



## Magnetism and vibrations in the phase $\epsilon$ of oxygen

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### ABSTRACT

Sandwiched between a set of magnetic phases at lower pressure, and a non magnetic phase at higher pressure, the magnetic state of phase  $\epsilon$  of oxygen has so far been elusive, together with its crystal structure. Neutron diffraction data indicate an absence of antiferromagnetism, but do not exclude a ferromagnetic order. The recent refinement of the internal atomic positions from single-crystal diffraction finally provides us with a correct structural model to study the possible occurrence of a magnetic ground state. By employing non-collinear spin-polarized density-functional theory we show that the ground state of  $\epsilon$ -O<sub>2</sub> is non magnetic. We also calculate vibrational spectra and show that  $\epsilon$ -O<sub>2</sub> possesses an additional vibron mode with large Raman cross section, not seen in experiments yet.

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### 1. Introduction

Among the diatomic molecules O<sub>2</sub> stands out for its magnetic moment ( $S = 1$ ) caused by the exchange interaction between electrons in the two-fold degenerate highest-occupied molecular orbitals. Intra and inter-molecular magnetic interactions play an important role in the structural, electronic, and magnetic properties of the solid phases of oxygen. The phase diagram of solid oxygen has been studied at pressures up to 130 GPa and temperatures up to 650 K, and six crystalline phases have been reported so far [1].

At low temperatures and below 1 GPa, solid oxygen exists in the  $\alpha$  phase, which has a monoclinic base-centered structure of space group  $C2/m$  and an insulating antiferromagnetic character [2]. With increasing temperature, the  $\alpha$  phase transforms into the paramagnetic  $\beta$  phase, in which thermal fluctuations destroy the long-range intermolecular magnetic order. At room temperature  $\alpha$ -O<sub>2</sub> transforms into a  $Fm\bar{3}m$  orthorhombic structure ( $\delta$ -O<sub>2</sub>) near 9.6 GPa [3], which again displays antiferromagnetic order. The  $\beta$  and  $\delta$  phases, as well as the low temperature  $\alpha$  phase, share

a similar arrangement of the oxygen molecules, whose centers of mass sit on layers, coincident with crystal planes, with their molecular axes perpendicular to the crystal planes. At about 10 GPa  $\delta$ -O<sub>2</sub> transforms into the  $\epsilon$  phase. The structure of  $\epsilon$ -O<sub>2</sub> has been the subject of several experimental and theoretical studies, which have only recently revealed, by single crystal diffraction, that molecules in  $\epsilon$ -O<sub>2</sub> group into O<sub>8</sub> ((O<sub>2</sub>)<sub>4</sub>) clusters [4,5]. The stability range of the  $\epsilon$  phase extends over a wide range of pressures, up to 96 GPa, where a transition to the non-magnetic, metallic  $\zeta$  phase occurs, which is associated with the insulator-metallic transition [6].

While the magnetic state of all the low-pressure phases of solid oxygen is well understood, and the high-pressure  $\zeta$  phase is non magnetic, the magnetic properties of the  $\epsilon$  phase remain unclear. Spin-polarized neutron diffraction experiments have shown that the antiferromagnetic peaks observed in  $\delta$ -O<sub>2</sub> disappear upon transformation into the  $\epsilon$ -O<sub>2</sub> phase [7]. This rules out an antiferromagnetic order similar to those observed in  $\delta$ -O<sub>2</sub> and  $\alpha$ -O<sub>2</sub>, but does not rule out the possibility of ferromagnetic order, nor the possibility of antiferromagnetic order within the unit cell, with an overall vanishing or small ferromagnetic moment per unit cell. The possibility of a magnetic state in  $\epsilon$ -O<sub>2</sub> is consistent in principle also with optical absorption experiments [8]. The lowest optical excitation in  $\delta$ -O<sub>2</sub> is in fact dominated by the intramolecular triplet-to-singlet transition, and is therefore controlled by the magnetic state of the molecule. Optical spectra show an increase of

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the excitation gap across the  $\delta$  to  $\epsilon$  transition, which is consistent in principle with a band mechanism adding up, in  $\epsilon$ -O<sub>2</sub>, to the triplet–singlet excitation, although a band mechanism alone could also be invoked in the absence of magnetism. First-principle spin-polarized molecular dynamics simulations with collinear spins [9] suggested a collapse of magnetism around 10–12 GPa, but later non-collinear static calculations showed that relaxing the collinear spin constraint leads to a geometrically frustrated magnetic state that is stable over the non magnetic state up to 50 GPa [10]. In contrast, another first-principle study [11] using a different structural model for phase  $\epsilon$  suggested a nonmagnetic insulating ground state. Differences in the theoretical results are to be attributed to different choices of the structural models for the  $\epsilon$  phase, none of which were consistent, in the theoretical studies discussed so far, with the actual structure of this phase, as determined in the recent diffraction experiments.

With the exact structure of  $\epsilon$  phase, the most recent theoretical study based on density functional theory [12] suggests a nonmagnetic state in this phase. However, the calculations of Ref. [12] have been performed in the collinear spin polarization limit, and cannot exclude that relaxing the collinear constraint a non-collinear magnetic ground state could develop, similarly to that observed in Ref. [10]. Therefore, we believe that it is necessary to perform non-collinear spin polarization calculations for a full understanding of the magnetic state of the  $\epsilon$ -phase.

Besides the unclear magnetic state, the vibrational spectra in the  $\epsilon$  phase show also a few interesting features. The room temperature Raman spectrum has been studied up to the insulator to metal transition [13] and has been shown to consist of three main bands: a vibron mode with frequency around 1590 cm<sup>-1</sup> (at  $P = 20$  GPa) and two low-frequency bands (below 500 cm<sup>-1</sup>) assigned as librons. The wave number of the vibron mode increases linearly with pressure. In addition, the frequency of the mid infrared vibron shows a peculiar behavior when the pressure increases [14,15]. It first decreases and reaches a minimum at 20 GPa and then grows slowly with an increasing pressure.

Our aim in this work is to perform the calculation in the most general case which is non-collinear spin polarized to study the magnetic property in the  $\epsilon$  phase. Furthermore, with the exact structure from the experiments [4,5], the vibration in this phase will be discussed in detail.

## 2. Methods

Calculations were performed within the density functional theory using the Perdew–Burke–Ernzerhoff exchange–correlation functional [16] and a plane basis set, as implemented in the Quantum-ESPRESSO code [17]. Noncollinear spin polarization calculations are performed as described in Ref. [10]. A Vanderbilt ultrasoft pseudopotential [18] with an energy cutoff of 30 Ry was used in all total-energy calculations. The vibrational spectra were calculated by density functional perturbation theory [19] using a norm-conserving pseudopotential with a kinetic energy cutoff of 80 Ry. A  $4 \times 4 \times 4$  Monkhorst–Pack  $k$ -point mesh [20] was sufficient to converge Brillouin zone sampling and was used throughout the calculations. The initial crystal structure and atomic positions were taken from the experimental data at 17.6 GPa [4]. Lattice and internal parameters were then fully optimized at different pressures. Magnetic calculations have been performed starting with several different initial directions and values of the magnetization for every molecule. Energy and magnetization were then calculated self-consistently for each initial structure.

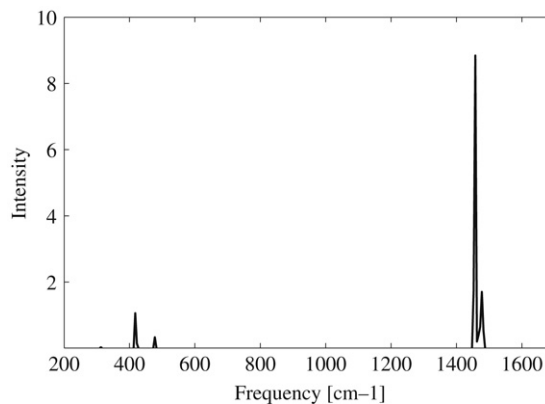


Fig. 1. Calculated infrared spectrum of  $\epsilon$ -O<sub>2</sub> at 20 GPa.

## 3. Results and discussions

### 3.1. Magnetism

In order to test the ability of our method to describe the magnetic state of solid oxygen, we first performed non-collinear calculations for the  $\delta$  phase. The  $\delta$  phase has a  $Fmmm$  orthorhombic structure and the lattice parameters were taken from the experiment [21]. Non-collinear calculation yielded a unique ground state, irrespective of the initial magnetization. The calculated ground state for  $\delta$ -O<sub>2</sub> is a collinear antiferromagnetic state, in excellent agreement with previous experimental [21] and theoretical [9] studies.

We then proceeded with the  $\epsilon$  phase and performed both collinear and non-collinear calculations at the experimental pressure 17.6 GPa. In both cases a non magnetic ground state was found. Because full lattice relaxation lead to a volume, at 17.6 GPa, which is 1% smaller than the experimental one, we repeated the calculations at the experimental volume, with and without optimization of the internal parameters, but again found a non magnetic ground state. Because magnetism is generally suppressed by compression, we also searched for a possible magnetic ground state at larger volumes, i.e. at pressures closer to the stability boundary of the  $\epsilon$  phase with the  $\delta$  phase. Calculations at 10 GPa however yielded again a non magnetic state. We therefore conclude that the  $\epsilon$  phase is indeed non magnetic.

### 3.2. Vibrational spectroscopy

For the  $\epsilon$ -phase with a primitive cell with four molecules, we have 21 optical modes, out of which, at the zone center, twelve are Raman active and nine infrared active. In Fig. 1 we show the infrared spectrum of the  $\epsilon$ -phase at 20 GPa. Consistently with the results of [14,15] we find a strong infrared peak in the far-IR, at 417 cm<sup>-1</sup>. In the vibron region we find an intense peak at 1457 cm<sup>-1</sup> and a weaker shoulder at 1477 cm<sup>-1</sup>. Only one peak is observed experimentally in that region. The weak shoulder disappears when the non-analytical part of the dynamical matrix responsible for the LO–TO splitting is removed, which indicates that the shoulder is a direct consequence of the LO–TO splitting. The calculated IR spectrum has been obtained as an isotropic average over the propagation directions, as different propagation directions yield different positions and intensities for the extra mode. In specific directions the mode intensity drops to zero, so we explain the experimental observation of a single IR active vibron to detection limits and to a possible preferred orientation of the crystal. In addition, our calculation shows that the infrared intensity of the vibron mode is much stronger than that of the far-IR mode, in agreement with the experimental data.

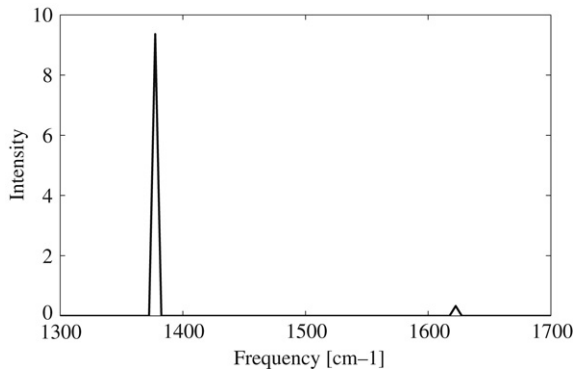


Fig. 2. Calculated Raman spectrum of  $\epsilon$ -O<sub>2</sub> at 20 GPa.

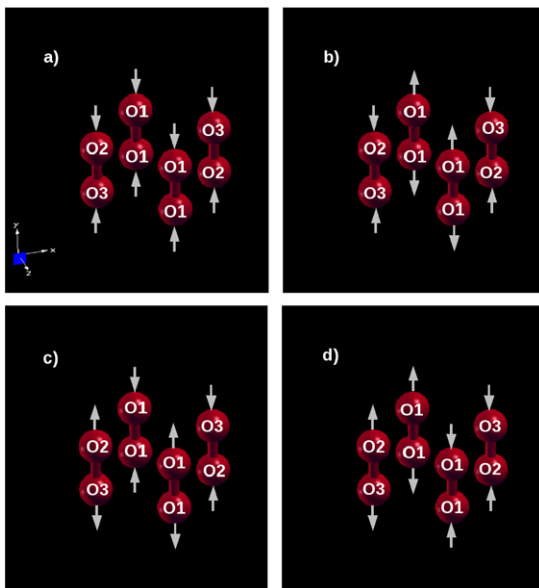


Fig. 3. Calculated vibrational patterns of the four vibron modes. Modes (a) and (b) are Raman active, modes (c) and (d) are IR active. Mode (a) and (b) correspond to the Raman vibrons with highest and lowest frequency in Fig. 2 ( $1622\text{ cm}^{-1}$  and  $1377\text{ cm}^{-1}$  at 20 GPa), respectively.

The Raman spectrum at 20 GPa in the vibron range of  $1300\text{--}1700\text{ cm}^{-1}$  is shown in Fig. 2. We find, in agreement with experiments [13], a vibron peak at around  $1600\text{ cm}^{-1}$ . However, we find that the Raman spectrum is dominated by a much stronger peak located at lower frequency ( $1377\text{ cm}^{-1}$  at 20 GPa). The peak is not visible in experiments as it lies in the frequency region hidden by the diamond anvil absorption.

Fig. 3 shows the vibrational patterns of the four vibron modes, two of which are Raman active and two are IR active. The weakest Raman peak, the only one seen in experiments, corresponds to an in-phase vibration of the four molecules, while the strongest Raman mode, not seen in experiments, corresponds to an out-of-phase oscillation with zero dipole moment. Regarding the IR active modes, they correspond to dipole-active out-of-phase oscillations. Their IR intensity obviously depends on the direction of propagation and on the polarization of the incoming light.

In Fig. 4 we present the pressure dependence of the frequencies of the main vibron modes. For the Raman modes, our calculations show a good agreement with the experimental data throughout the pressure range of stability of  $\epsilon$ -O<sub>2</sub>. For the IR mode, the calculation

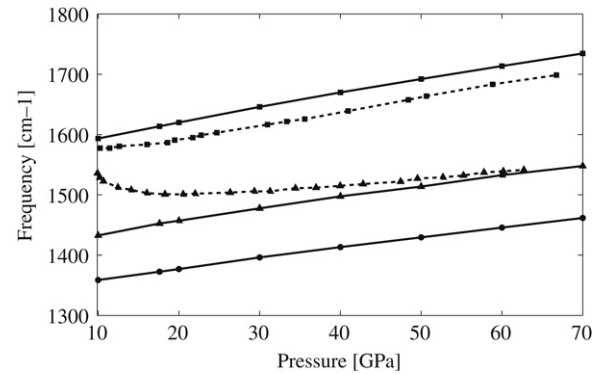


Fig. 4. Pressure dependence of the Raman and IR frequencies in the O<sub>2</sub> vibron region. Our work: solid line. Experiments [22]: dashed line. IR frequencies: triangles; Raman frequencies: squares and circles.

shows a good agreement with experiment only at high pressure (above 20 GPa). Below 20 GPa, we fail to reproduce the peculiar non-monotonic behavior of the IR frequency.

#### 4. Conclusions

In summary, our spin-polarized calculations indicate the absence of magnetism even in non-collinear configurations in  $\epsilon$ -O<sub>2</sub>. Our vibrational spectra agree well with available Raman and IR spectra on  $\epsilon$ -O<sub>2</sub>, and allow us to suggest the existence of an additional Raman peak in the vibron region of the spectra, not seen in experiments because it is hidden by the diamond Raman absorption window. The new peak is expected to possess a much higher Raman intensity than the higher-frequency peak seen in experiments. We fail to reproduce the non-monotonic dependence of the frequency of the IR vibron peak with pressure. Such an anomalous dependence has been theoretically explained as a result of a charge transfer mechanism in a O<sub>4</sub> cluster [14,15]. However, the analysis was based on the presence of a single Raman peak at lower frequency. Our finding of an additional, much stronger peak at lower frequency implies that the charge transfer model proposed in [15] may need to be revisited.

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