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Direct Determination of the Magnetic Structure of the Delta Phase of Oxygen

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Simple diatomic molecules exhibit a variety of exciting physical phenomena under high pressures, including structural transitions, pressure induced metallization, and superconductivity. Oxygen is of particular interest because it carries a magnetic moment. For the first time we studied the magnetic structure in solid oxygen under very high pressure by a direct method, namely, 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. We show that all structural transformations at pressures <7 GPa are driven by spin interactions; therefore, high-pressure oxygen should be considered as a unique "spin-controlled crystal."

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In many aspects solid oxygen is an unusual crystal. O_2 is the only elementary molecule that carries a magnetic moment. At ambient pressure solid oxygen is an antiferromagnetic insulator that crystallizes in α, β, and γ phases in the temperature ranges $T < 24$ K, $24 < T < 44$ K, and $44 < T < 54$ K, respectively. The γ phase is cubic and paramagnetic, the β phase is rhombohedral and short-range magnetically ordered, whereas the α phase is monoclinic and exhibits a long-range antiferromagnetic order [1,2]. It was argued that the α-β transition is actually driven by magnetic forces [3–6]. Magnetic interactions distort the triangular arrangements of the O_2 molecules in the β phase and therefore minimize the total free energy by releasing the topological frustration in the magnetic sublattice. Under pressure the temperature of the α-β transition rapidly increases and reaches 200 K at $P = 6$ GPa. At higher pressures oxygen transforms successively into an orthorhombic δ phase, then into a monoclinic ε phase [7–9], and finally into another monoclinic ξ phase which is metallic and superconducting [10–13]. Undoubtedly, magnetism should play an important role in these transformations. Unfortunately there is no direct experimental information on spin ordering in solid oxygen under high pressures. Optical spectroscopy suggests that spin interactions in α-O_2 are enhanced by pressure [14]. Additional vibrational modes in infrared spectra suggest that the δ phase should be antiferromagnetic [15], although no precise conclusion about the magnetic structure can be made.

Direct information on the interplay of magnetic and crystal structures can be obtained only through neutron scattering, since neutrons are sensitive to both crystal and magnetic structures. For a long time, such experiments were not feasible due to technical limitations for high-pressure neutron diffraction. Recently a new high pressure and neutron instrumentation has been developed at the Laboratoire Léon Brillouin (LLB), which allowed us to combine very high pressures and low temperatures [16,17]. Here we present the first results on neutron scattering in the α, β, and δ phases of solid oxygen under pressures up to 6.2 GPa. We obtained very surprising results.

We used the Kurchatov-LLB pressure cells [18] and the G6.1 high-pressure diffractometer installed on the ORPHEE reactor of the LLB [16]. Liquid oxygen was condensed at 77 K in a sealed volume. The sample was pressurized between two opposite anvils made from cubic boron nitride. 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 Ref. [19]. We estimate the absolute accuracy of the pressure measurement to be ± 0.2 GPa. The variation of pressure during heating or cooling was also within ± 0.2 GPa. The neutron beam was focused to the sample by special focusing systems. To characterize both magnetic and crystal structures, we used two values of the incident neutron wavelength $\lambda_1 = 4.74$ Å and $\lambda_2 = 2.37$ Å.

In Fig. 1 we show neutron diffraction patterns collected at $P = 6.2$ GPa. Above 100 K we observed the same α and β phases as found in previous x-ray diffraction experiments. Below 100 K we observed additional reflections that should be attributed to the orthorhombic δ phase. The α-δ transition is not complete even at the lowest temperature 4.3 K, probably because we were very close to the critical pressure of the α-δ transition. The structural parameters of the high-pressure phases are summarized in Table I. In the low-angle part of the diffraction patterns

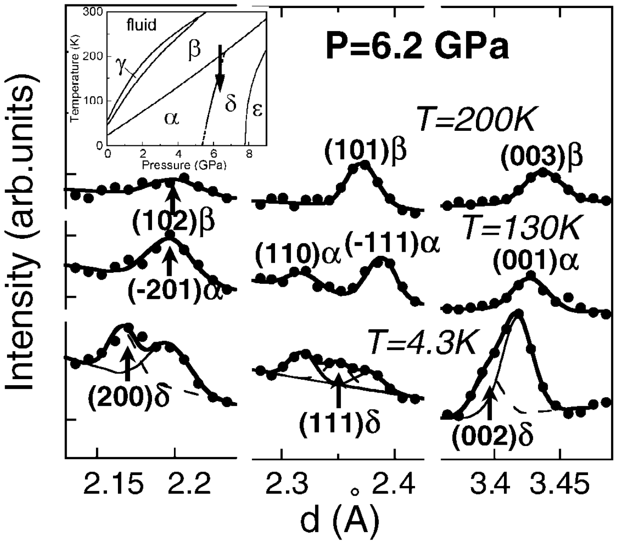

FIG. 1. Neutron diffraction data collected at $P = 6.2(2)$ GPa. Magnetic peaks are not shown. Peaks are indexed in the unit cells described in the table. Inset: the pressure-temperature phase diagram of solid oxygen derived from x-ray data [9].

measured in the region of stability of α-O_2, we observed diffraction lines that were not detected in x-ray diffraction experiments (Fig. 2). These lines should be attributed to a long-range magnetic ordering. The strongest peak can be indexed as a $(1\ 0\ -1)$ reflection in the monoclinic unit cell. The same reflection was observed in neutron diffraction experiments carried out in α-O_2 at $P = 0$ [1,2]. We conclude that the magnetic structure in α-O_2 at $P = 6.2$ GPa is essentially the same as at $P = 0$. In Fig. 3 we plot the integrated intensity of the $(1\ 0\ -1)$ magnetic reflection versus temperature at the pressures 3.8 and 6.2 GPa. We notice the remarkable increase of the temperature of transition towards long-range-ordered antiferromagnetic state (T_{LRO}) under pressure. We determined $T_{LRO} = 150(10)$ 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 $P = 0$. The disappearance of the magnetic signal exactly coincides with the α-β structural transition. As at $P = 0$ [2], we did not find any long-range magnetic order in β-O_2. Our results confirm the rapid increase of magnetic exchange interactions under pressure suggested before by optical spectroscopy [14] and prove the magnetic origin of the α-β transition for practically the whole range of stability of α-O_2.

The analysis of the neutron diffraction data collected in the range of stability of δ-O_2 reveals a very interesting and unexpected phenomenon. At $P = 6.2$ GPa and $T < 100$ K we observed a new magnetic peak that does not exist in the magnetic unit cell of α-O_2 and that was not found in the x-ray studies. This peak disappears at higher temperatures when δ-O_2 transforms into α-O_2 (Fig. 3). Obviously, this peak should be attributed to magnetic order in δ-O_2. It should be indexed as the $(1\ 0\ 0)$ reflection in the orthorhombic unit cell. Observation of the magnetic reflection that cannot be described in the primitive chemical unit cell provides a direct proof for the antiferromagnetic nature of δ-O_2. Below we use our neutron data to determine a precise spin arrangement in δ-O_2.

We notice the strong difference in positions of the magnetic peaks measured in α-O_2 and δ-O_2. The crystal structures of α and δ phases are very similar and can be described by the same monoclinic unit cell with only slightly different lattice parameters. One can naturally expect that the magnetic scattering in δ-O_2 will be essentially the same as in α-O_2 except for a tiny shift in the peak position due to the change in lattice parameters. Contrary to these expectations, neutron diffraction results show that the magnetic structures in α-O_2 and δ-O_2 are completely different. In Fig. 4 we show diffraction patterns calculated for different types of magnetic ordering in δ-O_2. One can see that the model assuming the same type of magnetic ordering in α-O_2 and δ-O_2 completely disagrees with our data [Fig. 4(a)]. We found only one possible model for magnetic order in δ-O_2 that agrees with our neutron data [see Fig. 4(b)]. The strong $(1\ 0\ 0)$ reflection and the weak $(0\ 1\ 1)$ 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-neighbor interplane spin orientation in α-O_2 is antiferromagnetic, whereas in δ-O_2 it is ferromagnetic.

The ferromagnetic coupling between the O_2 planes in δ-O_2 is highly surprising. It was not suggested by indirect measurements, and it was not found in *ab initio* calculations. In Ref. [8] authors suggested that δ-O_2 is magnetically disordered. This scenario is ruled out by our data. In Ref. [20] *ab initio* molecular dynamic simulation predicted the same antiferromagnetic stacking of the O_2

TABLE I. Structural parameters refined from our neutron data in the α-O_2, β-O_2, and δ-O_2 phases at $P = 6.2(2)$ GPa. β^* is defined in Fig. 4.

Phase	Space group	T (K)	a (Å)	b (Å)	c (Å)	β (°)	β^* (°)	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-3m	200	2.82(1)	···	10.31(4)	···	···	23.6(3)

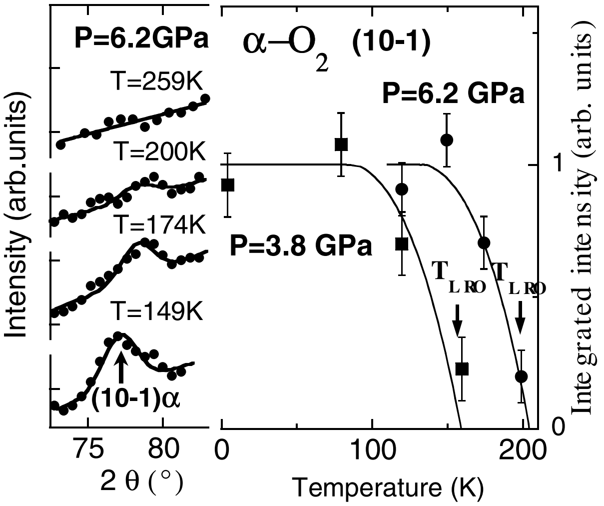

FIG. 2. Left: Evolution of the magnetic peak (1 0 − 1) measured in α-O_2 at $P = 6.2(2)$ GPa at different temperatures. Right: Integrated magnetic intensity of the (1 0 − 1) peak versus temperature at pressures of 3.8(2) GPa (squares) and 6.2(2) GPa (circles), showing the disappearance of the long-range magnetic order at the α-β transition.

planes in both α-O_2 and δ-O_2, which is also inconsistent with our experiment. It was generally assumed that exchange interactions between O_2 molecules are antiferromagnetic and rapidly decrease with distances [20]. This is consistent with the magnetic structure found in α-O_2, but fails to explain the magnetic structure of δ-O_2. We notice that Hartree-Fock calculations [21] suggest that the sign and the value of exchange interactions depend on the angle φ between the axis of the molecule and the vector connecting the centers of molecules. One can speculate that the variation of φ under pressure could be responsible for the magnetic transition. Nevertheless, we notice that φ changes only slightly under pressure. We determined $\varphi = 24.3°$ and 24.1° at $P = 6.2$ GPa in the α and δ phases, respectively, which should be compared with $\varphi = 26.3°$ in α-O_2 at $P = 0$ [2]. In an alternative model, the change of the interplanar magnetic stackings in the δ phases is driven by long-range magnetic interactions that are negligible at $P = 0$. In particular, we notice that the interactions between the third interplane neighbors can stabilize the ferromagnetic coupling of the O_2 planes even if all the exchange constants are negative (i.e., antiferromagnetic). The growing importance of the long-range magnetic interactions could be attributed to a partial delocalization of the O_2 orbitals under pressure. Whatever is the real origin of the magnetic transition, our

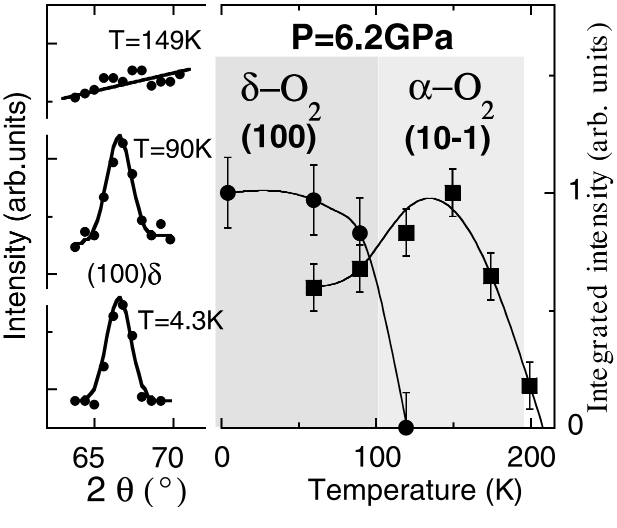

FIG. 3. Left: The magnetic peak (1 0 0) from δ-O_2 at $P = 6.2(2)$ measured at different temperatures. Right: Integrated intensities of the (1 0 − 1) magnetic peak from α-O_2 and the (1 0 0) magnetic peak from δ-O_2 versus temperature.

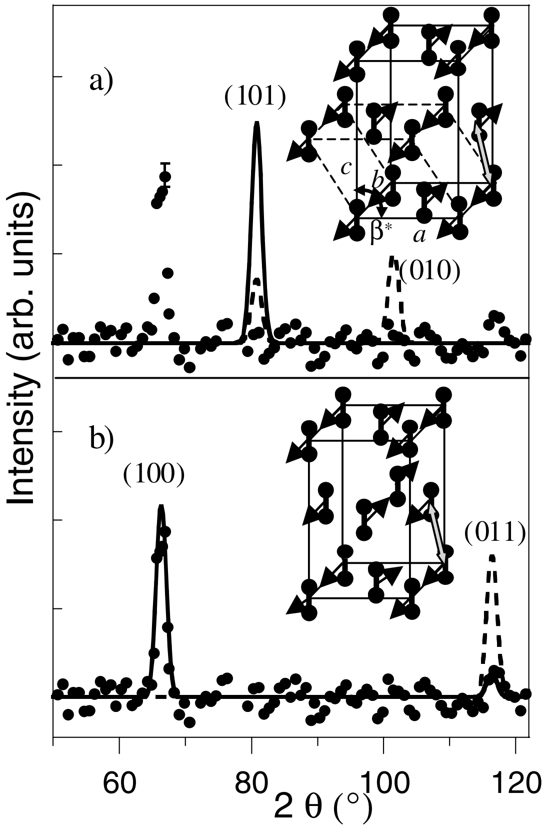

FIG. 4. Lines: calculated magnetic neutron scattering in δ-O_2. (a) O_2 planes are coupled antiferromagnetically, as it was found in α-O_2; (b) O_2 planes are coupled ferromagnetically. Solid lines correspond to magnetic moments directed along the b axis, whereas dashed lines correspond to magnetic moments directed along the a axis. The magnetic form factor was taken from Ref. [2]. Dots: Experimental data on magnetic neutron scattering in δ-O_2 ($\lambda = 4.74$ Å). In order to separate the α and δ phases we subtracted spectra measured in the temperature range above the α-δ transition. Insets: Dotted lines show the monoclinic unit cell. The double arrows show coupling between the interplane nearest neighbors.

results strongly change the understanding of magnetic phenomena in high-pressure oxygen.

The fact that α-O_2 and δ-O_2 order in completely different magnetic structures provides an 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 [22], even though the latest experimental data suggest that the α-δ transition is actually of first order [9]. In this sense, without the 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 why the α-δ transition is of first order. In contrast to the crystal structures, indeed, there is no smooth pass between the magnetic structures of α-O_2 and δ-O_2. Our results suggest that 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. Ongoing studies of the magnetic order in ε-O_2 should clarify how this "spin-controlled" crystal transforms into a metallic superconductor.

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