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Magnetism in solid oxygen studied by high pressure neutron diffraction

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Abstract This article reviews progress achieved over the last ~15 years in our understanding of magnetism in solid oxygen under high pressure with a particular emphasis on the contribution of neutron diffraction in the multi-GPa range. The paper highlights the unexpected complexity of magnetic structures in the δ phase at 5-8 GPa, presents data on the pressure dependence of diffuse scattering in β -O₂ and discusses potential magnetism in ε -O₂. High-resolution diffraction data of all three solid phases at ambient pressure are presented.

Keywords oxygen • magnetism • high pressure

1 Introduction

Among all elemental molecules oxygen is unique since it carries an electronic magnetic moment. The paramagnetic nature of gaseous oxygen was discovered by Faraday in 1847 [1] and later also found in the liquid [2]. Upon cooling below the melting point at 54 K, Perrier and Kamerlingh Onnes detected a strong drop in the magnetic susceptibility in solid O₂ and another “at approximately 33 K” [3]. These findings gave first evidence for magnetic order in solid oxygen, in two different phases. However, although the crystal structures of these phases (now called α - and β -O₂, γ -O₂ was overseen in this study) were soon investigated by x-ray studies, the magnetic structures remained unknown for half a century till the advent of neutron scattering. This revealed that only the low-temperature α phase, stable below 24 K, has magnetic long-range order whereas β -O₂ is magnetically frustrated [4,5,6]. By this time oxygen was also investigated under pressure; but it was only the development of the diamond anvil cell which allowed to generate pressures beyond ≈ 2 GPa to reach high pressure phases δ -O₂ and ε -O₂ at ≈ 6 GPa and ≈ 8 GPa respectively, and map out the phase diagram down to

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almost 0 K. These fundamental light scattering methods (including x-ray diffraction techniques carried out on synchrotrons) paved the way to neutron diffraction studies in 10 GPa range which became feasible from ≈ 2000 onward and which allowed a direct search for magnetic long-range order in δ -O₂ and ε -O₂ [7-9].

General aspects of magnetism in O₂ were discussed by the paper of DeFotis [10] which reviews the state of knowledge up to 1981. More recently, the properties of solid oxygen - including its magnetic properties - were reviewed in a very detailed and highly useful article by Freiman and Jodl [11]. There is also a more recent review by Freiman [12] with a focus on magnetism in solid O₂. To avoid unnecessary overlap with this and previous work, I will present here a detailed review of high pressure neutron scattering results published from 2004 on, obtained with techniques which allowed the investigation of the five phases of solid oxygen which exist in the 10 GPa range, i.e. α -, β - γ -, δ - and ε -O₂. The article is intended to be a critical review without claim for completeness. It contains also a number of unpublished neutron data on α -, β - and ε -O₂ which complement previous work by the author [9].

2 General aspects

It is useful to start with a brief discussion of the isolated O₂ molecule as well as the O₂-O₂ dimer which contain the essential physics to understand the binding and magnetism in solid oxygen.

Natural oxygen contains approximately 99.8 % ¹⁶O, the remainder being mostly ¹⁸O as well as a very small amount of ¹⁷O (less than 0.04%). The vast majority of experimental studies were carried out on the natural mixture. Neutron diffraction cannot distinguish between ¹⁶O and ¹⁸O since their scattering lengths are virtually identical.

Oxygen forms a diatomic molecule with a bond length of 1.21 Å. When two oxygen atoms bind, the individual 1s, 2s and 2p orbitals combine to molecular σ and π orbitals where the upper π_g^- orbital contains two electrons. According to Hund's rule, the two spins combine in the ground state to $S=1$ which makes O₂ paramagnetic with a magnetic moment of formally $2\mu_B$. For comparison, the two elemental gases next to oxygen, N₂ and F₂, have two electrons less (N₂) or two electrons more (F₂) which gives either an empty or a full π_g orbital, i.e. $S=0$ in both cases. The presence of a sizeable spin, combined with a relatively small quadrupole moment is the key to understanding oxygen's low-temperature phase diagram and its striking difference with nitrogen, for example. In fact, the interaction

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between spins in solid oxygen is of similar strength to the van der Waals forces and has thereby a significant influence on the crystal structures.

A lot of oxygen's binding behaviour can be learned by considering an isolated O₂-O₂ dimer. This is in fact a quasi-stable object which exists in the gas and even in the liquid over a timescale of picoseconds [13,14]. Both experiment and simulations reveal that at the equilibrium distance of ~ 3.5 Å and at zero magnetic field, the molecules align parallel to each other ('H-configuration') and the spins couple anti-ferromagnetically. In general, the intramolecular anisotropy tends to align the magnetic moment perpendicular to the molecular axis, a combined effect of spin-spin and spin-orbit interactions [10,11]. It turns out that this pattern – parallel molecules with antiparallel spin-alignment perpendicular to it – pertains in the three major low-temperature crystalline phases α -, β - and δ -O₂, as discussed in the following paragraphs.

3 Phase diagram and crystal structures

Figure 1 shows the currently accepted P - T phase diagram of oxygen [15]. At ambient pressure, liquid O₂ freezes into the cubic γ phase where the molecules are on an A15-type lattice ($Pm\bar{3}n$, $Z_{\text{mol}}=8$) and are able to rotate more or less freely [11,16]. This phase is stable over only 10 K and transforms at 44 K into hexagonal β -O₂. The transition is strongly first-order (5.5% volume change) and leads to an orientational ordering of the molecules to form O₂-planes with a nearest neighbor distance of ~ 3.2 Å. At this distance, the coupling of spins is antiferromagnetic [14,17]. Nevertheless, no long-range order occurs due to the well-known geometric frustration on a perfect triangular planar lattice. When β -O₂ is cooled to 24 K the magnetic frustration is lifted by a $\approx 10\%$ distortion in the a-b plane, accompanied by a small distortion along the hexagonal c-axis. This leads to the monoclinic α phase with space group $C2/m$ and 2 molecules per conventional unit cell ($Z_{\text{mol}}=2$). As expected for phase changes which involve structural distortions, the α - β transition is weakly first-order.

Under pressure both the α and β phases transform to orthorhombic δ -O₂ ($Fmmm$, $Z_{\text{mol}}=4$), at approximately 6-9 GPa. The transition was first discovered by visual observation as it is accompanied by a spectacular change in colour which gave δ -O₂ the name "orange phase". It involves again a distortion of either the α - or the β phase, depending on the temperature: when α -O₂ is compressed at 150 K, the monoclinic angle changes by $\approx 6^\circ$ over a pressure range of only 0.3 GPa, and the a/b ratio by $\approx 1.5\%$ [18]. This transition is one of the most interesting phase changes in

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solid oxygen since it reflects the competition between van der Waals and magnetic forces under variable pressure. The α - β transition is definitely first-order at low temperatures, for reasons given further below. Above ≈ 100 K the situation is still not clear, but evidence of a small jump in the vibron frequency [19] suggests a very weak first-order nature.

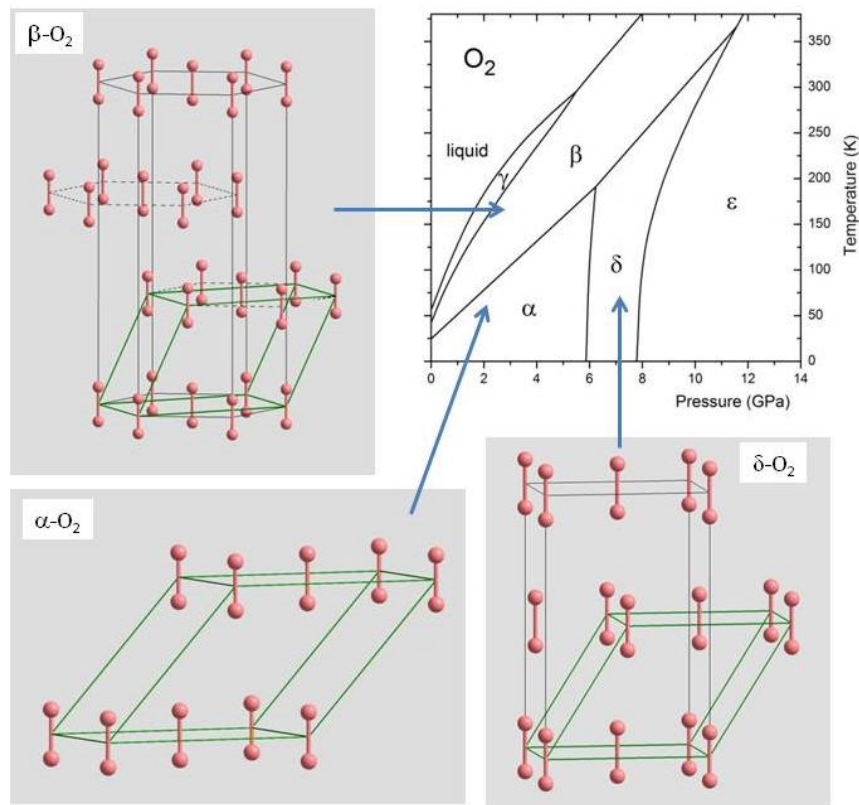


Fig. 1 Phase diagram of oxygen and crystal structures of phases β ($R3m$, upper left), α ($C2/m$, lower left), and δ ($Fmmm$, lower right). Note that the three phases are structurally related: Both phases α and δ can be derived by from the β phase by distortions. (Color figure online)

Further compression to 8-10 GPa leads to the monoclinic ϵ phase (space group $C2/m$, $Z_{\text{mol}}=4$) which has a reddish appearance when observed in a diamond anvil cell. Its crystal structure was only recently determined from single-crystal and powder x-ray diffraction [20,21] and consists of

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distinctive groups of 4 molecules which form $(\text{O}_2)_4$ clusters on each corner of the unit cell. This phase is extraordinarily stable: it transforms only at ≈ 96 GPa into the iso-structural ζ phase (not shown in Fig. 1) which is metallic and superconducting, though still molecular in nature. Little is known about magnetism in $\varepsilon\text{-O}_2$ but the experimental evidence from two neutron diffraction measurements is that $\varepsilon\text{-O}_2$ has no long-range magnetic order, as discussed in chapter 10.

4 Magnetic ordering at ambient pressure

The first neutron diffraction measurements on α - and $\beta\text{-O}_2$ were carried out in 1963 by Alikhanov [4] at the Russian reactor source in Dubna, but details of the structures were published only 4 years later [5]. In the meantime, Collins [6] measured at Harwell (UK) and concluded that $\alpha\text{-O}_2$ is antiferromagnetic whereas $\beta\text{-O}_2$ has only short-range order. Although the data quality is rather mediocre to current standards, these conclusions were later confirmed by Meier et al. [22] and are still uncontested. Figure 2 shows powder diffraction patterns of all three phases obtained recently [23] which suffer from much less texture and have no contamination from the sample environment compared to previous neutron diffraction patterns. The line through the data in the lower pattern is a Rietveld refinement. It leaves no doubt on the correctness of the currently accepted structure of $\alpha\text{-O}_2$. A remarkable feature in the pattern of $\gamma\text{-O}_2$ is the strong diffuse nuclear scattering at $2\text{-theta} \approx 38^\circ$ arising from the molecular orientational disorder. This phenomenon was studied in much detail by neutron scattering using single crystal samples [24,25]. From this it was concluded that molecules on the 2a and 6d sites of the A15 structure have spherical and disc-like disorder, respectively. It is interesting to note that the corresponding phase in solid nitrogen, $\delta\text{-N}_2$, shows exactly the same type of disorder, as derived from single-crystal x-ray diffraction [26]. In $\beta\text{-O}_2$ the short-range magnetic order produces a broad feature at $2\theta \approx 21^\circ$ ($Q = 1.2 \text{ \AA}^{-1}$). A rough estimation from the width $\Delta Q \approx 1 \text{ \AA}^{-1}$ gives a correlation length $\zeta = 2\pi/\Delta Q \approx 6 \text{ \AA}$ which corresponds to approximately 2-3 unit cell parameters in the a-b plane.

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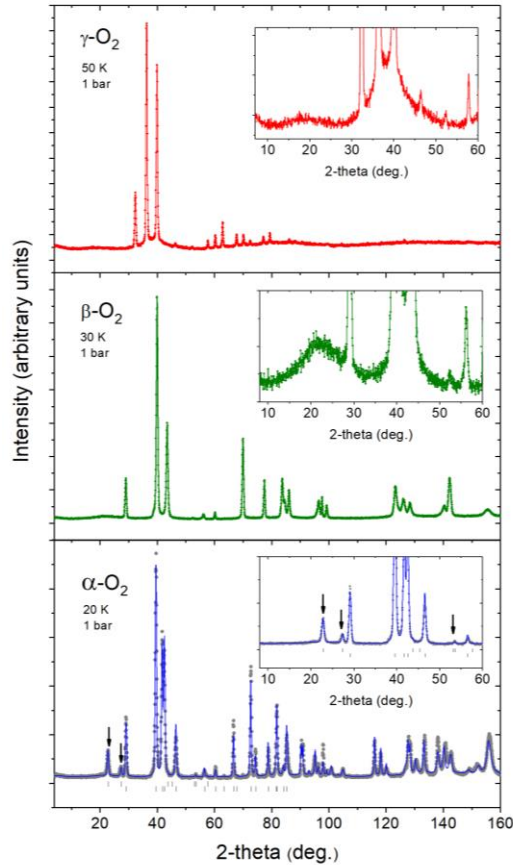


Fig. 2 Neutron diffraction patterns of the three solid ambient pressure phases of oxygen [23] ($\lambda=1.886$ Å). The insets show the low-angle part with the pronounced diffuse nuclear scattering in γ -O₂ at $2\text{-theta} \approx 38^\circ$, the magnetic diffuse scattering in β -O₂ at $2\text{-theta} \approx 22^\circ$, and the most intense purely magnetic Bragg reflections in α -O₂ (arrows). The line through the data in α -O₂ is a Rietveld fit. Upper and lower tick marks indicate positions of magnetic and nuclear reflections, respectively.

There has been much speculation about the detailed structure of the magnetic correlations in β -O₂ [11]. The most significant experimental contribution to this issue is the very detailed work by Dunstetter et al. [27] using spin-polarized neutron diffraction, a technique which can extract the purely magnetic part of a diffraction signal. From a careful analysis it was concluded that β -O₂ has a two-dimensional helicoidal order where the angle

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between neighboring molecules along the hexagonal *a*-axis is $\approx 140^\circ$ (or 280°), and that this correlation dies out beyond a correlation length of $\zeta \approx 5$ Å. This structure produces accurately the diffuse magnetic profile observed in neutron diffraction patterns at $Q \sim 1.2 \text{ \AA}^{-1}$ ($2\theta \approx 21^\circ$ in Fig. 2).

5 Experimental: High pressure neutron diffraction

The progress in the understanding of magnetism in δ - and ϵ -O₂ is entirely due to instrumental developments in the 1990s which allowed achieving routinely pressures of 5-10 GPa and collect useful data in this range and at low temperatures [28]. All these techniques applied so called “opposed anvil” devices where the sample is confined in a hole of a metallic disc (‘gasket’) which is compressed from both sides by two anvils made of some hard material.

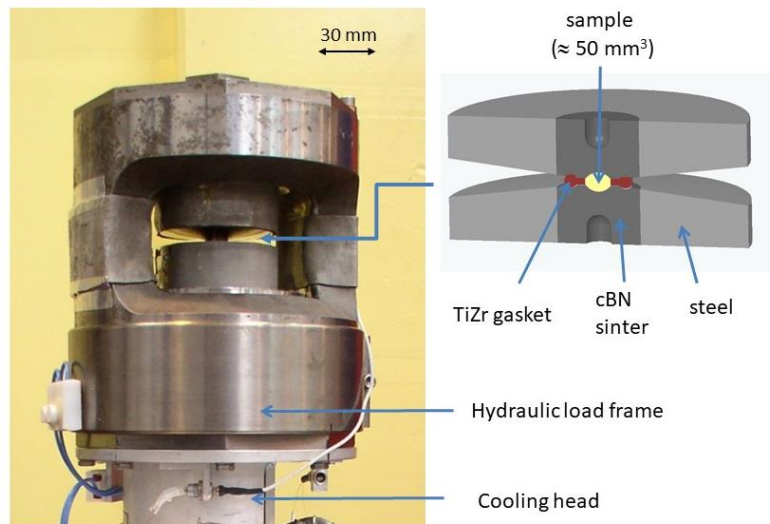


Fig. 3 High pressure cell for neutron scattering in the 0-30 GPa range (‘Paris-Edinburgh cell’) [28]. The drawing shows details of the gasket-anvil assembly. (Colour online)

Goncharenko and coworkers developed a clamp device [28] (‘Kurchatov-LLB cell’) which, for the study on oxygen, was mounted with conical anvils made of sintered cubic boron nitride (‘cBN’). This technique allows an initial sample volume of not larger than 1 mm^3 which naturally

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limits the data quality. Nevertheless, it was possible to make conclusions on the presence or absence of magnetic reflections and measure lattice parameters from the position of a few nuclear reflections. Data up to 9.5 GPa were collected at the French Orphée reactor source of the Laboratoire Léon Brillouin (LLB).

An alternative method uses the so-called ‘Paris-Edinburgh’ pressure cell [28,30,31] (Fig. 3), a device which has become standard equipment in most neutron facilities. The cell is more massive (35 kg) than the ‘Kurchatov-LLB’ cell, but still can reach 1.8 K with the associated cryogenic equipment [32]. A major advantage of this device is its relatively large sample volume of $\sim 50 \text{ mm}^3$ and the fact that the load frame is a hydraulic press which allows fine control of the pressure at almost any temperature [28]. For the study of O_2 cBN anvils with ‘cupped’ culet profiles were used. Such an anvil profile forms –together with the gasket - a spheroidal sample chamber which produces quasi-hydrostatic pressure conditions as demonstrated in numerous measurements on other molecular solids [33]. This aspect is quite important since solid O_2 is known to be highly sensitive to non-hydrostatic compression [15,18,19]. The use of null-scattering TiZr gaskets avoids Bragg reflections from the immediate sample environment. Data on oxygen in the multi-GPa range were collected at the D20 high-intensity diffractometer of the European neutron source ILL (Grenoble) [34]. This instrument is equipped with a radial oscillating collimator which removes all scattered signal from the cryogenic equipment. The combination of the specific high pressure equipment and the instrumental setup produces high resolution diffraction patterns which are free of contaminant signal from the environment and which can be analyzed by Rietveld refinement. These give both the crystallographic and the magnetic structures to high accuracy “in one shot” and hence allows a careful analysis of the mutual interplay between structural and magnetic parameters.

6 Short-range magnetic order in $\beta\text{-O}_2$ under pressure

The pressure dependence of short-range correlations was investigated only recently up to several GPa by the Paris group [23]. Slusarev et al. [11,35] gave a relation between the correlation length ζ , the temperature T , the lattice parameter a and the in-plane coupling constant J as:

$$\zeta \sim a \cdot [\exp(\pi J / (3^{1/2} T))]^{1/2}$$

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Since $J(r)$ and the in-plane compressibility is known [11], this relation predicts a strong increase of the correlation length under pressure with a coefficient of $d\zeta/\zeta/dP=15\%/kbar$ at 30 K.

This was recently tested by neutron diffraction to 2 kbar which found an increase of only approximately half of the predicted rate [23]. More generally, it appears that ζ is not a function of a single parameter $J/k_B T$, the ratio of the relevant energy scales, as it is in Slusarev et al.'s relation. In fact, Fig. 4 shows that at 150 K and 4 GPa diffuse magnetic scattering can no longer be detected despite the fact that $J/k_B T$ is approximately the same as at ambient pressure ($J/k_B T=1.3$), assuming published values for $J(p)$ [11]. It means that above 150 K (and maybe even somewhat below), magnetic correlations in β -O₂ become extremely short-range reaching hardly beyond one lattice parameter.

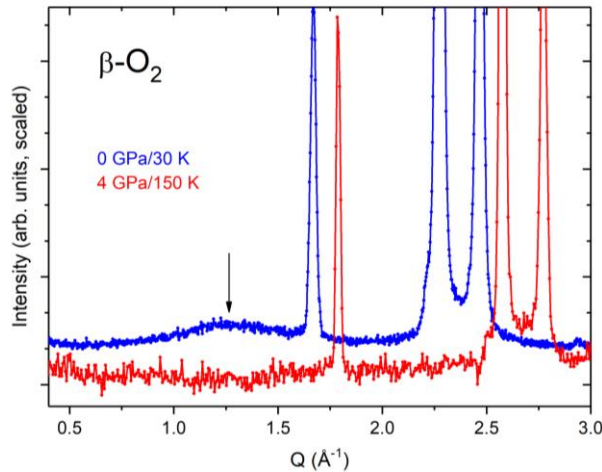


Fig. 4 Neutron diffraction patterns of β -O₂ at ambient pressure and 4 GPa. Data were collected at two different instruments, and intensities were scaled to approximately equal intensities of nuclear reflections. Note the absence of diffuse scattering at 4 GPa/150 K. (Colour online)

7 Magnetic ordering in δ -O₂

Solid oxygen under pressure was investigated by neutrons only from 2004 on when the phase diagram was sufficiently known and when strong evidence for magnetic ordering in δ -O₂ arose from optical spectroscopy [36]. The first data of δ -O₂ were obtained by Goncharenko et al. [7] who

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used a clamped opposed-anvil cell described above with a sample volume of less than 1 mm³. The setup allowed access to only few Bragg reflections and focused on the low-Q range where the magnetic signal was expected. In particular, the data could not be analyzed by Rietveld methods. Nevertheless, from essentially one single magnetic reflection it was concluded that at 4.2 K and 6.6 GPa (a) the coupling of spins within the *a-b* plane is antiferromagnetic with the spins pointing along the orthorhombic $\langle 010 \rangle$ direction (i.e. identical to α -O₂) and (b) that the coupling between nearest-neighbor spins in adjacent planes is ferromagnetic, contrary to what one would have guessed. This spin structure is nowadays called “low-temperature commensurate” (LTC) phase and shown in Fig. 6. Upon warming, Goncharenko et al. found a continuous decrease of magnetic intensity between 150 K and 200 K, from which it was concluded that phase δ is non-magnetic at high temperatures. No phase transitions were reported in the range 4-150 K.

The δ -phase was then investigated in much more detail by high-pressure neutron diffraction by Klotz et al. [9] which revised partially this picture. This group used a “Paris-Edinburgh” cell [28,30,31] which allows a ≈ 100 times larger sample volume, see the previous chapter for technical details.

Figure 5 shows diffraction patterns of a sample of δ -O₂ during slow cooling (~ 1 K/min) from 230 K to 20 K at approximately constant pressure (cooling at constant load in such a pressure device is essentially isochoric). The data reveal immediately a purely magnetic reflection at $2\theta \approx 30^\circ$ which cannot be indexed by Goncharenko et al.’s magnetic structure. This reflection disappears at ≈ 150 K where another Bragg reflection appears at $\approx 26.5^\circ$. It disappears at 20 K lower temperatures where a new strong reflection is visible at $\approx 25^\circ$. There are hence 3 different magnetic phases within one crystallographic phase, and the one at low temperatures is the phase previously observed by Goncharenko et al. [7].

A characteristic problem with oxygen is that its magnetic moment is rather delocalized compared to 3d or 4f elements. This leads to a rapid decrease of the form factor and hence a strong suppression of magnetic reflections as a function of Q (scattering angle). Nevertheless, the proposed structure of δ -O₂ predicts two reflections with non-zero intensity at $\approx 40^\circ$. These can in fact be observed in the data by Klotz et al. [9] if they are integrated over 10 hours (inset of Fig. 5). The slightly different intensity ratio is due to domain texture (preferred orientation) which was included in the Rietveld fits shown in Fig 5. This small but important detail gives strong support to the correctness of the proposed LTC magnetic structure.

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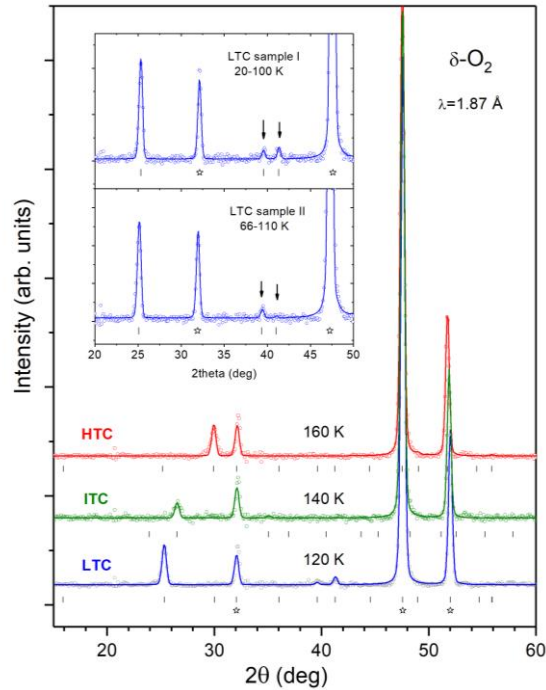


Fig. 5 Neutron diffraction patterns of $\delta\text{-O}_2$ collected during cooling at ≈ 7.8 GPa (main figure, sample 1). The insets show low-angle parts of patterns accumulated in the LTC phase over 10 hours, in two different samples. Tick marks and asterisks denote positions of magnetic and nuclear reflections, respectively. Note the weak magnetic Bragg reflections marked by arrows. (Color figure online)

The most surprising discovery in these measurements is that there are two other magnetic phases at higher temperatures (Fig. 6). It can be easily shown that the phase at high temperature (HTC) differs from the LTC phase only by the coupling between nearest neighbors in adjacent O_2 -sheets: it is antiferromagnetic and hence identical to the magnetic structure in $\alpha\text{-O}_2$. As for the phase between LTC and the HTC, the intermediate commensurate (ITC) phase, the stacking sequence of spins along the c -axis is alternating between ferromagnetic and antiferromagnetic. This requires a doubling of the unit cell along c .

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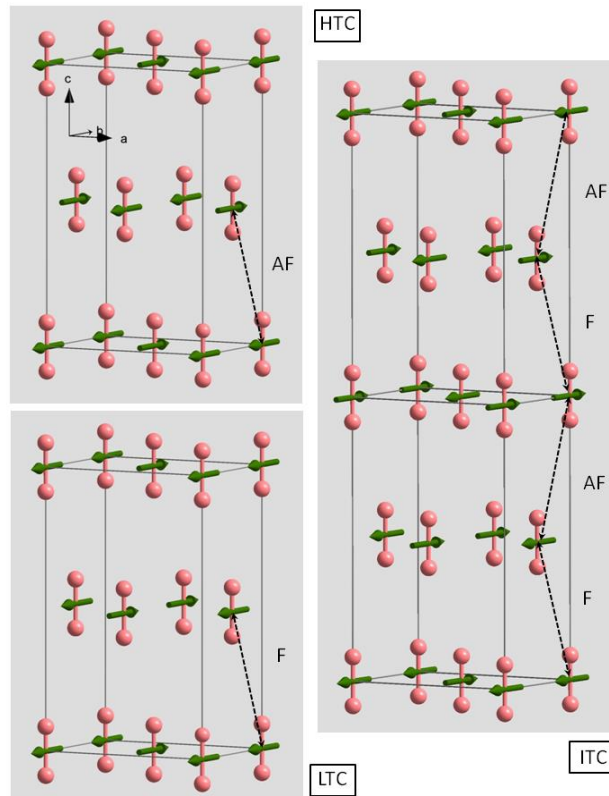


Fig. 6 Structures of magnetic phases LTC, ITC and HTC in δ -O₂. “F” and “AF” indicated ferromagnetic and antiferromagnetic coupling between nearest neighbor spins in adjacent O₂-planes, respectively (Color figure online)

The phase diagram of α - and δ -O₂ was investigated by the same group in various later neutron diffraction studies which confirm the existence of the three magnetic phases and which allow to draw a phase diagram as shown in Fig. 7. Note that according to this, the α - δ phase transition is necessarily discontinuous (‘first-order’) at low temperatures since it implies a discontinuous change in magnetic order.

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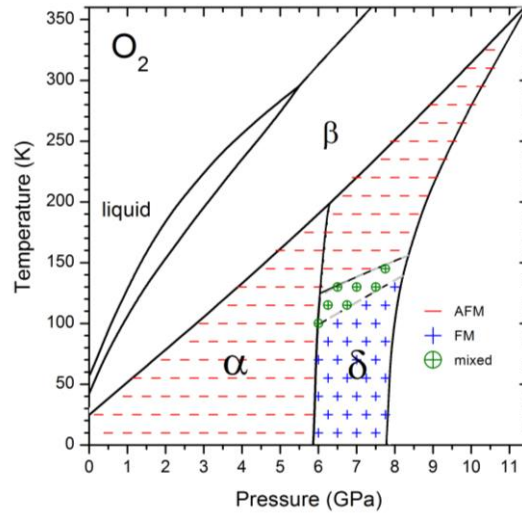


Fig. 7 Phase diagram of oxygen including magnetic phases as explained in the text. (Color figure online).

A noteworthy detail in these studies is that the refined magnetic moments of the α and δ phases (i.e. the magnetization, hence the order parameter) remains finite up to the temperature where the phase transition to the β phase occurs, see Fig. 8. The data points marked with arrows are phase mixtures, i.e. these points are exactly on the α - β and δ - β phase boundaries. Since in both cases the magnetic moment has a finite value, the Néel temperatures of both phases must be well above their respective stability regions. This was already pointed out by Collins [6] and Meier et al. [22] in their work on α - O_2 . An obvious corollary is that no evidence for a non-magnetic phase “ δ -II” at high temperatures was found, as reported previously [7]. This observation thereby confirms earlier conclusions derived from measurements by optical spectroscopy (see paragraph 8).

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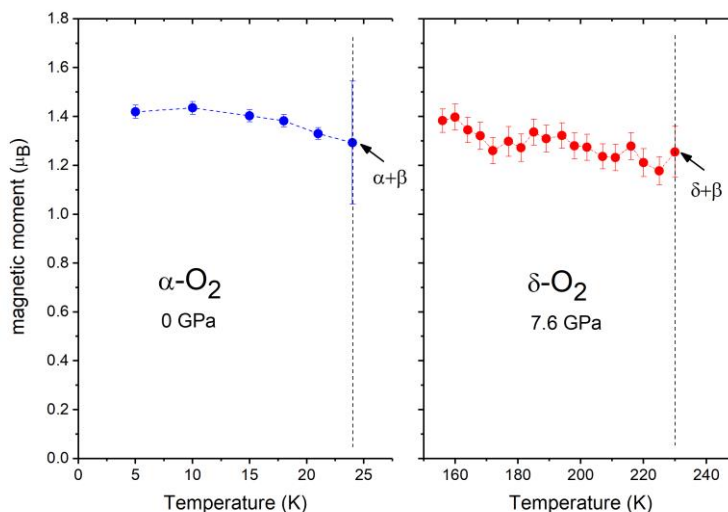


Fig. 8 Refined magnetic moments in α -O₂ and δ -O₂ upon approaching the α - β and δ - β phase boundary (vertical dashed line). Arrows indicate samples with phase mixtures. (Color figure online)

8 Evidence for magnetic ordering from optical spectroscopy

The existence of long-range magnetic order in phases α and δ is also visible by light scattering since it probes the collective excitations of the magnetic ground state, i.e. the magnons ('spin waves'). Convincing proof for magnons in α -O₂ came first from Raman [37,38] and far-infrared absorption measurements [39] which identified the two magnon branches at the zone-centre at 6.5 cm⁻¹ and 27 cm⁻¹. Later inelastic powder neutron scattering data gave information on their Q-dependence up to the zone boundary [40,41]. The high frequency magnon mode of α -O₂ was investigated under high pressure by Raman scattering in diamond anvil cells [42,43] up to 2.7 GPa. A characteristic observation in this work is the strong decrease of its intensity with pressure which made it undetectable beyond \approx 2.7 GPa [42,43]. This phenomenon is without doubt caused by a degrading (magnetic) micro-structure as the sample was compressed at low temperature: The neutron diffraction data show clearly the presence of magnetic long-range order in this pressure range, see discussion further above. Indirect proof for magnetism α - and δ -O₂ comes also from mid-

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infrared absorption spectroscopy. The magnetic order leads to a doubling of the primitive unit cell with two non-equivalent O₂ molecules. This allows the vibron to be infrared-active and produces a weak but sharp absorption line at $\sim 1550\text{ cm}^{-1}$. Gorelli et al. investigated this line from 2 GPa up into δ -O₂ and thereby gave strong evidence for antiferromagnetic order in δ -O₂ over its entire stability range [36], as later confirmed by neutron diffraction [9].

Recently, this issue was reinvestigated by a Paris-Florence collaboration using Raman scattering [46]. The low-energy spectrum of δ -O₂ shows a sharp line at $80\text{-}90\text{ cm}^{-1}$ (width approx. 2 cm^{-1}) which was so far interpreted as due to a minority ϵ phase [19,43], based on its proximity to a strong line which occurs in ϵ -O₂ at higher pressures. This appears however highly unlikely given the fact that it can be observed down to below 3 GPa, i.e. 5 GPa below the stability domain of ϵ -O₂. A more likely interpretation is that this is in fact a pure magnon mode: its position is on a perfect extrapolation of the magnon frequency in α -O₂ using the pressure dependence determined by Kreutz et al. [43] and Mita et al. [42]. These data show also significant changes in the libron-modes across the LTC-ITC-HTC phase boundaries [46]. In conclusion, these unpublished data give strong evidence that magnetic long-range order in δ -O₂ is detectable in Raman spectroscopy in the low-energy range.

9 Theory: Magnetism in δ -O₂

There is currently theory which describes structural and magnetic transitions across the δ - ϵ phase line and inside δ -O₂ comprehensively. This applies in particular for first-principles calculations with their well-known weakness to incorporate magnetism and van der Waals interactions. However, there are a few key results which merit to be mentioned here since they contain the essential physics to understand the behaviour of solid oxygen under variable density.

Van Hemert et al. [17] realized in one of the first ab initio (Hartree-Fock) calculations on an O₂-O₂ dimer that the exchange interaction between two molecules can be both positive and negative, depending on the orientation of the molecules with each other. They investigated a number of configuration named *H* (parallel), *A* (nearly parallel), *L* (linear), *X* (crossed), and *S* (shifted parallel) and realized that for the vast majority, the exchange is negative, i.e. favoring AF coupling. It is only for one relevant orientation (*S*) that the coupling is ferromagnetic.

Concerning the theoretical description of crystal phases α , β and δ , the fundamental work by Etters and coworkers should be mentioned [44,45].

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These authors use a semi-empirical model with a 6-12 Lennard-Jones potential and a Heisenberg Hamiltonian as essential ingredients to calculate structural and dynamical properties under pressure. Input parameters were taken from experiment, or were adapted to fit experimental observations. Although such a model seems completely outdated compared to current possibilities, this approach describes correctly the essential physics of solid oxygen under pressure. In particular, it describes the transition from α - to δ -O₂ and calculates the phonon (vibron and libron) dispersion [45]. Due to the doubling of the primitive unit cell in α -O₂, the model predicts four libron modes instead of two which should separate significantly in the δ phase. This has indeed been observed in recent Raman measurements [46]. The obvious shortcoming of this model is that the pressure dependence enters only via the r -dependence of the potential. This leads among others to a considerable underestimation of the α - δ transition (2.3 GPa instead of 6 GPa). A second shortcoming is that the magnetic interaction between molecules of adjacent planes is assumed to be negligible, i.e. only interactions between molecules in the “ H ”-configuration are considered. This model is hence *per se* unable to describe the magnetic transitions in δ -O₂ and assumes an HTC spin structure over the entire phase, as in α -O₂.

The above results give a hint on the microscopic origin of the LTC-ITC-HTC transitions in δ -O₂. Since the three phases occur at strictly the same crystal structure, and at fixed pressure and volume occur only as a function of temperature, they must be driven by entropy. The most important source of entropy in α - and δ -O₂ are molecular librations, as demonstrated by experiment and simulations which indicate that the molecule librates by typically ± 10 - 20° around the c -axis [44,45,47,48]. It was hence argued [9] that the most likely origin for the LTC-ITC-HTC resides in the orientation-dependence of the exchange coupling parameter J as explained further above: In the absence of large librational movements (close to $T=0$ K) the nearest-neighbor molecules in adjacent planes are in a “ S ” orientation with ferromagnetic coupling of spins, i.e. the preferred magnetic structure should be LTC, as observed. When the temperature increases, librations will lead to instantaneous orientations which deviate from the “ S ”-configuration and admix configurations with strongly antiferromagnetic coupling. Consequently, an HTC-type magnetic structure is expected at sufficiently high temperatures. For intermediate temperatures around 100 K the system seems to find a compromise with half of the couplings being ferromagnetic and the other half antiferromagnetic.

Gomonay and Loktev [49] presented a phenomenological model which includes exchange interactions up to 3rd neighbors between O₂ molecules in different planes. In this framework librational motion does not occur

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explicitly. Instead, the LTC-ITC-HTC transition sequence is interpreted as an effect of competing coupling constants which depend on temperature via the anisotropic thermal expansion. However, this model imposes a temperature dependent magnetization $M(T)$ which is taken from Goncharenko's measurements [8] and which was not confirmed neither by the neutron data by Klotz et al. [9] nor by IR spectroscopy [36]. Both indicate unambiguously magnetic order over the entire stability range of the δ phase, up to the δ - β phase boundary, see Fig. 8 and related discussion.

10 Potential magnetism in ϵ -O₂

The issue of magnetism in ϵ -O₂ has much been debated and is still not clear. A neutron diffraction measurement by Goncharenko [8] gave evidence for a magnetic collapse as the δ - ϵ phase boundary is approached. At 9.5 GPa, apparently in the ϵ phase, no Bragg reflections could be detected down to 1.5 K in the low-2-theta window where magnetic signal is expected. It therefore was concluded that ϵ -O₂ has no long-range magnetic order. Nevertheless, there is support for a survival of a $S=1$ molecular spin - probably over only a moderate pressures range - from theory. In particular, recent DFT calculations by Crespo et al. [50] claim a magnetic "plaquette" structure, where the $S=1$ spins are antiferromagnetically ordered over 4 molecules giving a zero net magnetic moment (singlet) of the (O₂)₄ unit as shown in Fig. 9. Based on the neutron evidence [8], the authors presumed that the interaction between such plaquettes is too weak to form long-range order. Also, the DFT calculations cannot tell anything certain about the direction of the spins (E. Tosatti; private comm.), i.e. the spin alignment shown in Fig. 9 is somewhat speculative. Some support for these DFT data comes from light scattering measurements, in particular infrared absorption data, by comparison with calculated mode frequencies in the 10-40 GPa range [50]. An interesting point in this work is the prediction that the magnetic moment will eventually disappear at ~ 20 GPa to give a spinless " ϵ_0 " phase which is stable up to 96 GPa. Clearly, this exciting issue needs more experimental input.

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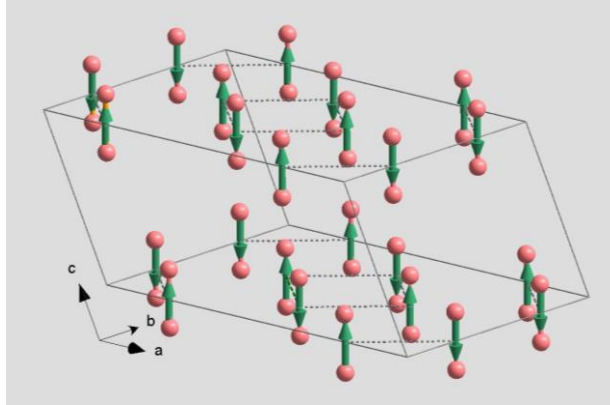


Fig. 9 Crystal structure of ϵ -O₂ (monoclinic, $C2/m$) with the magnetic structure as suggested from ab initio calculations [50]. The (O₂)₄ groups are indicated by dashed lines. Note that the direction of spins is not necessarily along the molecular axis. (Color figure online)

The issue of magnetism was investigated in more detail in neutron experiments using the Paris-Edinburgh technique described further above, see pattern Fig. 10 upper panel. The sample is clearly in the ϵ phase as shown by the Rietveld fit (line through the data) which give $a=8.231(4)$ Å, $b=5.900(2)$ Å, $c=3.887(2)$ Å, $\beta=116.63(2)^\circ$, $V=168.7(1)$ Å³, indicating a pressure of 10 GPa according to the x-ray data of Ref. [21]. The refinements (line through the data) assume only the known crystallographic structure [20,21] i.e. absence of magnetic order. Similar patterns were collected at lower temperatures (4 K) and different wave lengths resulting in considerably better statistics at low Q values. Given this experimental configuration, neutron diffraction patterns can be generated assuming long-range magnetic order with a moment of $m=1.6 \mu_B$ (as found in δ -O₂) and various different spin directions. Figure 10 middle panel gives the expected pattern according to the model by Crespo et al. [50] (spins point along the molecular axis, i.e. perpendicular to the a - b plane, see Fig. 9). Another, probably more obvious choice, is a spin alignment along the b -axis as found in α - and δ -O₂. This case would give a neutron diffraction pattern as shown in Fig. 10, lower panel. Various other configurations were tested; all of them give sizable Bragg reflections in the 2-theta window of Fig. 10. In conclusion, a comparison with the observed data (upper panel) gives no evidence for any magnetic order in ϵ -O₂ as long as the magnetic moment is larger than $\sim 0.2 \mu_B$ which is approximately the limit of detection.

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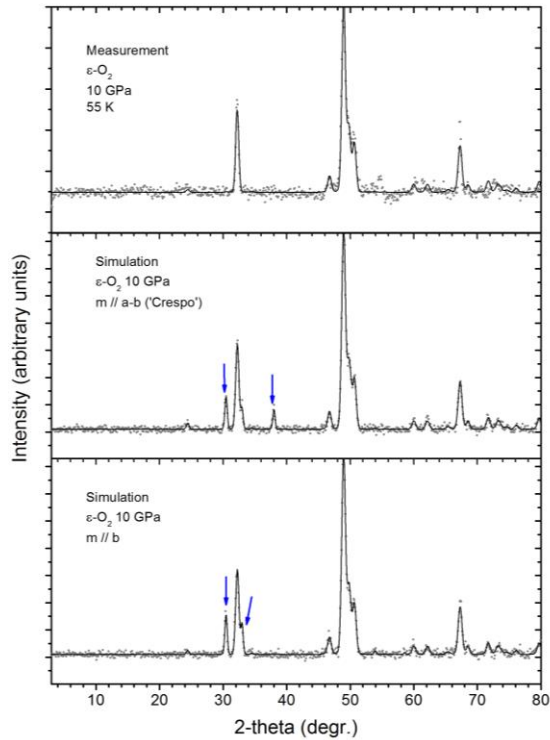


Fig. 10 Neutron diffraction patterns of ϵ -O₂. Upper panel: measured; the line is a Rietveld fit through the data (dots) assuming no magnetic long-range order. Middle panel: simulated, assuming long-range magnetic order and spin alignment according to Crespo et al. [50] (Fig. 9). Lower panel: same as above, but with spins aligned along b -axis. Arrows indicated strongest magnetic Bragg reflections. (Color figure online)

11 Conclusion and remaining issues

The technical progress allowing high pressure neutron scattering in the 10 GPa range and low temperatures has considerably improved our knowledge of magnetism in solid oxygen during the last decade. A key in the most recent investigations is the possibility to obtain high-quality diffraction patterns which can be treated by Rietveld refinement. Nevertheless, there are a few outstanding issues which need to be addressed.

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(A) There is still some doubt on the exact symmetry of δ -O₂. The single crystal studies at 300 K [48] assign it unambiguously to orthorhombic space group $Fmmm$, but powder x-ray diffraction at lower temperatures find evidence for a slight monoclinic distortion to $C2/m$ [18,51]. The most recent neutron diffraction data [8] support this observation: the neutron diffraction data shown in Fig. 4 can be fitted in $C2/m$ with a $\approx 0.2^\circ$ deviation from the ideal orthorhombic angle 90° . This deviation is small but significant and can be seen in Fig. 4 by a slightly larger width of the reflection at 47° (which is a doublet in $C/2m$) compared to the one at 52° (which is a singlet in $C/2m$). However, it is also observed that this monoclinic distortion is strongly dependent on the pressure-temperature history, and in particular that it decreases when the sample is annealed at high temperatures. The most likely interpretation is hence that the observed monoclinic distortion in δ -O₂ is not intrinsic but an effect of microstructure, possibly as a result of strain and non-hydrostatic pressure.

(B) A better understanding of potential magnetism in ϵ -O₂ in the 8-20 GPa range appears to be the most urgent issue. It is unlikely that neutron diffraction will provide further insight in the near future given the already rather conclusive results shown in the previous chapter. Myon spectroscopy would be an ideal technique to address this issue, but high pressure studies are so far limited to ~ 3 GPa [52].

(C) There are unpublished reports [53] from second harmonic generation spectroscopy indicating that δ -O₂ is not centrosymmetric, i.e. that the currently accepted crystal and/or magnetic structures (Fig. 6) are incorrect. It should be noted that the available x-ray and neutron diffraction data severely constrain the possible structures: the single crystal x-ray data by Schiferl et al. [48] are uncontested, and the evidence for the correctness of the magnetic structure (at least the LTC structure) is overwhelming, see Fig. 6 and related discussion. The only uncertainty concerns possible small static tilts of molecules which were so far interpreted as thermally induced librations [9,48]. It is indeed easy to show that periodic tilts (typically $\pm 5^\circ$) of two molecules in the unit cell in opposite directions can produce non-centrosymmetric structures which are nevertheless compatible with the x-ray data if they are small enough. A similar argument applies to the direction of the spins. It would therefore be interesting to address this issue by single-crystal diffraction at the P/T range of interest, i.e. ≈ 7 GPa/150 K.

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