Pressure-Induced Magnetic Collapse and Metallization of Molecular Oxygen: The ζ-O_2 Phase

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The behavior of solid oxygen in the pressure range between 5–116 GPa studied with *ab initio* simulations, shows a spontaneous phase transformation from the antiferromagnetic insulating δ-O_2 phase to a nonmagnetic, metallic molecular phase. The calculated static structure factor of this phase is in excellent agreement with x-ray diffraction data in the metallic ζ-O_2 phase above 96 GPa. We thus propose that ζ-O_2 should be base centered monoclinic with space group $C2/m$ and four molecules per cell, suggesting a reindexing of the experimental diffraction peaks. Physical constraints on the intermediate-pressure ϵ-O_2 phase are also obtained. [S0031-9007(98)06326-1]

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The high-pressure behavior of simple molecular systems (H_2, N_2, I_2, and O_2) has recently attracted special interest, as it can shed light on fundamental aspects of the pressure effects on chemical bonding (molecular dissociation, metallization, etc.), and is now amenable to study with high brilliance x-ray synchrotron sources. Among the simple molecular systems studied so far, solid oxygen has the unique property of retaining molecular magnetism up to relatively high pressures. The ground state of the free O_2 molecule has two unpaired electrons in the doubly degenerate π^* level, requiring by Hund's rule a spin-1 $^3\Sigma_g$ ground state. Magnetism persists in the condensed phases of O_2 and complicates considerably its phase diagram. Solid oxygen is expected to be an antiferromagnetic Mott-Hubbard insulator at low pressures, because of the strong intramolecular Coulomb repulsion ($U \sim 10$ eV) within the π^* state. Magnetism in the low-pressure phases α, β, and γ can thus be phenomenologically modeled by simply adding a Heisenberg-type interaction between neighboring molecules [1]. With increasing pressure, however, electron hopping and band formation will finally lead to a nonmagnetic metallic state, a transition expected when the bandwidth is of the order of U.

Experimentally, solid O_2 has been studied up to a pressure of 130 GPa. The monoclinic α-O_2 phase (space group $C2/m$) at low pressures and temperatures is, as discussed, an insulating (collinear) antiferromagnet. At about 3 GPa, α-O_2 transforms to orthorhombic δ-O_2 (space group $Fmmm$), also insulating and also believed to be antiferromagnetic [2], although by indirect evidence. The stability range of δ-O_2 extends up to nearly 10 GPa, where it transforms into a third insulating phase, ϵ-O_2, with a sizeable decrease in volume ($\Delta V/V \sim 6\%$ at the transition). X-ray diffraction [3] has suggested that ϵ-O_2 could be monoclinic (space group $A2/m$) with eight molecules per cell, but an orthorhombic unit cell with four molecules has also been proposed [4] (in either case, the relative positions of the molecules in the cell were not determined). Optical absorption [2] in ϵ-O_2 indicates a shrinking gap, and indirectly suggests that a magnetic moment might still be present, but the ordering is unclear. Finally, at a pressure of 96 GPa, ϵ-O_2 transforms to the metallic phase ζ-O_2 [5]. The similarity between the x-ray diffraction profiles of ϵ-O_2 and of ζ-O_2, and the small volume change ($\Delta V/V \sim 1.4\%$), suggests that ϵ-$O_2 \rightarrow \zeta$-O_2 might be a weak isostructural transformation [5], with minor lattice changes. By contrast, near-infrared reflectivity [6], Raman [7], and, more recently, evidence for metallic conduction and even for superconductivity [8] indicate that the transition is accompanied by major electronic changes. Metallization of O_2 at high density has recently been discussed theoretically [9], based, however, on a rather unrealistic rescaling of the zero-pressure α-O_2 structure, with no attempt to obtain the new structure.

We have undertaken *ab initio* deformable-cell molecular dynamics (MD) simulations [10], proven to be effective in the study of structural transformations among crystalline phases in a variety of systems [11]. General details on the method can be found elsewhere [10]. In order to deal with magnetism in oxygen, we have extended the calculations to include spin within the local spin density approximation (LSDA). Strongly correlated systems, such as Mott-Hubbard insulators, are not generally tractable in this approximation, where the insulating gap is strictly tied to magnetic long range order. This inadequacy is expected to be much less serious at very high pressures, where band behavior should eventually apply. Recently, LSDA has been used to describe the magnetic collapse of transition metal oxides (also Mott-Hubbard insulators in normal conditions) at very high pressures [12]. We used LSDA with Becke-Perdew gradient corrections [13], a fully nonlocal [14] pseudopotential [15], and a plane wave cutoff of 80 Ry.

We first studied the isolated O_2 molecule, and found the correct $^3\Sigma_g$ ground state, with a very good bond length of 2.30 a.u. (expt. 2.29 a.u.). Omitting α-O_2, which is well understood (and whose low density would imply an extremely large basis set), our MD simulations of solid oxygen were carried out starting from the δ-O_2 phase at a pressure of 7 GPa. We used an orthorhombic simulation box with eight molecules, a time step of 0.24 fs, and Γ point sampling of the Brillouin zone. Further refinement of k-point sampling, necessary for a quantitative description of the unknown final phases, is carried out subsequently, as described further below. The system was initially equilibrated at 200 K and 7 GPa for a period of 2 ps. In agreement with experiment, the δ-O_2 phase was found to be stable in this regime. The stable state is antiferromagnetic, with the collinear spin structure shown in Fig. 1(a), and a sublattice magnetization (Fig. 2) of about $0.5\mu_b$/molecule at 200 K (the $T = 0$ value was only slightly higher). A very similar collinear antiferromagnetic order is known for α-O_2. The magnetic order of both α and δ-O_2 can be interpreted as the result of competition between elastic forces, favoring an in-plane triangular lattice of molecules (ratio of the in-plane lattice parameters is $b/a = 0.577$), and antiferromagnetic exchange J, frustrated in that lattice. Partial removal of frustrations is obtained by increasing b/a, whose value in α-O_2 is in fact 0.64. For δ-O_2 we get $b/a \sim 0.8$ at 10 GPa, the rapid increase of J with pressure causing a larger deviation from 0.577. We also obtain the electronic structure of δ-O_2 at 10 GPa, [Fig. 3(a)]. Bands are weakly dispersive, with molecular levels still clearly identifiable. As is well known, LSDA always underestimates the insulating gap, which is in this case $\sim$1 eV, to be compared with the experimental optical value 2.2 eV [2]. The bands are split by magnetic exchange, as levels are in the free molecule. The $\pi \rightarrow \pi^*$ (interband) excitation energy is reduced from 7 eV in the molecule to 4 eV in δ-O_2. We find it further decreasing with pressure, with a rate of about 0.13 eV/GPa. This compares quite well with the redshift for increasing pressures of the ultraviolet broadband observed in δ-O_2 and ϵ-O_2 by Nicol and Syassen [2] of about 0.15 eV/GPa.

From this stable δ-O_2 state we increased the pressure at a rate of about 30 GPa/ps for other 3.5 ps, as shown in Fig. 2. At about 12 GPa, an abrupt collapse of the magnetization occurred (see Fig. 2), followed by a gradual structural transformation into a new orthorhombic phase. The observed transition path had both intraplanar and interplanar components. An interplanar sliding led molecules belonging to different planes into a distorted hcp configuration [Figs. 1(c) and 1(d)]. This new geometry optimizes the packing of molecules at high pressures and appears to reflect the increasing role of interplanar interactions with pressure. The intraplanar displacement was more complex. It finally led to a molecular arrangement [Fig. 1(d)] very similar to the initial one [Fig. 1(a)], however, with an important rescaling of the a and b axes. By analyzing the structure factor, we found it characterized by the emergence of a new (201) peak, absent in the δ-O_2. In Fig. 2 we show the behavior, during the simulation, of the intensity of the (201) peak of the nonmagnetic high-pressure orthorhombic phase. By comparison with the sublattice magnetization, we see that the magnetic collapse is fast, and precedes the structural transformation, which is slow. Thus, the structural transition seems to be driven by magnetic collapse and metallization. Because of this, the new phase obtained is very likely related to the ζ-O_2, and the simulation appears to have skipped the intermediate ϵ-O_2. While for a proper description of the approach to magnetic collapse in the ϵ-O_2 phase an accurate description

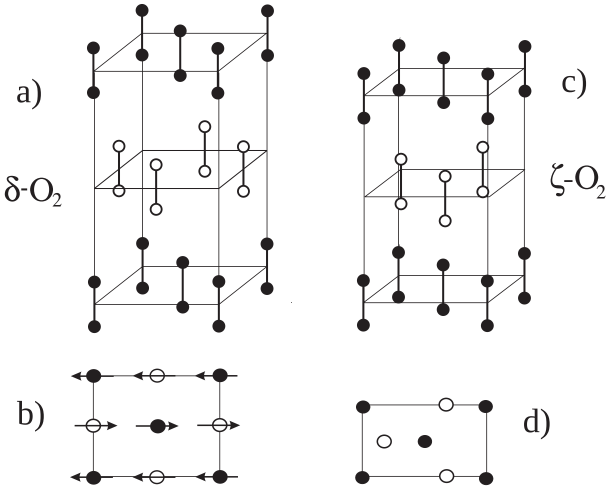

FIG. 1. (a) Side view of the conventional unit cell of the δ-O_2 phase. (b) Top view of the δ-O_2 phase; arrows represent spins structure found in the simulations. (c) Side view of the conventional unit cell of the ζ-O_2 phase. (d) Top view of the ζ-O_2 phase as found in the simulation. Black and white circles denote O atoms in adjacent planes.

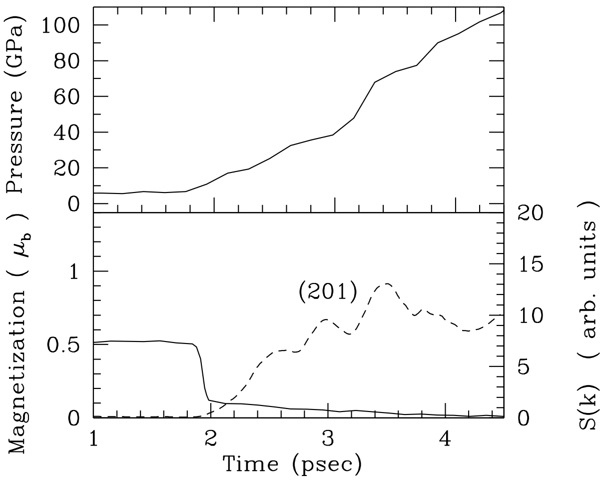

FIG. 2. Upper panel: pressure variation during the simulation. Lower panel: behavior of the magnetization (solid line) and of the intensity of the (201) peak (dashed line) along the simulation. Magnetic collapse occurs at 2 ps, followed by a slow lattice rearrangement.

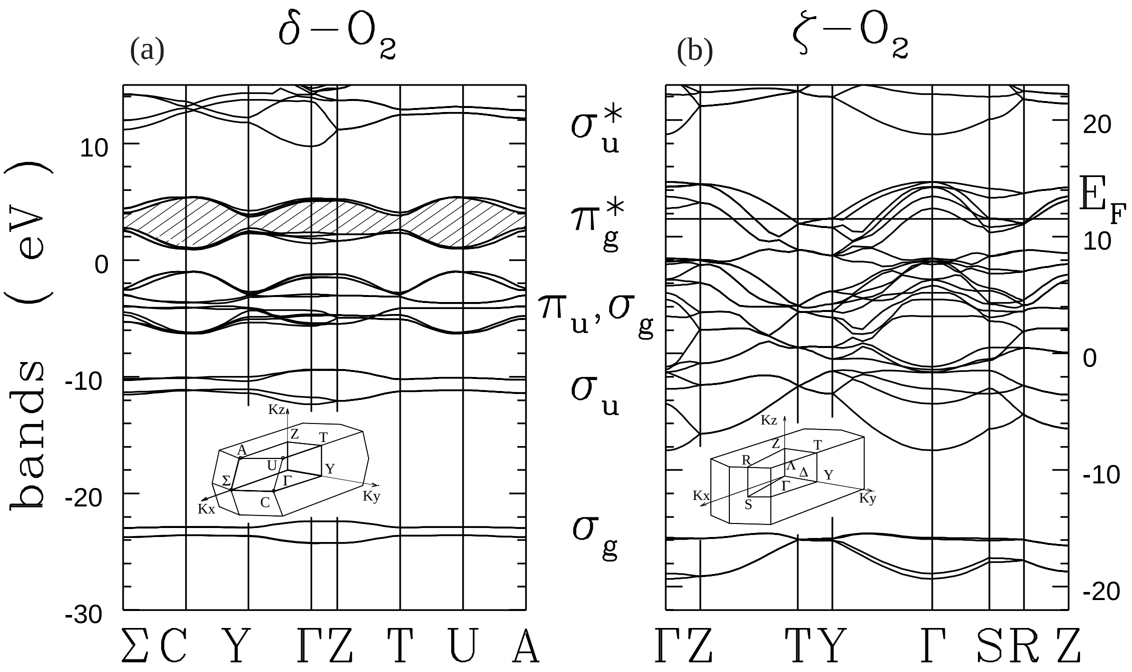

FIG. 3. Band structure of (refined) δ-O_2 at 10 GPa (a) and ζ-O_2 at 116 GPa (b). The band gap of antiferromagnetic δ-O_2 is dashed; paramagnetic ζ-O_2 is fully metallic. Their respective Brillouin zones are shown in the insets.

of this phase is required (a point to be discussed later), we can nonetheless proceed to a full characterization of the ζ-O_2. In order to extract accurate predictions for ζ-O_2, we must refine the simulation results, which are affected by approximations, particularly the Γ point sampling of electronic wave functions, which is too poor for such a small simulation cell.

We then carried out an independent and very accurate optimization of the electronic and crystal structures of the found novel high-pressure metallic O_2 phase. This was done by increasing the number of k points to 216 in the full Brillouin zone. For completeness we also did the same for the insulating δ-O_2. After k-point sampling refinement, we find for δ-O_2 at 10 GPa a cell volume of 12.61 cm^3/mole, against 10.89 cm^3/mole for Γ point only (expt. 12.55 $\text{cm}^3/\text{mole}/\text{mole}$). The critical pressure at which magnetic collapse set in is unaffected by the refinement. The refined structure, shown in Figs. 1(c) and 1(d), possesses a base-centered orthorhombic structure, with four molecules in the conventional unit cell. Its space group is $C2mm$, and the layered structure typical of solid O_2 is preserved. Molecules are still aligned perpendicular to nearly triangular molecular planes, as in α-O_2 and in δ-O_2. The absence of tilting in the nonmagnetic phase confirms previous speculations that quadrupolar interactions in oxygen are negligible [1], but contradicts the earlier hypothesis [16] that tilting is hindered by magnetic interactions.

Similarity of the static form factor calculated for the nonmagnetic phase at 96 GPa, with the experimental data of Akahama *et al.* [5] at the same pressure, is encouraging, and confirms that the nonmagnetic phase found by simulation should be identified with the observed ζ-O_2 phase. The agreement with the experimental data improves further by adding a tiny (up to 4%) monoclinic distortion to our calculated orthorhombic cell (see Table I). Comparison with the x-ray diffraction data of Akahama *et al.* [5] at 116 GPa is shown in Fig. 4. The monoclinic cell of space group $A2/m$ previously proposed by Akahama *et al.* [5] is no longer satisfactory, once the calculated internal structure of the molecules is taken into account. With that cell, we tried different molecular arrangements, requiring for the internal structure the same local coordination of molecules which we calculated to be optimal (in particular, preserving the absence of tilting). We systematically found in this way a structure factor dramatically different from the experimental one. Moreover, the discrepancies remain even when tilting of molecules within the cell (compatible with the $A2/m$ space group) is allowed. Our new base-centered monoclinic cell has $C2/m$ symmetry and only four molecules per unit cell. With our proposed structure, the assignment

TABLE I. Lattice parameters of ζ-O_2 at 116 GPa. The unit cell is monoclinic, and contains four molecules with bond length 2.26 Å (2.292 Å for the δ-O_2 at 10 GPa). Calculated (Calc.) values refer to our results, while distorted (Dist.) values refer to the distortion required to match experimental data.

	a (Å)	b (Å)	c (Å)	α
Dist.	3.56	2.18	5.97	90.5°
Calc.	3.62	2.10	6.11	90°

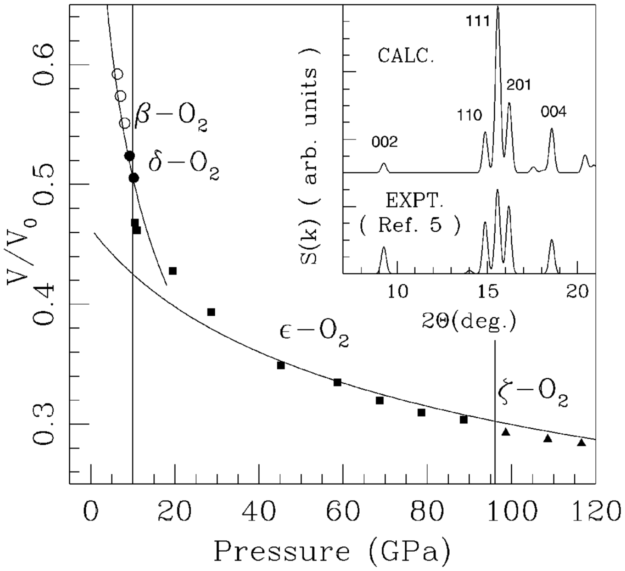

FIG. 4. Relative volume (referred to the molar volume of gas-liquid-solid triple point at 54 K, $V_0 = 24.21$ cm^3) versus pressure as obtained from our k-point converged calculation for δ-O_2 and ζ-O_2. Open circles, solid circles, squares, and triangles concern data of Akahama *et al.* [5] relative to β-O_2, δ-O_2, ϵ-O_2, and ζ-O_2, respectively. Inset: static structure factor of ζ-O_2 at 116 GPa, with our new peak assignment, compared to the experimental data of Akahama *et al.* [5].

of the experimentally observed peaks of Fig. 4 becomes $d(002) = 2.9852$ Å, $d(110) = 1.8601$ Å, $d(111) = 1.7782$ Å, $d(201) = 1.7119$ Å, $d(004) = 1.4925$ Å.

We now focus on the electronic structure of ζ-O_2 at 116 GPa, shown in Fig. 3(b). Bands are now considerably broader, with significant mixing of different molecular orbitals. At 100 GPa the original σp, π, and π^* states are completely hybridized, and the gap between the π and π^* orbitals has disappeared. The insulating gap within the π^* band characteristic of the low-pressure phase has collapsed along with magnetism. The metallic behavior is in agreement with the observed Drude-type reflectivity of ζ-O_2 at these pressures [6] and with the recent observation of a jump in the static conductivity across the $\epsilon \rightarrow \zeta$ transition [8]. Good agreement is also found between calculated and experimental pressure-volume curve (Fig. 4) below 12 GPa, i.e., within the stability domain of δ-O_2, and above 96 GPa, where ζ-O_2 becomes stable.

We are presently missing a description of ϵ-O_2 , stable at intermediate pressures, since in our simulations δ-O_2 prematurely transformed directly to ζ-O_2. This could perhaps be attributed to an overestimate of the binding energy of the metallic phase relative to the magnetic insulator, a typical weakness of the LSDA. There is, however, a more interesting possibility. Let us assume, as suggested by experiment, ϵ-O_2 to be essentially isostructural with ζ-O_2. If this were the case, then, reinterpreting the ϵ-O_2 x-ray diffraction data with our proposed monoclinic cell, we find an in-plane b/a ratio of 0.61, that is much closer to the "triangular" value in ϵ-O_2 than it was in δ-O_2. We might thus speculate that collinear antiferromagnetism is, in ϵ-O_2, strongly frustrated by the triangular in-plane structure. In a triangular Heisenberg lattice, the ground state has a different magnetic long range order, based on three sublattices with moments at 120°, a noncollinear spin configuration. By construction, noncollinear spin configurations are not allowed by our present LSDA calculations. We plan to verify in the near future whether inclusion of noncollinearity could possibly explain ϵ-O_2, as we now conjecture, or not.

In conclusion, we have obtained fresh theoretical insight into the high-pressure phases of solid O_2. In particular, we present the first qualitative and quantitative proposal for the structure and the electronic properties of the recently discovered metallic ζ-O_2 phase above 96 GPa.

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