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Evidence for a Magnetic Collapse in the Epsilon Phase of Solid Oxygen

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Solid oxygen is the only elementary molecular magnet. Under the very high pressure of 96 GPa oxygen transforms into a metal and a superconductor. Theory predicts a nonmagnetic state occurring before the transition into the superconducting ξ phase. Nevertheless, until now there was no direct evidence of a magnetic collapse in high-pressure oxygen. For the first time direct information is provided on magnetic properties of the ε phase, which is sandwiched between the antiferromagnetic δ phase and the superconducting ξ phase. We used magnetic neutron diffraction. The data show that the long-range magnetic order disappears at the δ-ε transition. The magnetic collapse occurs at $P \approx 8$ GPa, far below the pressure of the insulator-metal (superconductor) transition. The collapse is preceded by a decrease in temperature of transition towards the long-range magnetically ordered state (T_{LRO}) in the δ phase, at $P = 7.6$ GPa.

While at ambient pressure solid oxygen is an antiferromagnetic insulator [1–3], under very high pressure it becomes a metal and a superconductor [4,5]. Local magnetic fields destroy Cooper's pairs; therefore, magnetism rarely coexists with superconductivity. One should expect that oxygen loses its magnetic properties before it transforms to the superconductive state. Indeed, the growing hybridization of molecular orbitals under pressure, which leads to the insulator-metal transition, could also destroy the localized magnetic moments. The P-T structural phase diagram of oxygen is shown in the inset of Fig. 1. At low temperature and low pressure ($P < 6$ GPa) oxygen crystallizes in a monoclinic antiferromagnetic α phase [1–3]. The ground state of the O_2 molecule is a triplet, and the molecule carries spin $S = 1$. At high temperatures, the α-O_2 transforms into magnetically disordered (or short-range ordered) rhombohedral β-O_2. At $P \approx 6$ GPa, the α-O_2 phase transforms into an orthorhombic δ-O_2 [6,7]. A recent neutron-diffraction study [8] proved that the δ phase orders in an antiferromagnetic structure, while different from the magnetic structure of α-O_2. At $P \approx 8$ GPa, δ-O_2 transforms into monoclinic ε-O_2 [9,10], which is stable in the wide pressure range $8 < P < 96$ GPa, until it transforms into the superconducting ξ phase [11,12]. The ε phase, sandwiched between the antiferromagnetic δ and the superconducting ξ phases, is probably the most intriguing phase in solid oxygen. First-principles theoretical studies based on the density functional theory (DFT) and the local spin density approximation [13,14] suggest that the magnetic collapse occurs at the ε-ξ transition [13] or somewhere in the range of stability of the ε phase [14], following the band gap closure. In contrast, the most recent DFT study suggests a nonmagnetic insulating ground state in the ε phase [15]. Until now only indirect optical probes were used to characterize the molecular and magnetic states in ε-O_2 [16–21]. The results are quite controversial. Some studies [17–19] suggest that the magnetic collapse might occur at the δ-ε transition or somewhere in the

pressure range 8–20 GPa. In this pressure range, the optical data show strong modifications of the vibrational modes [16–18] and the low-energy electronic excitations [19,20]. These modifications were interpreted [17,19] on the basis of the formation of an O_4 lattice which would have a nonmagnetic singlet ground state. In contrast, in Ref. [21] the Raman modes of the ε and ξ phases were interpreted on the basis of an O_2 lattice, with relatively weak changes in molecular bonding, so there is no consensus on the molecular state in ε-O_2. Analysis of the P-T phase diagram makes the situation even more intriguing. Pressure of the δ-ε transition increases with temperature; therefore, for any constant pressure in the range $8 < P < 12$ GPa the ε phase transforms into the δ phase as temperature increases above some critical value $T_{\varepsilon\text{-}\delta}$. Consequently, the hypothesis that the magnetic collapse occurs at the δ-ε transition should imply a transition from a nonmagnetic low-temperature ground state ($T < T_{\varepsilon\text{-}\delta}$) into a magnetically ordered state ($T > T_{\varepsilon\text{-}\delta}$) at elevated temperatures. While not forbidden from first principles, such "temperature induced" magnetism had been never observed experimentally.

The only direct method to study magnetic ordering in high-pressure oxygen is magnetic neutron diffraction. Recently neutron diffraction in α- and δ-O_2 had been studied up to the pressure of 6.2 GPa [7]. No evidence for a magnetic collapse had been found in this pressure range. Moreover, T_{LRO} increases under pressure from 24 K at $P = 0$ up to 200 K at $P = 6.2$ GPa. In the present study the pressure range in neutron-diffraction studies of solid oxygen was extended up to 9.5 GPa, i.e., to the range of stability of the ε-O_2. Neutron-diffraction experiments on high-pressure oxygen, having weak magnetic scattering amplitudes and very high penetrating abilities, are extremely difficult. We used the Kurchatov-Laboratoire Léon Brillouin pressure cell [22]. Liquid oxygen was loaded at 77 K. About 0.5 mm³ of oxygen was sealed between two opposite anvils made from cubic boron ni-
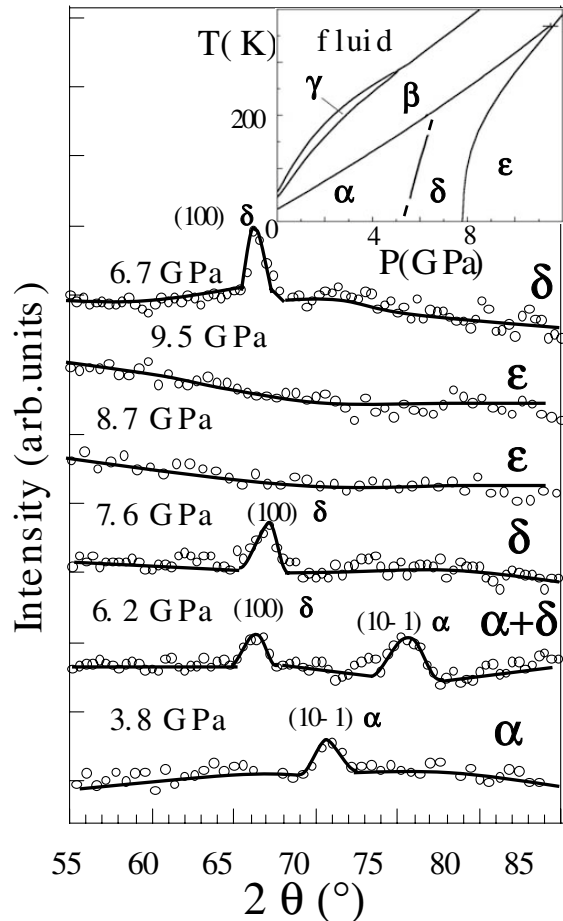
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FIG. 1. Magnetic neutron-diffraction patterns measured at the lowest temperatures 1.5–4 K and different pressures. In order to separate magnetic and structural contributions, spectra measured in the paramagnetic range ($T > T_{\alpha,\delta-\beta}$) were subtracted from the low-temperature data. Inset: the P-T structural phase diagram of solid oxygen derived from x-ray data [7].

tride. For each pressure, we collected several diffraction patterns at different temperatures $1.5 < T < 300$ K. Pressure was monitored by measuring the diffraction lines from a small piece of NaCl placed into the sample volume, similar to the procedure described in Ref. [8]. Accuracy of the pressure measurement is estimated to be ± 0.2 GPa. Variations of pressure with temperature were also within ± 0.2 GPa. Neutron data were collected on the G6.1 high-pressure diffractometer installed on the ORPHEE reactor of the Laboratoire Léon Brillouin [23,24]. The neutron beam was focused to the sample by special focusing systems.

In Fig. 1 we show magnetic neutron-diffraction patterns obtained at different pressures. The spectra collected in the temperature range 1.5–4.5 K were subtracted from the spectra measured in the paramagnetic range. At $P = 3.8$ GPa the same α type of magnetic ordering as at ambient pressure was observed. At $P = 6.2$ GPa, a new

magnetic peak appears which is associated with the δ type of magnetic ordering. The α- and δ-magnetic orderings are similar except the interplanar coupling between the antiferromagnetic O_2 planes. While in the α phase the nearest interplanar neighbors are antiferromagnetic, in the δ phase they are ferromagnetic [8]. At $P = 7.6$ GPa, the α ordering disappears completely and we observe only δ ordering. At higher pressures $P \geq 8$ GPa the sample transforms into the ε phase. The structural transition is accompanied by a drastic change in the magnetic scattering. At $P = 8.7$ ($T = 4$ K) and 9.5 GPa ($T = 1.5$ K) we did not observe *any* magnetic diffraction peaks. In this pressure range, diffraction patterns show only a smooth background. When pressure was released from 8.7 to 6.7 GPa, the sample recovered long-range magnetic ordering (Fig. 1). In order to confirm the reproducibility of our results we made two experimental runs with two different samples. They give similar results. Theoretical calculations [14] suggest a noncollinear triangular magnetic structure in the ε phase. Nevertheless, such a noncollinear magnetic structure is incompatible with the present study since it should give magnetic peaks on neutron-diffraction pattern [namely $(1/3, 1/3, 0)$ and $(1/3, 1/3, 1)$ reflections] which were not observed experimentally. In Fig. 2 we show more details on neutron-diffraction data collected at $P = 8.7$ GPa. In the inset to Fig. 2 we show the temperature evolution of the structural peak $(002)/(001)$ (indices are given in the orthorhombic/monoclinic unit cell). As temperature decreases,
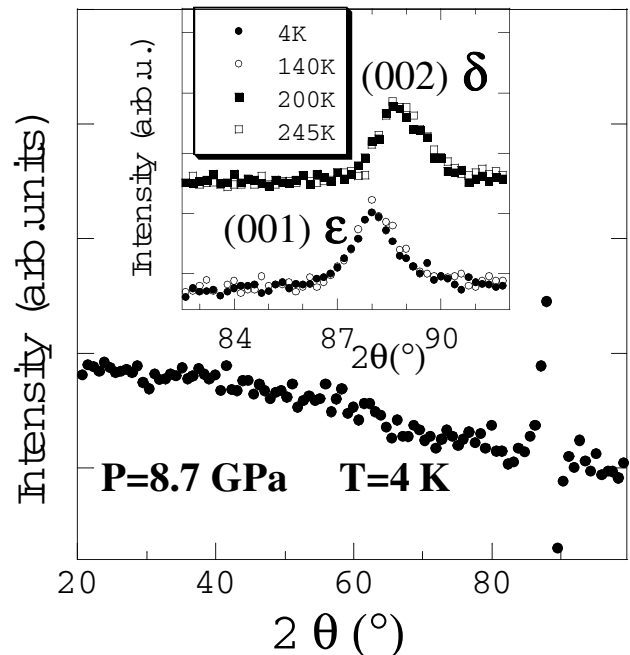

FIG. 2. Magnetic neutron scattering at $P = 8.7$ GPa and $T = 4$ K. Spectra measured in the paramagnetic range ($T > 250$ K) were subtracted from the low-temperature data. Inset: evolution of the structural peak $(002)/(001)$ in the δ/ε phase with temperature.

the sample crosses the δ-ε phase line on the P-T diagram. The phase transition is evidenced by a sudden displacement of the structural peak, associated with the monoclinic distortion of the unit cell. The magnetic neutron-diffraction pattern, measured at $T = 4$ K in the wide range of d spacings $2.7 < d < 27$ Å and subtracted from the paramagnetic spectra measured in the temperature range $T > 250$ K, does not show any magnetic peaks. The anomaly at $2\theta \approx 88°$ arises from the subtraction of the temperature dependent $(001)/(002)$ structural reflection. We conclude that the ε phase has no long-range magnetic order.

In Fig. 3 data on temperature evolution of magnetic peaks in δ-O_2 ($P = 6.2$ and 7.6 GPa) are shown. In the whole pressure range $P < 6.2$ GPa, T_{LRO} increases with pressure, from 24 K at $P = 0$ up to 200 K at $P = 6.2$ GPa. Surprisingly, at 7.6 GPa the magnetic order occurs at lower temperature (150 K) than at 6.2 GPa. While in the pressure range $P < 6.2$ GPa the long-range magnetic ordering occurs at the same temperature as the structural transition from the high-temperature rhombohedral β phase to the low-temperature α and δ phases ($T_{\alpha,\delta\text{-}\beta}$), at $P = 7.6$ GPa the magnetic and structural transitions are decoupled. At 7.6 GPa, T_{LRO} is lower by about 80 K than the temperature of the δ-β transition (which is about 230 K at this pressure). One should conclude that the δ phase exists in two different modifications: the low-temperature magnetic modification (δ-I) and the high-temperature nonmagnetic or magnetically disordered modification (δ-II). The two phases have essentially the same orthorhombic crystal structure. We cannot exclude the presence of short-range magnetic correlations (static or dynamic) in the ε- and δ-II phases. On neutron-diffraction patterns, such correlations would give only broad diffuse peaks, which cannot be separated from the experimental background. The upper limit for ordered magnetic moment in the ε- and δ-II phases is estimated to be $0.5\mu_B$ (compared to $2\mu_B$ at $P = 0$).
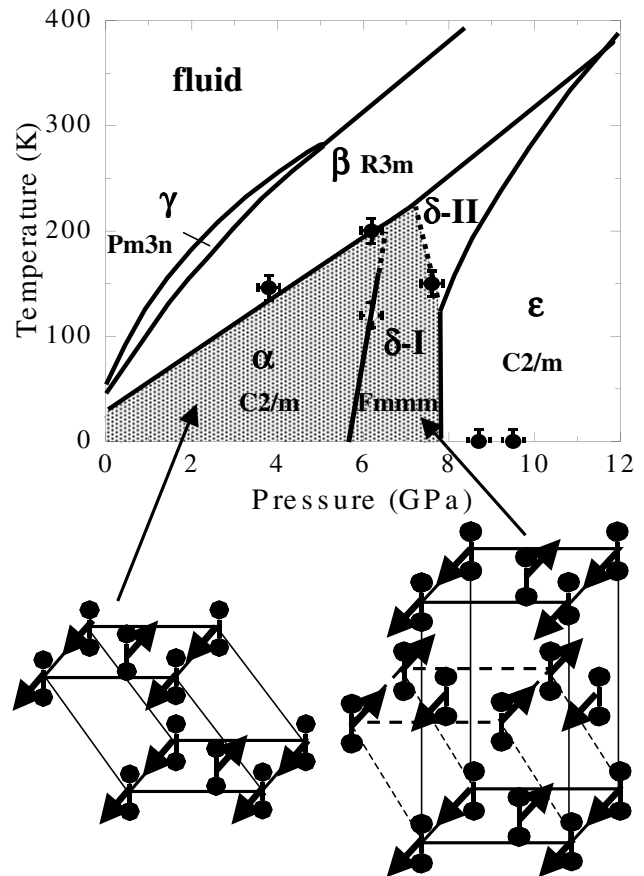
FIG. 4.   Magnetostructural P-T phase diagram of oxygen, based on the neutron measurements (Ref. [8] and the present study), the optical, and the x-ray experiments [6,7,10]. The space groups correspond to crystal structures and do not include magnetic symmetry. The shadowed area and unshadowed areas correspond to long-range magnetic ordering and the nonmagnetic or short-range ordered state, respectively. Filled circles: experimentally measured values of temperature of long-range magnetic ordering (T_{LRO}). Open circle: temperature of transition from the α to δ type of magnetic order. The dotted phase lines are extrapolations from the values measured at 6.2 and 7.6 GPa; they were drawn taking into account the optical data measured at $P = 7$ GPa [25]. At the bottom of the figure we show magnetic structures in the α and δ-I phases from Ref. [8].
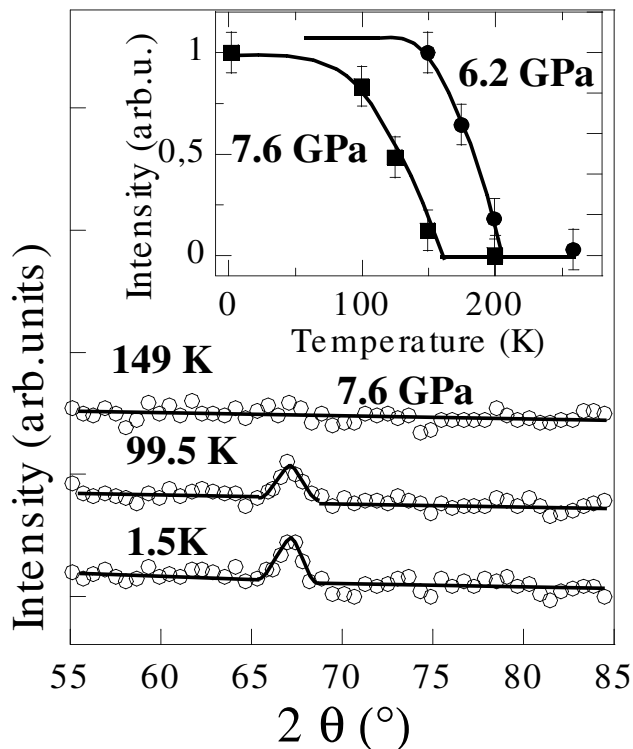

FIG. 3.   Temperature evolution of magnetic neutron scattering at $P = 7.6$ GPa. Inset: integrated magnetic intensities of the (10-1) and (100) in the α phase at $P = 6.2$ GPa and the δ phase at $P = 7.6$ GPa, respectively, versus temperature.

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Our data provide a consistent picture of magnetic phenomena in high-pressure oxygen (Fig. 4). In the low-pressure range $P < 7$ GPa the molecular magnetic moments are stable and, as pressure increases, the growing exchange between the molecules favors higher values of T_{LRO}. This is in agreement with the data provided by indirect optical probes [19,25]. In the pressure range $7 < P < 8$ GPa, the magnetic sublattice shows the first signs of instability. T_{LRO} decreases and the magnetic and structural transitions decouple. At higher pressures $P > 8$ GPa the long-range magnetic order disappears completely and oxygen transforms into the ε phase. The fact that the δ phase exists in the magnetically ordered (δ-I) and nonmagnetic or magnetically disordered (δ-II) modifications removes the contradiction discussed above between a nonmagnetic ground state (ε phase, $T < T_{\delta\text{-}\varepsilon}$) and the magnetically ordered state which might occur at elevated temperatures in the pressure range $8 < P < 12$ GPa (δ phase, $T_{\delta\text{-}\varepsilon} < T < T_{\delta\text{-}\beta}$). Actually, as the temperature increases, the nonmagnetic ε phase transforms not into the magnetic δ-I phase, but into the nonmagnetic δ-II phase (see Fig. 4), which poses no problem for theory.

The magnetic breakdown occurs at pressures by order of magnitude lower than the pressure of the insulator-metal transition (96 GPa). While being in contradiction with the earlier theoretical works [13,14], this result is in a good agreement with the optical data, suggesting an O_4 singlet ground state in the ε phase [17,19] and the most recent DFT calculations [15]. The DFT calculations suggest formation of herringbone-type chains of O_2 molecules in the ε phase. The strong electronic hybridization inside the chains can suppress the local magnetic moments. Indeed, total energies calculated for spin- and nonspin polarized models were found to be essentially the same; therefore, the ε phase was claimed to be nonmagnetic [15]. The presented data require one to reexamine the common point of view on magnetostructural phenomena in solid oxygen. In the α, δ, and ε phases, the O_2 lattice is distorted within the a, b planes regarding an ideal triangular lattice ($b/a = 0.68$–0.71 in the pressure range $6 < P < 10$ GPa, to be compared with $b/a = 0.577$ in the triangular lattice). The distortion was commonly assigned to an influence of the magnetic interactions. In a nondistorted triangular lattice, no spin arrangement can satisfy first-neighbor antiferromagnetic interactions. Through the distortion, the system gains some exchange energy in a long-range-ordered magnetic structure. Nevertheless, the fact that the O_2 lattice remains distorted in the ε- and δ-II phases having no long-range magnetic order requires an alternative explanation for the anisotropy in the (a, b) plane. Such explanation can be probably provided on the basis of Ref. [15] which suggests anisotropic molecular bonding in the (a, b) plane in a nonmagnetic ground state under pressure.

In conclusion, we show that the magnetic properties of solid oxygen undergo profound modifications in the pressure range $6 < P < 8$ GPa. These modifications result in a complete breakdown of the long-range antiferromagnetic order at $P \approx 8$ GPa. In agreement with the most recent first-principles theoretical study [15], the present work shows that the antiferromagnetic and metallic ground states in solid oxygen are separated by a vast pressure range $8 < P < 96$ GPa.

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