalpy for the O_4 system is lower than for the O_2 unit-cell, but from 1TPa the enthalpy per atom of the O_2 is better by a few hundredth electronvolts.

3.2. Molecular solid oxygen at finite temperature

At extreme conditions of pressure and temperature, similar to those found at planetary interiors, the thermodynamical behaviour of the materials plays a significant role in the description of their physical properties. Accurate calculations regarding the effects related to lattice dynamics can be done by using the Quasi-Harmonic Approximation (QHA) [36, 37]. In the QHA, the contribution to the vibrational part of the free energy is determined by:

$$F_{vib} = \frac{1}{2} \sum_{qs} \hbar \omega(qs) + k_B T \sum_{qs} \ln[1 - \exp(-\hbar \omega(qs)/k_B T)] \quad (1)$$

And the entropy can be derived as: $S = -(\partial F / \partial T)_V$. We performed finite temperature calculations from $T=0K$ to $T=2500K$ to study the phase-transition boundary from Cmcmm to Fmmm that occurs around 9.3TPa at zero temperature, according to [18]. The most remarkable feature of our findings was that even without the zero-point energy contribution, there was a shift to the left of the non-molecular phases transition point. We found that while the temperature is increasing, the merging from Cmcmm to Fmmm occurs at lower pressures due to purely to entropic contributions (see Figure 2).

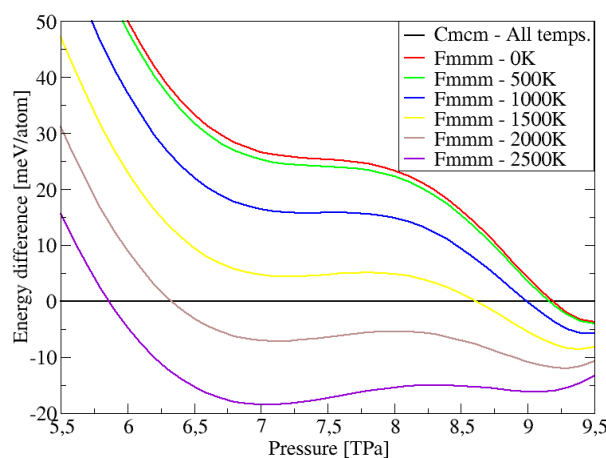


Figure 2. Enthalpy difference for the Fmmm structure at finite temperature from 0 to 2500K. Cmcmm structure is the reference.

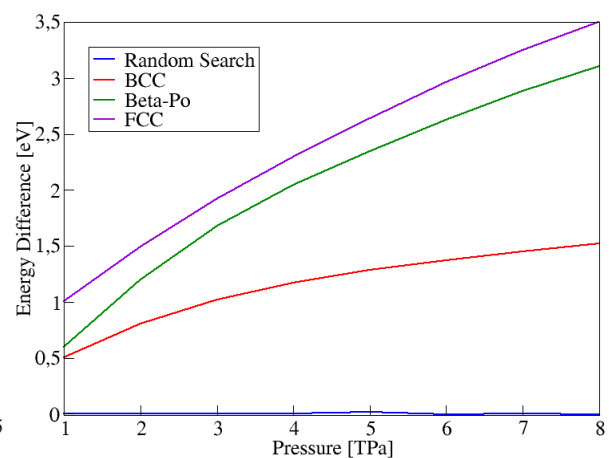


Figure 3. Enthalpy difference for several monoatomic oxygen structures from 1TPa to 8TPa. Fmmm structure is the reference.

3.3. Monoatomic oxygen (special case)

Up to 9TPa solid oxygen remains molecular while other chalcogen elements (group 16 of the periodic table) take a monoatomic rhombohedral β -Po structure after being compressed [38-40]. Going beyond, when further compression is applied on Se and Te, a BCC structure is formed after their β -Po-type structure [40-42], however a layered monoatomic crystalline phase for oxygen has been predicted to occur only above 9TPa [18]. Given that oxygen exhibits several different structures [18], such as chain-like I41/acd at 2TPa, a Cmcmm zigzag structure at 3TPa, and finally a monoatomic Fmmm structure at 9.3TPa, we decided to complete the picture of oxygen as a chalcogen by making an structural search for

monoatomic oxygen up to 8TPa, and then adding a comparison between those structures that we found and the β -Po, BCC and FCC (see Figure3).

For this study we used a slightly different approach in order to make our findings comparable with the results reported in [18]. We used Perdew-Burke-Ernzerhof (PBE) generalized gradient (GGA) exchange-correlation functional, a k-point grid of $20 \times 20 \times 20$ due to the very small cells involved and a plane wave kinetic cutoff energy of 60Ry. Also, for the most stable structures from the random search, we performed very well converged calculations using hard Norm-Conserving pseudopotentials and nonlinear core corrected projector augmented-wave (PAW), with the same exchange-correlation functional.

We found that for pressures above 1TPa, the most stable structure is Fmmm. In fact, it is evident that for higher pressures the enthalpy difference increases for all the other structures that were analysed. Although they are metastable, the BCC structure was observed as a post- β -Po phase same as for Te and Se [40-42]. We made calculations that are not shown in Figure 3 in order to establish the pressure at which the transition from β -Po to BCC takes place, and we found that it is slightly above of 0.9TPa. Even if this pressure is much higher than the ones determined for Te and Se, it is clear that oxygen follows the same trend and therefore it has something in common at some level with other chalcogen elements.

4. Conclusions

Due to technical limitations, hydrostatic compression experiments can reach pressures up to 300GPa, value that is close to the pressure in the Earth's inner core. At that pressure regime, oxygen keeps its molecular form. Using computational approaches, we were able to study this system at pressures that today are impossible to obtain in a laboratory.

The dramatic changes found for molecular solid oxygen at pressures below 1.50TPa were also observed by Sun *et al.* [18], but we offered more detailed calculations that are necessary for a better understanding of the structural and physical changes that occur under those conditions. The structural search calculations were complemented with a tool for prediction of the thermal properties, such as QHA. The finite temperature calculations which include the vibrational entropy show that the pressures for molecular dissociation are not as high as those predicted by [18] at the temperatures of interest for planetary interiors.

Regarding the structural search calculations done for monoatomic oxygen, we observed that it is not like other chalcogen element. Our curves comparing the stability of the Fmmm structure found in [18] with other possible monoatomic structures observed in chalcogens, reveal that there is no point above 1TPa where any of those structures are more stable than Fmmm. Indeed, the fact that the energy difference between them actually grows with pressure, discards any possible resemblance of oxygen to other chalcogens, even going to higher pressures. It is however interesting that at least as metastable structures the β -Po oxygen is lower in enthalpy with respect to BCC until BCC takes over at around 0.9TPa, and this sequence at least is consistent with the behaviour found in Se and Te.

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