MAGNETIC ORDER IN HIGH-PRESSURE OXYGEN

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While being one of the most casual elements in our planet, elementary oxygen shows many unusual features. O_2 is the only elementary molecule which carries a magnetic moment (S=1). At ambient pressure, solid oxygen is an antiferromagnetic insulator. Magnetic interactions between O_2 molecules are comparable with weak intermolecular forces, therefore magnetism plays an important role in stabilization of a particular crystal structure. In this respect, oxygen is different from any other solid. Magnetic interactions were claimed to be responsible for a structural transition from the rhombohedral β-phase to a monoclinic α-phase at T=24K and ambient pressure. Under high pressures, solid oxygen transform successively into an orthorhombic δ-phase (P=6 GPa), then into a monoclinic ε-phase (P=8 GPa) and finally to a metallic and superconducting ξ-phase (P=96 GPa, T_C=0.6 K [1]).

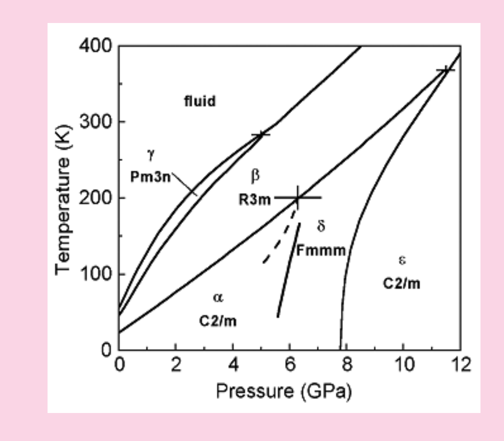

Figure 1. Pressure-temperature phase diagram of solid oxygen at P<12 GPa [2].

Undoubtedly, magnetism should play an important role in these transformations**.** Pressure could change a balance between the intermolecular and magnetic interactions. Under very high pressures, hybridisation between molecular orbitals could lead to a partial suppression of the localized magnetic moments. Finally, before the transition to the superconductive state one might expect a complete magnetic collapse. Even more intriguing, magnetic properties of dense oxygen are directly related to the fundamental properties of the diatomic molecules under pressure. Do they transform directly from a diatomic state to a metallic monoatomic state? Are there any intermediate "polymerised" states? Magnetic properties give a possibility for monitoring of the molecular state. Formation of a "molecular polymer" or multi-atomic molecules X_n (n>2) are expected to break the magnetic order.

Until now there was no any direct information on magnetic order in high-pressure oxygen. Measuring of vibron modes by optical spectroscopy suggested that solid oxygen remain antiferromagnetic up to 7 GPa [3]. No evidence for new magnetic structures was found by the indirect probes and theoretical simulations.

Only neutron diffraction could answer the question about magnetic orderings in high-pressure oxygen. Due to high penetration, relatively low intensity of magnetic peaks and problems of preferable orientation, neutron studies of high-pressure oxygen is a difficult task. At the LLB, we carried out a first neutron diffraction study of magnetic order in solid oxygen under pressures up to 7 GPa [4]. We used the original pressure and neutron setups developed at the LLB and allowing to study magnetic orders under pressures as high as 50 GPa and temperatures as low as 0.1 K. Liquid O_2 was loaded in the pressure cell with anvils made from superhard boron nitride. Neutron diffraction spectra in the temperature range 4-300 K were measured on the specialized high-pressure diffractometer G6.1 "MICRO".

In the region of stability of the α-phase (P<6.2 GPa) we found a remarkable enhancement of magnetic interactions between O_2 molecules. Temperature of transition towards to long-range ordered antiferromagnetic state increases by order of magnitude, from 24 K at P=0 up to 200 K at P=6.2 GPa (T_{LRO}). The disappearance of the magnetic signal exactly coincides with the α-β structural transition. Our results provide a direct confirmation of the magneto-structural origin of the α-β transition in a wide range of interatomic distances.

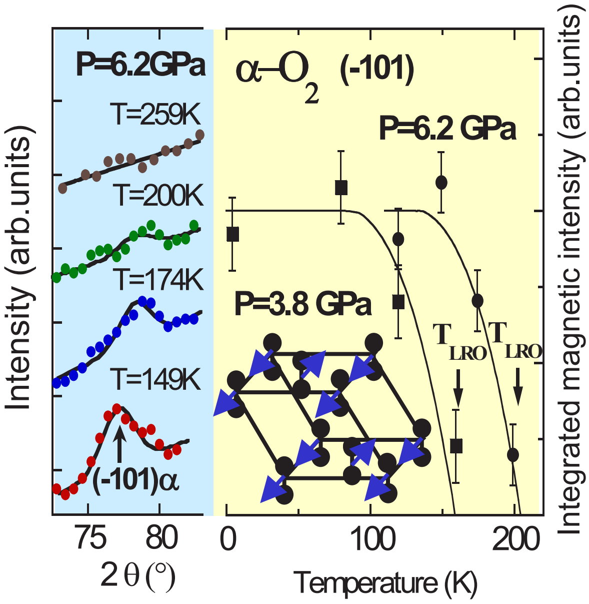

Figure 2 Left: temperature evolution of the magnetic peak (10-1) measured in α-O_2 at P=6.2 GPa. Right: integrated magnetic intensity of the (10-1) peak versus temperature at pressures of 3.8 GPa (squares) and 6.2 GPa (circles). In inset: magnetic structure of α-O_2.

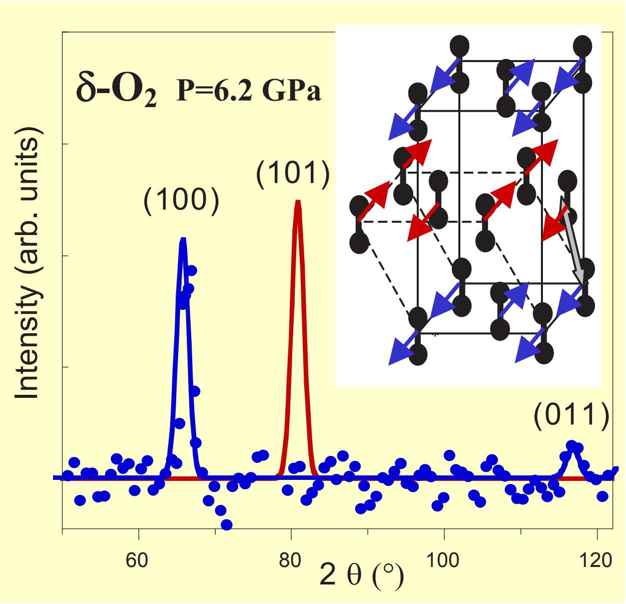

Figure 3. Dots: experimental data on magnetic scattering in δ-O_2 at P=6.2 GPa and T=4 K. Lines: calculated profiles assuming the same type of magnetic structure as in α-O_2 (in red) and new type of magnetic structure shown in inset (in blue).

At P=6.2 GPa we crossed the transition line between the α- and δ- phases. At this pressure and low temperature (<100 K) we observed new diffraction peaks which were not found in previous X-ray measurements and should be attributed to a magnetic order in the δ phase. Surprisingly, the magnetic peaks from α- and δ phases are located at completely different scattering angles. The crystal structures of α- and δ-O_2 are very similar and can be described in 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 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 (Fig. 3). In Fig. 3 we show calculated scattering profiles assuming the same type of order as in the α-phase and new type of order with ferromagnetic stacking of the O_2 plane. The first model completely disagrees with our experiment whereas the later model fits perfectly our data.

The magnetic structure of δ-O_2 is very intriguing. It was not suggested by indirect measurements and it was not found in ab-initio calculations. Especially ferromagnetic coupling between the nearest off-plane neighbours (Fig. 3) is very surprising. Simple quantum considerations suggest negative sign of exchange constant favouring antiparallel spin arrangements. One can think that the interplanar magnetic stackings in the δ-phase is driven by long-range magnetic interactions with second and third off-plane neighbours, which are negligible at P=0. The growing importance of the long-range magnetic interactions should be attributed to a growing delocalisation of the O_2 orbitals under pressure and could be a first sign of a magnetic collapse expected at higher pressures. In conclusion, we show that practically all phase transitions in solid O_2 at pressures P<7 GPa have magneto-structural character. Neutron diffraction study of magnetic order in ε-O_2, now in progress, should clarify how this “spin controlled” molecular crystal transforms into a metallic superconductor

References

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