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PRESSURE-INDUCED MAGNETIC COLLAPSE
AND METALLIZATION OF MOLECULAR OXYGEN:
THE ζ-O$_2$ PHASE

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Abstract

The behaviour of solid oxygen in the pressure range between 5-116 GPa is studied by *ab-initio* simulations, showing a spontaneous phase transformation from the antiferromagnetic insulating $\delta - O_2$ phase to a non-magnetic, metallic molecular phase. The calculated static structure factor of this phase is in excellent agreement with X-ray diffraction data in the metallic $\zeta - O_2$ phase above 96 GPa. We thus propose that $\zeta - O_2$ should be base centered monoclinic with space group C2/m and 4 molecules per cell, suggesting a re-indexing of the experimental diffraction peaks. Physical constraints on the intermediate-pressure $\epsilon - O_2$ phase are also obtained.

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The high pressure behavior of simple molecular systems (H_2, N_2, I_2 and O_2) has recently attracted a 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 in comparison with other simple molecular systems. Crudely, solid oxygen is expected to be an antiferromagnetic Mott-Hubbard insulator at low pressures, because of the strong intra-molecular 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, increases in electron hopping and band formation will finally lead to a non-magnetic metallic state, a transition expected when the bandwidth W is of the order of U.

Experimentally, solid O_2 has been studied up to a pressure of 130 GPa. The monoclinic $\alpha - O_2$ phase (space group $C2/m$) at low pressures and temperatures is, as discussed, an insulating (collinear) antiferromagnet. At about 3 GPa $\alpha - O_2$ transforms to orthorhombic $\delta - O_2$ (space group $Fmmm$), also insulating, and also believed to be antiferromagnetic[2], although by indirect evidence. The stability range of $\delta - O_2$ extends up to nearly 10 GPa where it transforms into a third insulating phase, $\epsilon - O_2$, with a sizeable decrease in volume ($\Delta V/V \sim 6\%$ at the transition). X-ray diffraction[3] has suggested that $\epsilon - O_2$ could be monoclinic (space group $A2/m$) with 8 molecules per cell, but an orthorhombic unit cell with 4 molecules has also been proposed[4] (in either cases, the relative positions of the molecules in the cell were not determined). Optical absorption[2] in $\epsilon - O_2$ 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, $\epsilon - O_2$ transforms to the metallic phase $\zeta - O_2$[5]. The similarity between the X-ray diffraction profiles of $\epsilon - O_2$

and of $\zeta - O_2$, and the small volume change ($\Delta V/V \sim 1.4\%$) suggest that $\epsilon - O_2 \rightarrow \zeta - O_2$ 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, including metallization. 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.

Our goal is a comprehensive description of the evolution of structural, electronic, and magnetic properties of O_2 at high pressure, in particular, of the mechanism underlying the observed insulator to metal transition. 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)[12] with gradient corrections (GC) to the exchange correlation potential. 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. However, this inadequacy is expected to be much less serious at very high pressures, where band behavior should eventually apply. Recently, LSDA+GC has been used to describe the magnetic collapse of transition metal oxides, (also Mott-Hubbard insulators in normal conditions) at very high pressures[13]. We used LSDA with Becke-Perdew GC[14] and a pseudopotential description of the electron-ion interaction within the Kleinman-Bylander scheme[15], and Troullier-Martins pseudopotentials[16] with $E_{cut} = 80$ 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 $\alpha - O_2$ 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 $\delta - O_2$ phase at a pressure of 7 GPa. We used an orthorhombic simulation box with 8 molecules/box, a time step of 0.24 fs and Γ point sampling of the Brillouin Zone. 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.
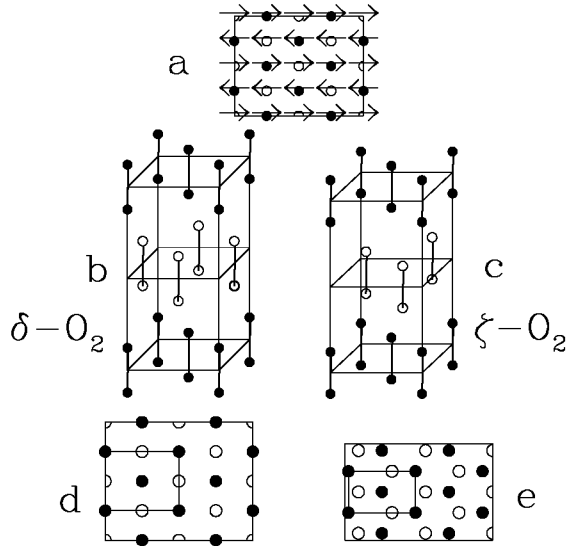

FIG. 1. a): Top view of the $\delta - O_2$ phase, arrows represent spins structure found in the simulations. b): side view of the conventional unit cell of the $\delta - O_2$ phase. c): side view of the conventional unit cell of the $\zeta - O_2$ phase. d): Top view of the $\delta - O_2$. Conventional orthorombic cell is also shown. e): Top view of the $\zeta - O_2$ phase as found in the simulation. Black and white circles denote O atoms in adjacent planes.

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 μ_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 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. 3a). 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
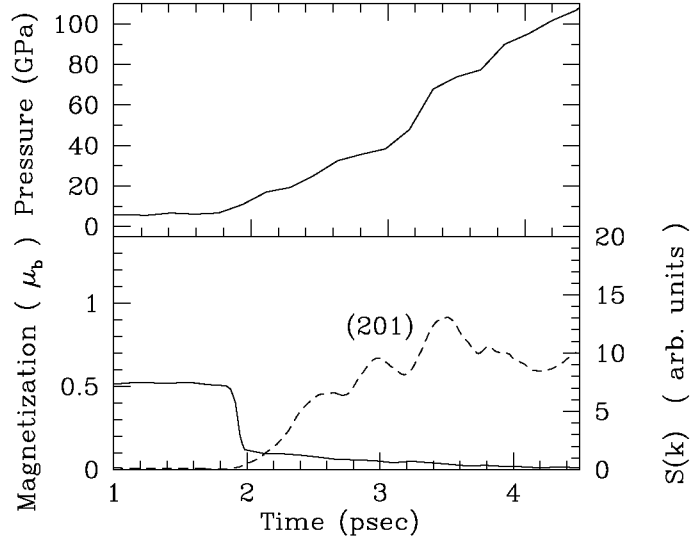
optical value, 2.2 eV.

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

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 red shift for increasing pressures of the ultraviolet broad band observed in $\delta - O_2$ and $\epsilon - O_2$ by Nicol and Syassen[2], of about 0.15 eV/GPa.

From this stable δ-O_2 state we increased the pressure at a constant rate of 32 GPa/ps for other 3.5 ps. At about 12 GPa, an abrupt collapse of the magnetization occurred, 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. 1c,e). 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. 1e) very similar to the initial one (Fig. 1d), however with an important rescaling of the a and b axes. By analysing the structure factor, we found that it is characterized

by the emergence of a new (201) peak, absent in the $\delta - O_2$. In Fig. 2 we show the behavior during the simulation, of the intensity of the (201) peak of the non-magnetic 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 $\zeta - O_2$, and the simulation appears to have skipped the intermediate $\epsilon - O_2$ (a point to be discussed later). In order to extract accurate predictions for $\zeta - O_2$, we must define
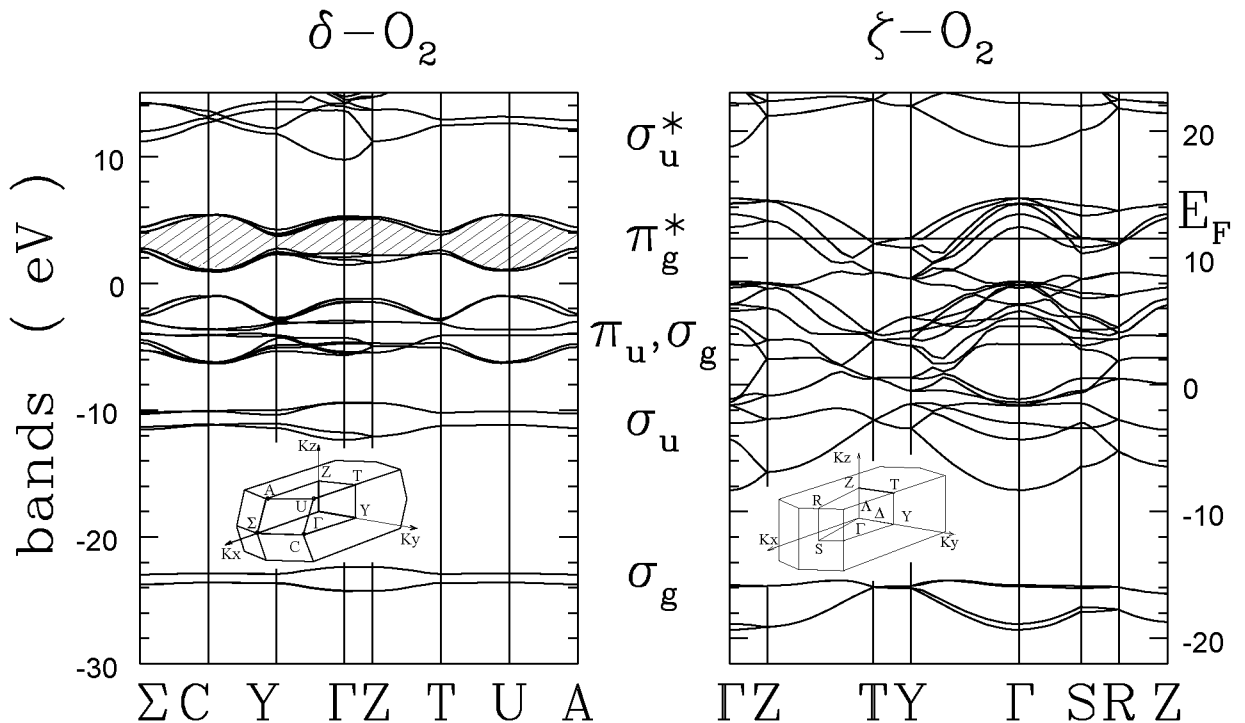

FIG. 3. Bands structure of δ-O_2 at 10 GPa and of ζ-O_2 at 116 GPa. The band gap of antiferromagnetic δ-O_2 is dashed; paramagnetic ζ-O_2 is fully metallic. Their respective Brillouin Zones are shown in the insets.

the simulation results, which are affected by approximations, particularly the Γ point sampling of electronic wave functions, which is too wide 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 zone Brillouin Zone. For completeness we also did the same for the insulating $\delta - O_2$. Apart for a rescaling of volumes and pressures, and removal of minor residual distorsions induced by the dynamics, the magnetic and structural properties of the two phases were not significantly altered. In particular, the optimal high pressure paramagnetic metal possesses a based centered orthorhombic structure, with 4 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 non magnetic phase confirms previous speculations that quadrupolar interactions in oxygen are negligible[1], but contradicts the hypothesis by Freiman et al.[17] that tilting is hindered by magnetic interactions.

Similarity of the static form factor calculated for the non-magnetic phase at 96 GPa, with the experimental data of Akahama et al.[5] at the same pressure is encouraging, and confirms that the non magnetic phase found by simulation should be identified with the observed ζ-O_2 phase.
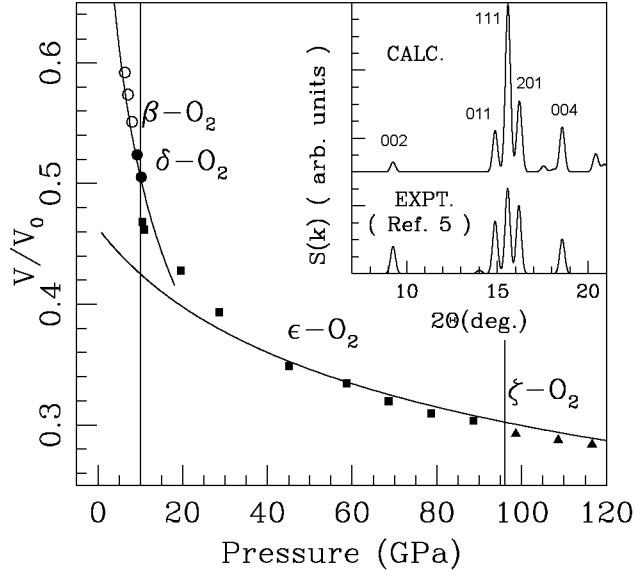
FIG. 4. Relative volume (referred to the molar volume of gas-liquid-solid triple point at 54 K, $V_0 = 24.21$ cm^3) versus pressure as obtained from our k-converged calculation for δ-O$_2$ and ζ-O$_2$. Open circles, full circles, squares and triangles concern data of Akahama et al.[5] relative to β-O$_2$, 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].

The agreement with the experimental data improves further by adding a tiny monoclinic distortion to our calculated orthorhombic cell. Comparison with the X-ray diffraction data of Akahama et al.[5] at 116 GPa is shown in Fig.4. The best agreement with their data has been obtained using the values of the lattice parameters reported in Table I. The distorted parameters differ at most by 4% from the calculated ones, the difference being probably due to the intrinsic limitations of the LSDA. 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) are allowed. Our new base-centered monoclinic cell has the same space group of that of Akahama, $C2/m$,

but only four molecules per unit cell. With our proposed structure, the assignment of the experimentally observed peaks of Fig. 4 becomes $d(002) = 2.9852$ Å, $d(011) = 1.8601$ 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. 3b. 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 pressures phase has collapsed along with magnetism. The metallic behaviour 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 $\epsilon \to \zeta$ transition. 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 $\zeta - O_2$ 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 $\zeta - O_2$. 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.

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

TABLE I. Lattice parameters of ζ-O_2. The unit cell is monoclinic, and contains four molecules. Calculated (Calc.) values refer to our LSDA results, while disorded (Dist.) values refer to the distorsion required to obtain agreement with experimental data.
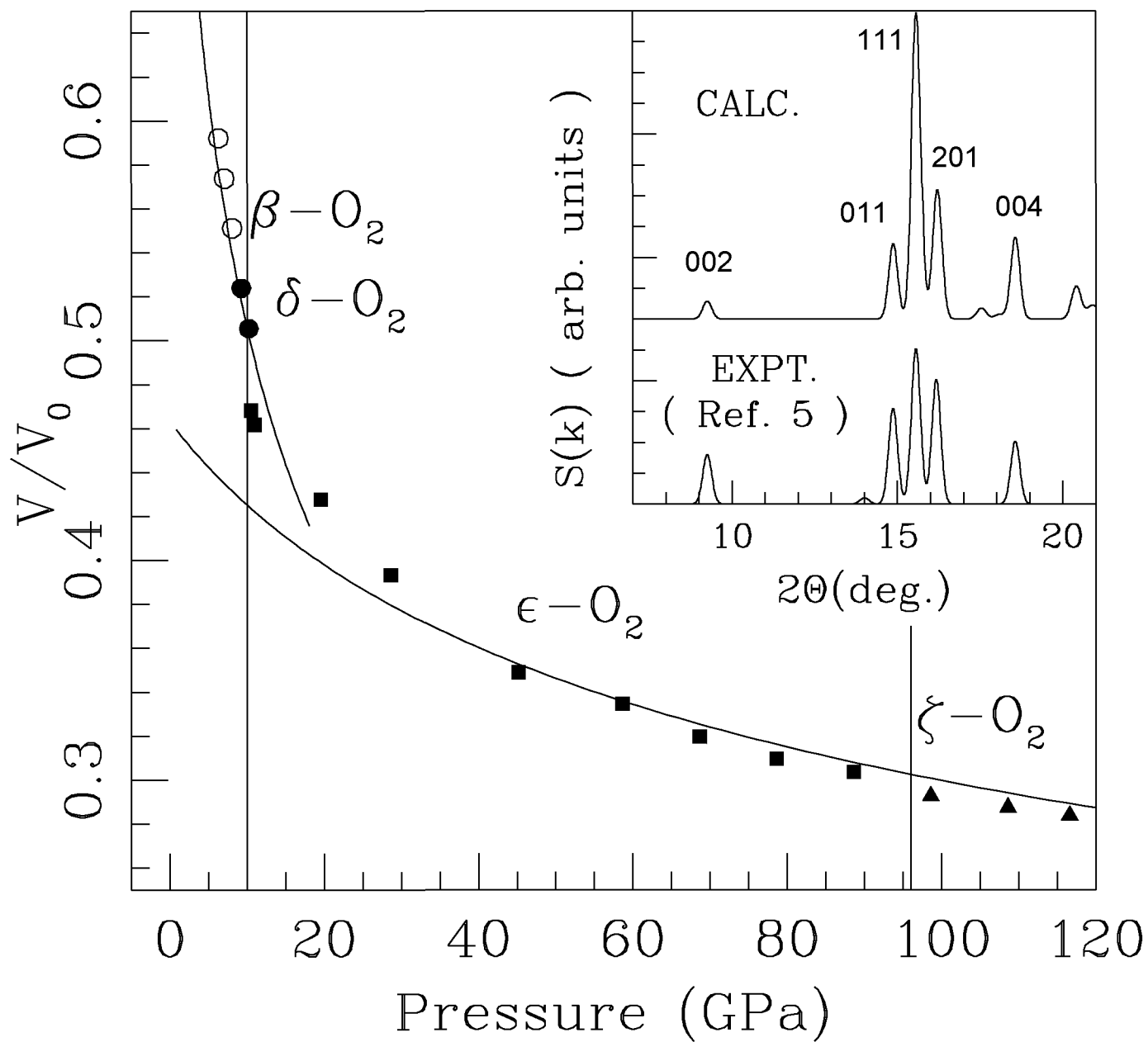
We might thus speculate that collinear anti-ferromagnetism is, in ϵ-O$_2$, strongly frustrated, by the triangular in-plane structure. In a triangular Heisenberg lattice, the ground state has three sublattices with moments at 120 degrees, a non-collinear spin configuration. By construction, non-collinear spins configuration are not allowed by our present LSDA calculations. We plan to verify in the near future whether inclusion of non-collinearity could possibly explain ϵ-O$_2$, as we now conjecture, or not.
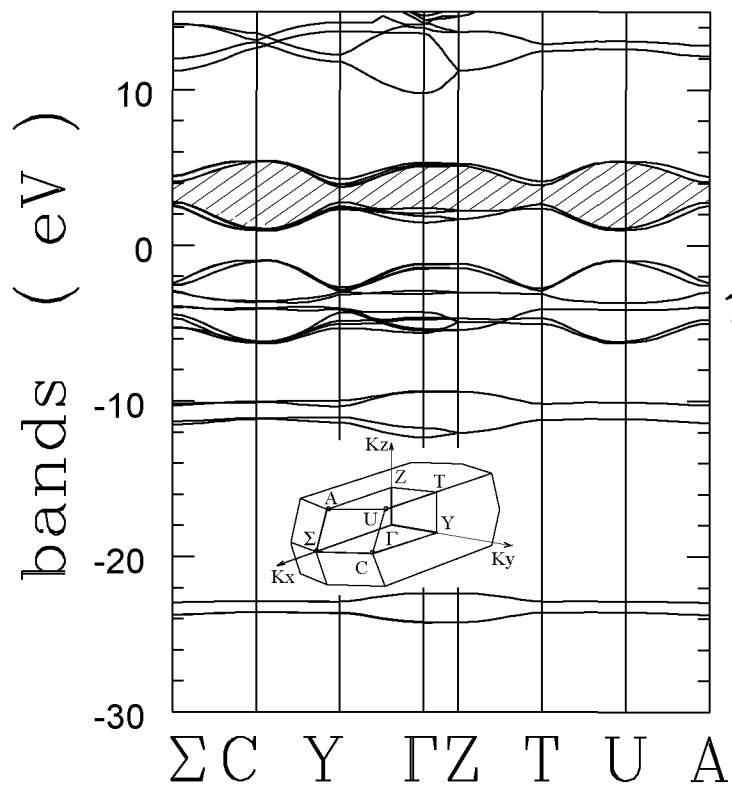
In conclusion, we have obtained fresh theoretical insight into the high pressure phases of solid O$_2$. In particular, we present the first qualitative and quantitative proposal for the structure and the electronic properties of the recently discovered metallic ζ-O$_2$ phase above 96 GPa.

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$\delta - O_2$

$\zeta - O_2$

bands (eV)

σ_u^*

π_g^*

π_u, σ_g

σ_u

σ_g

E_F

Σ C Y Γ Z T U A

Γ Z T Y Γ S R Z

a

b

$\delta - O_2$

c

$\zeta - O_2$

d

e