High-pressure oxygen: a non-conventional magnet studied by means of neutron diffraction

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Abstract
While being among the most casually treated elements on our planet, elementary
oxygen shows many unusual features at low temperatures and high pressures.
At low pressure, oxygen is the only elementary molecular magnet. Under high
pressures solid oxygen undergoes several structural transformations and finally
becomes a metal and superconductor under the very high pressure of 96 GPa.
For the first time, we studied magnetic ordering in solid oxygen under very high
pressures by a direct method, namely by means of neutron diffraction. A new
type of magnetic order with ferromagnetic stacking of the antiferromagnetic
O_2 planes was discovered in δ-O_2 at $P = 6.2$ GPa. The structural transitions
from α-O_2 to β-O_2 and δ-O_2 correlate with the magnetic transitions; therefore
in the pressure range $P < 7$ GPa, oxygen should be considered as a unique
'spin-controlled crystal'.

1. Introduction

Dense oxygen is a very unusual solid. O_2 is the only elementary molecule which carries a
magnetic moment. The ground state of the O_2 molecule is a triplet; therefore it carries the
non-compensated spin $S = 1$. At ambient pressure solid oxygen is an antiferromagnetic
insulator [1, 2]. Magnetic interactions between O_2 molecules are comparable with weak
intermolecular forces; therefore magnetism plays an important role in the stabilization of a
particular crystal structure. In this respect, oxygen is different from any other solid. At ambient
pressure oxygen crystallizes in three different structural modifications: α, β and γ [3]. The γ
phase exists in a narrow temperature range $44\,\text{K} < T < 54\,\text{K}$. It has $Pm3n$ structure with eight
molecules in the unit cell, which is very different from the structures of the α and γ phases.
Whereas the centres of the O_2 molecules form perfectly ordered structure, the orientations of
the molecular axes are random. Molecules located in the different crystallographic positions
can be described as spheres (full orientational disorder) or discs (partial orientational disorder).
No long-range magnetic order is expected to occur in this orientationally disordered phase. In
the temperature range $24\,\text{K} < T < 44\,\text{K}$ oxygen crystallizes in a rhombohedral β phase. In this
phase, the O_2 molecules are located in the triangular planes with the molecular axis ordered

a)

b)
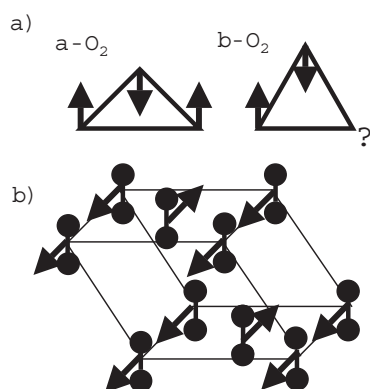
Figure 1. (a) The triangular arrangement of O_2 molecules in the basal plane of α- and β-O_2. The perfect triangular lattice (right) is topologically frustrated whereas the distorted lattice is not. (b) The magnetic structure of α-O_2.
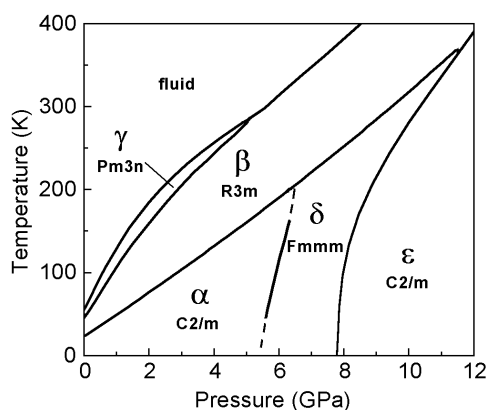
Figure 2. The pressure–temperature phase diagram of oxygen derived from x-ray data [9].

and directed perpendicular to the planes. The first-neighbour distances between molecules located within the same plane are much smaller than the shortest distances between molecules located in the neighbouring planes; therefore β-O_2 could be considered a two-dimensional crystal. One should note that in the Ising model the two-dimensional triangular lattice is topologically frustrated as regards first-neighbour antiferromagnetic interactions; i.e., no one spin arrangement can minimize the free energy (figure 1(a)). The topological frustration could suppress the long-range magnetic order. Neutron diffraction studies found only short-range magnetic correlations in β-O_2 [2]. At $T = 24$ K rhombohedral β-O_2 transforms into monoclinic α-O_2. The α–β structural transition coincides with the magnetic transition from a short-range ordered state to a long-range antiferromagnetic order. It was argued that magnetic exchange interactions could be responsible for the structural transition [4–7]. In the α phase the triangular nets are distorted and therefore non-frustrated topologically, so the total free energy could gain from magnetic exchange. The magnetic unit cell of α-O_2 consists of two molecules and coincides with the chemical unit cell [2]. Every O_2 molecule has four nearest neighbours in the same plane with antiparallel spin orientation (figure 1(b)). Four closest molecules in the neighbouring planes also have antiparallel spin orientations.

High-pressure properties of solid O_2 are even more intriguing. The pressure–temperature phase diagram is shown in figure 2. At $P = 6$ GPa and low temperature oxygen transforms into an orthorhombic δ phase [8, 9]. The orthorhombic unit cell consists of four O_2 molecules. The crystal structures of the α and δ phases are very similar. The crystal structure of the δ phase can be also described with a monoclinic unit cell (similar to the unit cell of the α phase) with some particular ratio of lattice parameters, namely $-\cos(\beta) = c/2a$ where β is the monoclinic angle. At higher pressures $P > 7.8$ GPa the δ phase transforms to the ε phase [10, 11]. In the pressure range 15 GPa $< P <$ 96 GPa the ε phase is the only stable phase of solid oxygen. The exact crystal structure of ε-O_2 is unknown. Finally at $P = 96$ GPa the ε phase transforms to the ξ phase [12, 13]. Very high pressures affect the electronic properties of dense oxygen. At ambient pressure oxygen is a wide-gap insulator. The orange colour of the ε phase indicates reduction of the gap. Finally, the ξ phase is metallic and shows superconducting properties at $T < 0.6$ K [14, 15]. Undoubtedly, magnetism should play some role in the above transformations. It is unlikely that a magnetically ordered state

could coexist with the superconducting state in the ξ phase, so one should expect to find that in the pressure range $P < 96$ GPa solid oxygen loses its magnetic properties. Different scenarios had been suggested for the evolution of the magnetic properties in the pressure range $P < 96$ GPa. In one of these scenarios, electronic shells of O_2 molecules are gradually losing their localized character with pressure [16]. Partial delocalization results in a gradual decrease of the microscopic magnetic moment. In this scenario, one should expect a smooth decrease of the magnetic ordering temperature in the some pressure range, while the O_2 molecular lattice remains practically intact. In another scenario, pressure favours chemical bonding between the molecules, resulting in the formation of a polymeric multi-molecular state or a multi-atomic O_n ($n > 2$) molecular lattice. The multi-atomic molecules or polymeric states are expected to carry compensated spins. If diatomic molecular states are ever broken by pressure, one should expect a drastic collapse of magnetic properties. The O_4 molecular lattice was suggested for the ε phase [17].

Would the magnetic state found in solid oxygen at ambient pressure be stable over a wide pressure range? Will the magnetic interactions play some role in the pressure induced structural transitions? Neither of these questions could be addressed without a direct study of magnetic ordering in high-pressure oxygen. Before the present study, only indirect information on magnetic interactions in solid oxygen obtained by optical methods was available. Optical spectroscopy suggests that spin interactions in α-O_2 are enhanced by pressure [18]. Additional vibrational modes in infrared spectra suggest that the true symmetry (structural + magnetic) of the δ phase is lower than that found from x-ray measurements; therefore an antiferromagnetic state similar to that found in α-O_2 was suggested for the δ phase [19]. The optical properties of the ε phase were found to be completely different from the optical spectra of the α and δ phases. On the basis of this difference, an O_4 lattice was suggested for ε-O_2 [17]. None of the above suggestions was based on a direct experimental method. Only a neutron diffraction study could answer the question of the magnetic order in high-pressure oxygen. Unfortunately, due to the relatively low amplitudes of magnetic neutron scattering in solid O_2, problems with preferred orientation and difficulties of compressing considerable amounts of highly penetrating O_2, such studies were not possible until now. Here we present the first neutron results on magnetic and structural transitions in high-pressure oxygen. A short description of these results was recently published in [20].

2. Experimental details

General features of the pressure technique are described in [21]. A modification of the 'Kurchatov–LLB' pressure cell (figure 3) was used. The cell was able to accommodate a maximal load up to 150 kN, about three times higher than our standard 'Kurchatov–LLB' cell, while keeping almost the same diameter (48 mm) and therefore being compatible with our standard He flow cryostat ($T_{min} = 1.4$ K). Bevelled springs allow a smooth loading and minimize variations of pressure with temperature. About 1 mm^3 of solid oxygen was pressurized between two anvils made from polycrystalline cubic boron nitride. Being highly absorbing of neutrons, boron nitride anvils did not contribute any diffraction lines to the diffraction patterns. Incident and scattered neutron beams passed through the gasket made from steel. Pressure was estimated by measuring the diffraction lines from a small piece of NaCl placed into the sample volume. We used the equations of state $V(P, T)$ for NaCl from [22]. The absolute accuracy of the pressure measurement was estimated as ± 0.2 GPa. Pressure variations were monitored during cooling or heating. The variations of pressure with temperature were within ± 0.2 GPa.

Figure 3. Left: the pressure cell with anvils made from cubic boron nitride. Right: the container used to load liquid oxygen into the cell.

Liquid oxygen was condensed at 77 K in a sealed container (figure 3). The container was placed into a liquid nitrogen bath. Before condensation, the volume was evacuated and the condensation took place at an oxygen pressure slightly above the atmospheric pressure—in order to avoid any contamination with N_2 or H_2O. The pressure cell was inside the container, immersed in liquid oxygen. When liquid oxygen filled all free space in the container, a small pressure was applied by means of special screws at the top of the container and a liquid sample was sealed off in the pressure cell. Then the container was opened and pressure was increased up to the final value. In the first experiments pressure was increased at $T = 300$ K and then the pressure cell was cooled down in order to study the magnetic ordering. In this case in the pressure range $4\,\text{GPa} < P < 7\,\text{GPa}$ oxygen crystallized from the liquid state to the β phase and then, with cooling, to α or δ phases. It was found that the above procedure does not produce a good polycrystalline sample. The samples consisted of several big crystals and the intensities of the Bragg peaks were strongly affected by the particular orientations of the crystals. The phase transition between β and α (or δ) phases, having closely related symmetries and almost no difference in volume, did not improve the sample quality. Therefore in the experiments described below, pressure was applied at $T = 200$ K. In this case, the sample first crystallized into the γ phase and then passed through a $\gamma–\beta$ transition. The very different crystal structures of the γ and β phases and a huge volume effect at the $\gamma–\beta$ transition helped us to obtain good polycrystalline samples.

The neutron scattering was measured using a specialized high-pressure diffractometer G6.1 'MICRO' at the Laboratoire Léon Brillouin, installed on a cold neutron guide of the ORPHEE reactor [23]. A monochromatic neutron beam was focused onto the sample by means of a double-stage focusing system made from Ni–Ti supermirrors [24, 25]. Special efforts were taken to decrease the neutron background. Diffraction patterns were registered by a 400-cell multi-detector. To characterize both magnetic and crystal structures, two values of the incident neutron wavelength $\lambda_1 = 4.74$ Å and $\lambda_2 = 2.37$ Å were used. Typical counting times were from 2 to 12 h per spectrum.
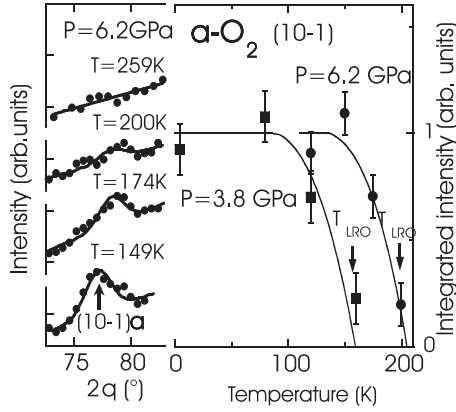
Figure 4. On the left: evolution the magnetic peak $(10\bar{1})$ measured in α-O_2 at $P = 6.2$ GPa at different temperatures ($\lambda = 4.741$ Å). On the right: integrated magnetic intensity of the $(10\bar{1})$ peak versus temperature at pressures of 3.8 GPa (squares) and 6.2 GPa (circles), showing the disappearance of the long-range magnetic order at the α–β transition.
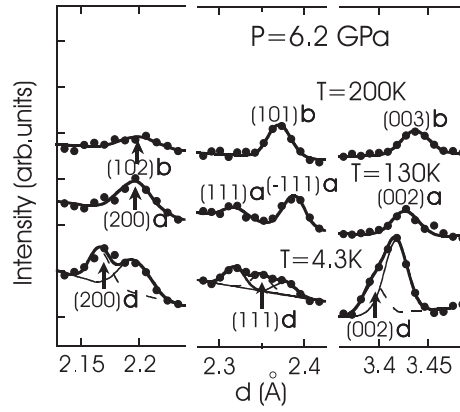
Figure 5. Neutron diffraction data collected at $P = 6.2$ GPa. Magnetic peaks are not shown. Peaks are indexed in the unit cells described in the table.

Table 1. Structural parameters refined from our neutron data for α-, β- and δ-O_2 at $P = 6.2$ GPa. β^* is defined in figure 9.

| Phase	Space group	T (K)	a (Å^3)	b (Å^3)	c (Å^3)	β (deg)	β^* (deg)	V/molecule (Å^3)
δ	$Fmmm$	4.3	4.33(2)	3.06(2)	6.83(4)	—	90	22.6(3)
α	$C2/m$	130	4.41(3)	3.05 (2)	4.23(3)	125.9(5)	94.7(5)	23.0(4)
β	$R\bar{3}m$	200	2.82(1)	—	10.31(4)	—	—	23.6(3)

3. Results

In figure 4 we show intensities of the magnetic diffraction peak $(10\bar{1})$ measured in the region of stability of the α phase at $P = 3.8$ and 6.2 GPa at different temperatures. The magnetic structure of α-O_2 at $P = 6.2$ GPa is essentially the same as that at ambient pressure. No difference was found between the neutron data measured at high and ambient pressures, except the difference in magnetic ordering temperature and lattice parameters. The temperature of transition to the long-range ordered antiferromagnetic state (T_{LRO}) shows a remarkable increase under pressure. From our data, $T_{LRO} = 150(10)$ K at $P = 3.8$ GPa and $T_{LRO} = 200(10)$ K at $P = 6.2$ GPa, which should be compared to $T_{LRO} = 24$ K at ambient pressure. The disappearance of the magnetic signal exactly coincides with the α–β structural transition. As at ambient pressure [2], no long-range magnetic order was found in β-O_2.

At $P = 6.2$ GPa and low temperature one should expect to cross the transition line between the α and δ phases. At this pressure, some changes in neutron diffraction patterns were observed in the temperature range below 100 K (figure 5). This changes should be attributed to the formation of the orthorhombic δ phase. The α–δ transition is not complete even at the lowest temperature 4.3 K, probably because the pressure was very close to the critical pressure of the α–δ transition. The structural parameters of the α and δ phases at $P = 6.2$ GPa are summarized in table 1. They are very close to the values obtained in the previous x-ray measurements.
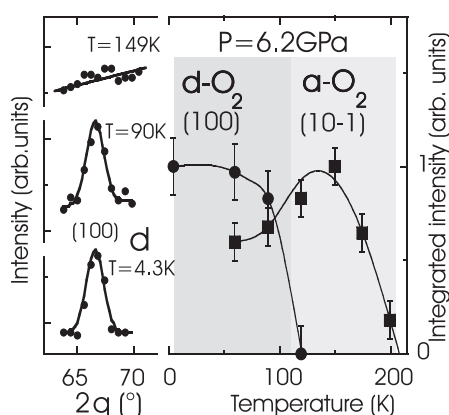
Figure 6. On the left: the magnetic peak (100) from δ-O_2 at $P = 6.2$ GPa measured at different temperatures. On the right: integrated intensities of the $(10\bar{1})$ magnetic peak from α-O_2 and the (100) magnetic peak from δ-O_2 versus temperature.
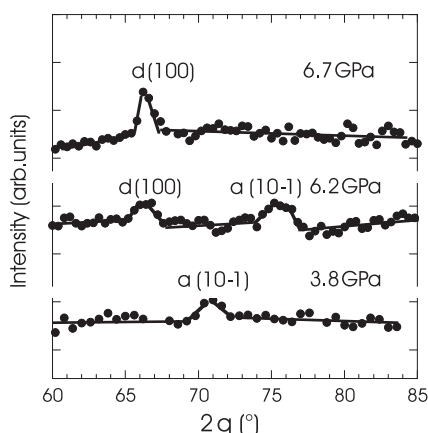
Figure 7. Magnetic neutron diffraction in solid oxygen ($\lambda = 4.741$ Å) measured at pressures of 3.8, 6.2 and 6.7 GPa and temperature 4 K.

Besides the structural peaks, additional diffraction peaks were observed for the δ phase. These peaks are superstructural as regards the symmetry of the chemical unit cell and were not found in the previous x-ray measurements. In figure 6 we show the temperature evolution of such an additional reflection at the pressure 6.2 GPa. The peak disappeared at $T \approx 100$ K when the δ phase transformed into the α phase. Obviously, this peak should be attributed to magnetic order in the δ phase. In figure 7 one can see the magnetic neutron scattering measured at pressures of 3.8, 6.2 and 6.7 GPa and $T = 4$ K. At 3.8 GPa we observed only 'α-type' magnetic scattering. At $P = 6.2$ GPa the new peak appeared. This peak was indexed as (100) in the orthorhombic unit cell of δ-O_2. At this pressure, it coexists with the magnetic peak from α-O_2, as could be expected for an incomplete α–δ transition. At $P = 6.7$ GPa the transition is complete; any scattering from the 'α-type' of magnetic order disappeared and only the 'δ-type' of magnetic order was observed.

The strong difference in positions of the magnetic peaks measured for α-O_2 and δ-O_2 is very surprising. As was mentioned in the introduction, the crystal structures of α and δ phases are very similar and can be described with the same monoclinic unit cell with only slightly different lattice parameters. One would naturally expect the magnetic scattering in δ-O_2 to be essentially the same as that in α-O_2—except a tiny shift in the peak position due to the change in lattice parameters. Contrary to these expectations, neutron diffraction shows that the magnetic structures in α-O_2 and δ-O_2 are completely different. In figure 8 diffraction patterns calculated for different models of magnetic ordering in δ-O_2 are shown. The model assuming the same type of magnetic ordering in α-O_2 and δ-O_2 completely disagrees with our data (figure 8(a)). The agreement did not improve when spins were rotated in the basal plane. The strongest magnetic peak from δ-O_2 does not exist in the 'α-type' model of magnetic ordering. To explain our diffraction data one has to assume a new type of magnetic structure in δ-O_2 (figure 9). The strong (100) reflection and the weak (011) reflection suggest that the magnetic moments in δ-O_2 are directed along the b-axis. Although the magnetic order *within* the $O_2(a, b)$ planes is similar in α-O_2 and δ-O_2, the *interplane* order is just the opposite. The first-neighbour *interplane* spin orientations in α-O_2 are antiferromagnetic whereas in δ-O_2 they are ferromagnetic. The proposed magnetic structure fits perfectly to our neutron data (figure 8(b)).
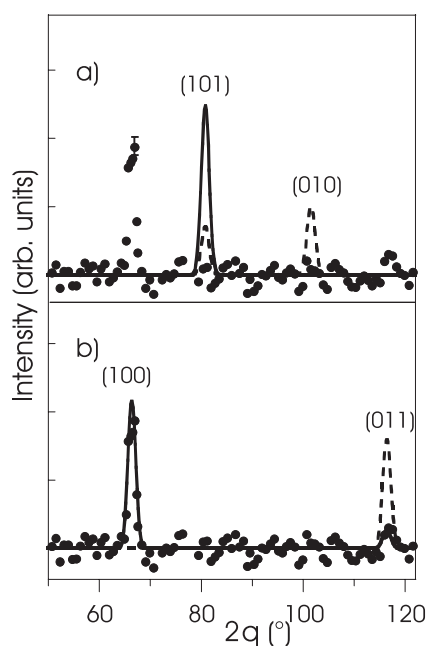
Figure 8. Curves: calculated magnetic neutron scattering in δ-O_2. (a) O_2 planes are coupled antiferromagnetically, as was found in α-O_2; (b) O_2 planes are coupled ferromagnetically. Solid curves correspond to magnetic moments directed along the b-axis whereas dashed curves correspond to magnetic moments directed along the a-axis. The magnetic form factor was taken from [2]. Dots: experimental data for the magnetic neutron scattering in δ-O_2 at $P = 6.2$ GPa. In order to separate α and δ phases we subtracted spectra measured in the temperature range above the α–δ transition.

4. Discussion

Our results confirm the rapid increase of magnetic exchange interactions under pressure (by an order of magnitude at $P = 6.2$ GPa) suggested before from optical spectroscopy and prove the magnetostructural character of the α–β transition for practically the whole range of stability of α-O_2.

The magnetic structure found in δ-O_2 is highly surprising. It was not suggested by indirect measurements and it was not found in *ab initio* calculations. In [8] the authors suggested that δ-O_2 is magnetically disordered. This scenario is ruled out by our data. In [26] *ab initio* molecular dynamic simulation predicted the same antiferromagnetic stacking of the O_2 planes in α-O_2 and δ-O_2, which is also inconsistent with our experiment. In elementary insulating magnets, exchange interactions are expected to arise from an overlap of molecular orbitals ('direct exchange'). Simple quantum considerations suggest a negative sign of the exchange constant, favouring antiparallel spin arrangements. The absolute value of the exchange interaction decreases rapidly with distance; therefore it should be sufficient to consider only nearest in-plane and off-plane neighbours to describe the three-dimensional magnetic ordering in solid oxygen. The magnetic structure of α-O_2 fits perfectly to the above scheme. In this structure, in-plane and off-plane first-neighbour spin orientations are antiferromagnetic. In contrast, the ferromagnetic coupling between nearest off-plane neighbours in δ-O_2 cannot be explained.

One should note that in a molecular crystal spin interactions could depend on the angle φ between the axis of the molecule and the vector connecting the centres of the molecules.
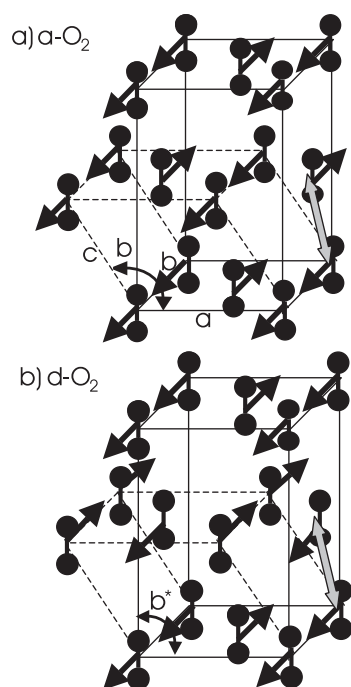
Figure 9. Magnetic orderings in the α and δ phases. Dotted lines show the monoclinic unit cell, common to α-O_2 and δ-O_2. The double arrows show coupling between the off-plane nearest neighbours.

Hartree–Fock calculations [27] suggest that for some values of φ exchange interactions in solid oxygen could become positive, favouring ferromagnetic spin alignment. One could speculate that the variation of φ under pressure could be responsible for the magnetic transition from the α type of order to the δ type of order. Nevertheless, angle φ changes only slightly under pressure. At $P = 6.2$ GPa, $\varphi = 24.3°$ and $24.1°$ in the α and δ phases respectively which should be compared with $\varphi = 26.3°$ in α-O_2 at ambient pressure. In an alternative model, the change of the interplanar magnetic stackings in the δ phases is driven by long-range magnetic interactions which are negligible at ambient pressure. In this case, the δ type of magnetic order can be stabilized even if all exchange interactions are negative (i.e. antiferromagnetic). In figure 10 one can see how the interactions with second and third off-plane neighbours can stabilize the δ-type coupling of the O_2 planes. The growing importance of the long-range magnetic interactions should be attributed to a growing delocalization of the O_2 orbitals under pressure. Therefore in this model the magnetic transition from the α–δ transition should be considered as a first sign of magnetic instability which could be followed by magnetic collapse at higher pressure (probably in the ε phase) and, finally, by a transition to a metallic state at much higher pressures.

The fact that α-O_2 and δ-O_2 order in completely different magnetic structures provides insight into the possible microscopic origins of the α–δ transition. The crystal structure of δ-O_2 can be obtained from the crystal structure of α-O_2 through a smooth displacement of the O_2 planes; therefore some authors argued that this transition should be of second order [8] or even assigned the whole low-temperature region of the phase diagram (from ambient pressure up to the transition to the ε phase) to the α phase [28], even though the latest experimental data
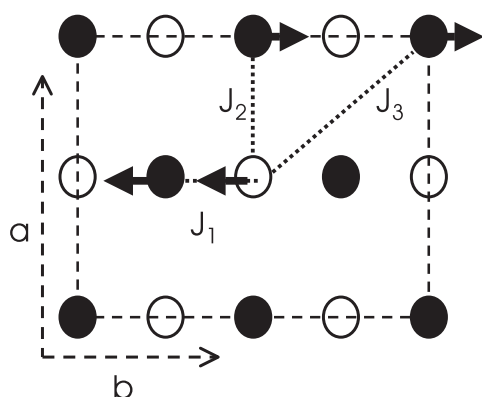
Figure 10. Spin orientations and magnetic interactions between first, second and third off-plane neighbours in the δ phase. The open and filled spheres indicate molecules located in the neighbouring planes.

suggest that the α–δ transition is actually of first order [9]. In this sense, without information on the magnetic order in δ-O_2, the stability of the δ phase looked somewhat mysterious. Our data prove that the δ phase is fundamentally different from the α phase and give a natural explanation of why the α–δ transition is of first order. In contrast to the crystal structures, indeed, there is no smooth passage between the magnetic structures of α-O_2 and δ-O_2. Probably not only the α–β transition but also the α–δ transition is actually driven by magnetic forces. In this case the whole phase diagram of solid oxygen at $P < 7$ GPa (except, probably, the narrow range of stability of the γ phase) is described through an interplay of magnetic and intermolecular interactions.

Solid oxygen at $P < 7$ GPa could be described as a 'spin-controlled' crystal. What should we expect at higher pressures? It is unlikely that the balance between the intermolecular and magnetic forces would extend up to very high pressures, >10 GPa. The absolute values of the exchange constant might continue to increase under pressure, but the values of the magnetic moments are expected to decrease as molecular orbitals become less localized; therefore the total magnetic energy $\Sigma J_i S S_i$ is expected to decrease at some pressure. One should expect that at some critical pressure the structural and magnetic transitions will become decoupled. At even higher pressures, magnetic order could disappear completely. Ongoing studies of the magnetic order in ε-O_2 should clarify this question.

In conclusion, we carried out a first neutron diffraction study of solid oxygen under pressures up to 6.7 GPa. New and unexpected magnetic structure had been found at $P > 6$ GPa. Our results strongly modify the interpretation of the well-established phase diagram of solid O_2 under pressures <7 GPa. Once more, solid oxygen demonstrated its intriguing features.

Acknowledgments

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