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Noncolinear spin polarization from frustrated antiferromagnetism: A possible scenario for molecular oxygen at high pressure

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We perform density-functional calculations of the magnetic properties of a simplified structure aimed at capturing some of the features of the elusive ϵ phase of molecular oxygen at high pressure. Starting with the δ phase—which is a quasi-two-dimensional distorted triangular arrangement of antiferromagnetically ordered molecules—pressure could decrease the b/a ratio in the basal planes pushing it toward the ideal triangular value of $1/\sqrt{3}$, thus increasing magnetic frustration. We conjecture that when frustration takes over, the magnetic order may turn into a 120° planar spin-spiral structure inside the ϵ phase, until at higher pressures band-overlap metallization suppresses magnetization in the ζ phase. This conjecture is substantiated by calculations that also represent the attempt to apply state-of-the-art pseudopotential techniques to the magnetic properties of a frustrated antiferromagnet.

I. INTRODUCTION

Most magnetic materials are characterized by atomic moments (or electronic spins, in an itinerant picture) all aligned, parallel or antiparallel, to the same direction everywhere in space. A number of notable exceptions to this rule exist, in which the direction of the magnetization varies from point to point in space. Such exceptions include, e.g., spin spirals in the lanthanides and the complex structures occurring in topologically frustrated antiferromagnets.

Density-functional theory (DFT) calculations of noncolinear magnetic structures have been available for more than a decade.[1] Most of these studies, however, rely on some kind of atomic-sphere approximation (ASA) in which different spin quantization axes are chosen within different spheres. The stable magnetic structure is then determined *a posteriori* as the one that minimizes the total energy with respect to the directions of the quantization axes chosen as inputs of the calculation. Although spin colinearity may be broken even within individual atoms by, e.g., spin-orbit effects,[2] the concept that the same direction of magnetization is associated with each atom is physically well motivated, and it has been recently confirmed by calculations on iron clusters performed without requiring ASA.[3] Nevertheless, going beyond the ASA treatment of magnetic noncolinearity is important, because only releasing all prior constraints on the magnetic structure (such as, notably, that on the relative orientation of different quantization axes within different atomic spheres) can DFT calculations display their full predictive power.

In this paper we present a fully unconstrained calculation of the magnetic structure of a topologically frustrated antiferromagnet, following an approach whose bases are conceptually similar to that of Ref. 3. The system we choose to study is a layered triangular arrangement of oxygen molecules aimed at capturing some of the features of the hitherto ill-characterized ϵ phase of molecular oxygen at high pressure.

II. OXYGEN AT HIGH PRESSURE

In the gas phase, the ground state of the O_2 molecule is a triplet, as required by Hund's rule. In solid, and Mott-Hubbard insulating, O_2, at low temperature and moderate pressure, weak electron hopping gives rise to antiferromagnetic intermolecular superexchange, whose magnitude rises considerably with pressure,[4,5] from the zero-pressure value of 5 meV (Ref. 6) to hundreds of meV at tens of GPa.[7] The relevant pre-1990 work on high-pressure phases and magnetism of oxygen is reviewed by Freiman.[8] Antiferromagnetic order is realized in the insulating low-temperature crystalline phase α-O_2,[9] which is stable up to ≈ 1 GPa. With temperature this converts to β-O_2, which is magnetically disordered.

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At low temperature but increasing pressure one obtains, in the range $1<P<8$ GPa another phase, δ-O_2. Even if strictly speaking a direct proof of magnetic order in δ-O_2 is still lacking, there is widespread belief, also supported by calculations,[10] that molecules are still magnetic, and that ordering is again colinear antiferromagnetic. Molecules in δ-O_2 are arranged in layers, with the molecular axis normal to the layer, and a planar arrangement inside each layer, which is elongated triangular, with a b/a ratio of about 0.70, substantially larger than the ideal triangular value of $1/\sqrt{3}\approx 0.577$. In analogy with many other similar systems, it is precisely this deviation of the planar structure from triangularity that makes antiferromagnetic spin order possible in δ-O_2, by removing frustration.[8,11] This conjecture is further supported by the observation that in β-O_2—obtained by heating either δ-O_2 or α-O_2—and where magnetic order is thermally lifted, the ideal triangular structure is recovered. At much higher pressures, $P>96$ GPa,[12] a new molecular, metallic structure[13,14] state is reached, ζ-O_2. For this state, which is believed to be nonmagnetic, we previously optimized a structure[10] whose b/a ratio is 0.58, again close to perfectly triangular. Hence, there appears to be a close connection between structural elongation in the planes, causing a deviation from triangularity, and colinear magnetic order.

Sandwiched between δ-O_2 and ζ-O_2 (i.e., for $8<P<96$ GPa) there is yet another, much more elusive and intriguing phase, namely, ϵ-O_2.[15] Optical data[16] indicate that ϵ-O_2 is still insulating, and also suggest indirectly that it is probably still magnetic, like δ-O_2, and unlike ζ-O_2. X-ray diffraction suggests a sizable ($\sim 8\%$) volume change between δ-O_2 and ϵ-O_2 at 10 GPa and room temperature,[17] and only a minor one ($<0.3\%$) between ϵ-O_2 and ζ-O_2 at 96 GPa,[12] indicating that ϵ-O_2 may be structurally closer (or even isostructural[12]) to ζ-O_2 than to δ-O_2. There are also other features of ϵ-O_2, such as a high infrared (IR) activity,[18] which further indicate a large unit cell, and which we shall not concern ourselves with at this stage.

Even without that complication, the relationship between insulating versus metallic behavior, magnetism versus nonmagnetism, and stretched versus triangular planar structure of the high-pressure phases of oxygen appears to be very intriguing, and largely unexplained. In recent *ab initio* local-spin-density (LSD) calculations[10] we failed to retrieve an ϵ-O_2 phase, obtaining instead, unrealistically, a straight δ-$O_2 \rightarrow \zeta$-O_2, insulator → metal transition. Our calculated transition was accompanied by collapse of magnetism and a substantial triangularization, as mentioned above. However, the calculations did require antiferromagnetism, if present, to be strictly *colinear*, and thus strongly hindered by the topological frustration arising in a triangular lattice. Noncolinear magnetic structures for oxygen were speculated upon before for oxygen,[8,11,19] but not in connection with ϵ-O_2.

The aim of this work is to use density-functional methods to investigate the possibility that noncolinear spin ordering might occur in the high-pressure phase diagram of molecular O_2 at high pressure. Since not only volume but also the b/a ratio appears to decrease with pressure, both spin frustration and antiferromagnetic couplings are expected to increase thereby. We argue that the region where noncolinear antiferromagnetic order could be favored should fall inside the ϵ-O_2 phase. Unfortunately no direct experimental evidence of the ϵ-O_2 spin structure is available. Spectroscopic data,[16] indicate that intermolecular coupling increases dramatically upon the δ-$O_2 \rightarrow \epsilon$-O_2 transition. The progressive growth of the optical absorption peak intensity close to 2.4 eV,[16] and the appearance in ϵ-O_2 of novel features at 1.6 eV, likely due to weak spin-forbidden triplet-singlet transitions, progressively allowed by increased magnetic coupling, are only indirect hints. Because we lack reliable data for the precise molecular structure of ϵ-O_2, our calculations will be based on assuming a crude model structure, with only two molecules per cell. Owing to this deliberate oversimplification we will not be able to provide a realistic description of important properties such as the IR activity. Nonetheless, we will be able to show that spiral antiferromagnetism can indeed arise in high-pressure oxygen, by studying our model structure by *ab initio* LSD calculations, when the possibility of noncolinear magnetic order is allowed for.

Taking advantage of the above mentioned similarity between ϵ-O_2 and ζ-O_2, we can use the structure of ζ-O_2 as the starting point for a crude guess of the structure to be used to mimic the ϵ-O_2 phase. The ζ-O_2 crystal structure obtained in the simulation of Ref. 10 was monoclinic ($C2/m$), distortion of a base-centered orthorhombic ($C2mm$) unit cell, with two molecules per primitive unit cell. The layered structure (with molecules oriented perpendicular to the planes) common to most phases of O_2 appears to be conserved in ζ-O_2. Comparing the structure of ζ-O_2 with that of δ-O_2 (Ref. 17) we note two major differences. First, the relative stacking of molecular planes differs because molecules in nearby planes are in a *bridge* position in δ-O_2, and *centered* (hcp-like) in ζ-O_2. Moreover, the in-plane b/a ratio, 0.70 in δ-O_2,[17] collapses to 0.58 in ζ-O_2, closer to the ideal triangular lattice value of $1/\sqrt{3}\approx 0.577$. If the ϵ-$O_2 \rightarrow \zeta$-O_2 transition were indeed nearly isostructural, then also the b/a ratio of ϵ-O_2 would be close, at least at pressures close to 96 GPa, to the triangular value.

We built our tentative model structure starting with the structure of ζ-O_2, and modifying it so as to fit x-ray data for ϵ-O_2 at 16.6 GPa.[20] With the monoclinic cell shown in Fig. 1, characterized by $a=4.46$ Å, $b=2.69$ Å, $c=6.61$ Å, and $\alpha=90.3°$, we obtain a reasonable agreement of calculated and experimental x-ray intensities for this structure as displayed in Fig. 2. With this unit cell the computational effort would, however, still be rather heavy. In view of the overall uncertainties on the details of the structure and in order to keep the model structure as simple as possible, we further selected a smaller monoclinic cell containing only one independent plane of molecules, stacked fcc-like, instead of hcp-like, whose in-plane lattice parameters are the above ones. The possibility that molecules may be tilted with respect to the perpendicular to the planes has been ignored, although it cannot be strictly excluded. We note, however, that no tilting was found to be stable in ζ-O_2, even when allowed by calculations.[10] Moreover, the experimental vibron frequency[21] displays a monotonic increase with pressure, possibly related to the calculated[10] monotonic decrease of the O_2 bond length with pressure, suggesting a pressure-induced strengthening of the molecular bond. It is natural to attribute this bond strengthening to the strong interplanar coupling resulting from the absence of tilting. In cases where

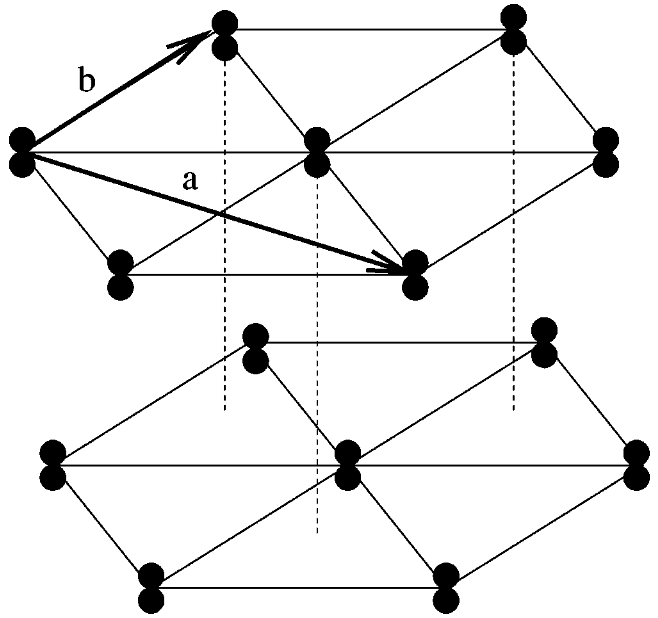

FIG. 1. Tentative structure for ϵ-O_2. Molecules (filled circles) lie perpendicular to the distorted hexagonal planes.

tilting is known to occur, such as in H_2 and N_2, there is pressure-induced softening of the vibron: tilted molecules can in that case release stress by simply varying the tilting angle, without altering the bond length.

III. GENERALIZED LOCAL SPIN-DENSITY APPROXIMATION

In order to substantiate our speculations, we decided to apply to our model structure for ϵ-O_2 a newly developed LSD method,[22] capable of accounting for general, noncolinear magnetic structures. This method is similar to that presented in Ref. 3, the main improvement being represented by our ability to properly deal with infinite systems and Fermi-surface sampling by using the special-point Gaussian-smearing technique.[23] In this approach, which we name *generalized local-spin-density* approximation (GLSD), each Kohn-Sham orbital is treated in full generality as a two-component spinor. The local magnetization is then found self-consistently by calculating the expectation values of the Pauli spin matrices using these spinors: $\boldsymbol{m}(\boldsymbol{r}) = \mu_B \Sigma f_i \psi_i^\dagger(\boldsymbol{r}) \boldsymbol{\sigma} \psi_i(\boldsymbol{r})$. Here the f's are the occupation numbers of the different electronic levels, the ψ's the corresponding spinor Kohn-Sham orbitals, μ_B is the Bohr magneton, and $\boldsymbol{\sigma} = (\sigma_x, \sigma_y, \sigma_z)$ are the Pauli matrices. The spatial components of the spinors are represented independently using a plane-wave basis set. The local direction of the magnetization is therefore unconstrained, unlike most present approaches to noncolinear magnetism where the direction of the local quantization axis within different atomic spheres is taken as an input quantity. The magnetization and charge density are then found in the usual way by self-consistently minimizing the total energy. In the presence of noncolinear magnetism, the Kohn-Sham Hamiltonian takes the form

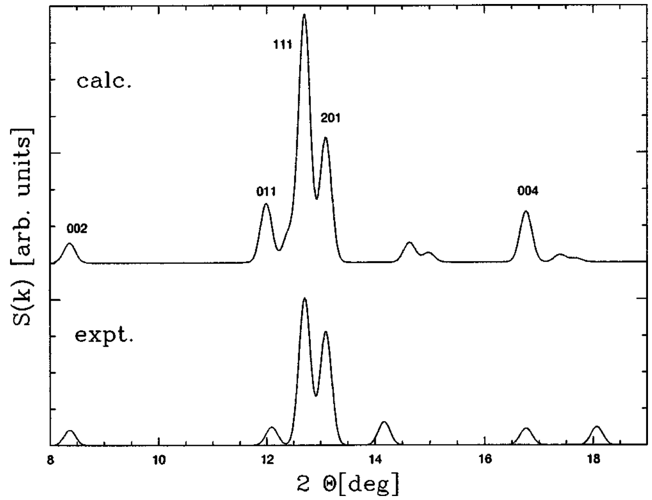

FIG. 2. Comparison of the calculated and measured structure factor for ϵ-O_2 at 16.6 GPa. The calculated curve corresponds to the $C2/m$ monoclinic structure described in the text and depicted in Fig. 1.

$$H_{KS} = \left(-\frac{1}{2}\nabla^2 + V_{ext}(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \right) \mathbf{I} + \boldsymbol{B}_{xc}(\boldsymbol{r}) \cdot \boldsymbol{\sigma}, \tag{1}$$

where V_{ext} and V_H are the external and Hartree potential, respectively, $\mathbf{I}$ is the unit (2×2) matrix, and V_{xc} and $\boldsymbol{B}_{xc}$ are the exchange-correlation scalar potential and *magnetic field* respectively: $V_{xc}(\boldsymbol{r}) = \partial E_{xc}(n, |\boldsymbol{m}|)/\partial n|_{n=n(\boldsymbol{r})}$, $\boldsymbol{B}_{xc}(\boldsymbol{r}) = \partial E_{xc}(n, |\boldsymbol{m}|)/\partial \boldsymbol{m}|_{\boldsymbol{m}=\boldsymbol{m}(\boldsymbol{r})}$. In the Hamiltonian (1), the last term corresponds formally to an external magnetic field, which stems from the magnetization dependence of the exchange-correlation energy. It is this term in the Hamiltonian that mixes the up and down components of the spinors if the magnetization is not aligned with the z axis.

The self-consistent cycle is initialized with a magnetization and charge density from a superposition of the atomic densities. The initial direction of the magnetization for every molecule is chosen at random. These initial choices define the Hamiltonian H_{KS}, Eq. (1). Once the corresponding Kohn-Sham spinors ψ are calculated, they can be used to obtain a new charge density and magnetization, and the cycle is iterated to self-consistency.

In this GLSD formalism, spin-orbit coupling is neglected. One consequence of this is that the direction of the magnetization is not coupled to the crystal lattice and the energy of the system is therefore not affected by a global rotation of the magnetization. This is why our GLSD calculations cannot predict the global direction of the magnetization, but only the relative orientation of the magnetization at different points in space, and in particular the angle between the integrated magnetic moments around different molecules. The energy that is associated with a relative rotation of one molecular moment with respect to another is small in comparison with the energies associated with a change of the charge density or the absolute value of the magnetization. This small energy scale gives rise to a slow convergence of the self-consistent cycle, and our GLSD calculations need generally more iterations than usual LSD calculations, where the direction of the magnetic moments is fixed.

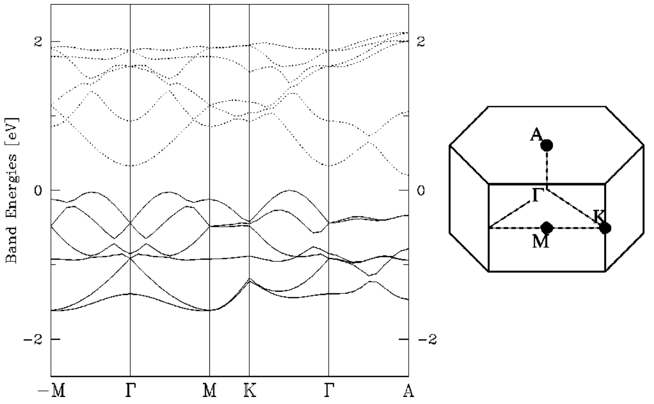

FIG. 3. Band structure near the Fermi level, for the expanded ϵ-O_2 structure ($V=13.35$ cm^3/mol, the Fermi energy is set to 0 eV).

IV. RESULTS

Calculations were perfomed using a gradient-corrected local-density approximation (GC-LDA), within the plane-wave pseudopotential method. The exchange and correlation functionals were taken after Refs. 24 and 25, respectively, while pseudopotentials were generated using the recipe by Troullier-Martins[26] with core radii $r_s=r_p=0.74$ Å, and the p channel taken as the local reference. Nonlocal contributions to the pseudopotential were treated using the Kleinman-Bylander technique.[27] Plane waves up to a kinetic-energy cutoff of 90 Ry were include in the basis sets. The sums over the occupied states were performed by the Gaussian-smearing special-point technique,[23] using a Gaussian broadening $\sigma=0.54$ eV. 125 special $\mathbf{k}$ points were necessary to achieve convergence in the sampling of the Brillouin zone.

Since we deal at best with a reasonable tentative structure, and in view of extremely demanding computer requirements, our strategy has been to purposely avoid total-energy structural optimizations, and to restrict to a rigid volume grid, to cover different pressure regimes. In order to accommodate the proposed 120° spin-spiral structure, calculations were performed using a unit-cell containing three independent molecules arranged in one plane.

We started by considering a strictly triangular structure (with a b/a ratio of $1/\sqrt{3}$) and a volume of 12.1 cm^3/mol, which corresponds to a pressure of about 10 GPa. In this case, we found that constraining the magnetization to be colinear—which is achieved using a conventional GC-LSD approach—results in a nonmagnetic ground state. However, as soon as we allowed the frustrating constraint of spin colinearity to be lifted (by using GC-GLSD), we found a magnetic ground state, which exhibits precisely the expected 120° spin-spiral geometry. Going next from the ideal triangular structure with $b/a=0.577$, to our tentative model for ϵ-O_2—which has a b/a ratio of 0.603—we found the same spin geometry. In Fig. 3 we report the resulting band structure which displays an indirect band gap, corresponding to a transition between a HOMO located along the ΓK line and a LUMO at the A point. Interestingly enough, neglecting any gradient corrections to the LDA density functional would yield a semimetallic band structure, contrary to experimental evidence. In Table I we report the values of the band gap and of the molecular magnetic moment, as calculated for different values of the molar volume. In this table the entry ''gap'' indicates the energy difference between the states which are LUMO and HOMO in the insulating phase, which becomes negative when at higher pressures the conduction and the valence bands start to overlap, and the system becomes semimetallic. With increasing pressure the metallic character increases and the molecular magnetic moment decreases, until the conduction and valence bands lose their identity, and the magnetic moment eventually vanishes. The values of the magnetic moment reported in Table I were obtained by integrating the magnetization density inside the Voronoi polyhedron around the molecules. In Ref. 10, where the molecular moments of colinear δ-O_2 were reported to be of the order of $0.5\mu_B$, the density was integrated in a small sphere around the molecules. The difference between the reported moments is due to this difference of the integration volume. When the same integration technique is used, our results are essentially the same as those in Ref. 10. The calculated triangular magnetic structure is visually presented in Fig. 4.

TABLE I. The volume dependence of the band gap and the magnetic moment per molecule from GC-GLSD calculations.

Volume (cm^3/mol)	Band gap (meV)	Magnetic moment (μ_B)
12.1	200	1.52
11.0	−320	1.29
10.0		0.79
8.5		<0.01

V. DISCUSSION

Our results suggest a possible scenario for the sequence of structural changes induced by increasing the applied pressure

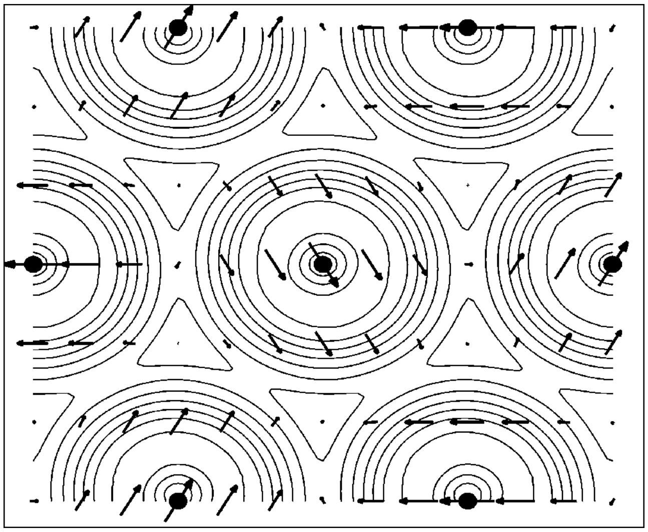

FIG. 4. Magnetization in the plane of the molecules, calculated in ϵ-O_2 at a molar volume of 12.1 $Å^3$. The arrows indicate the direction and relative magnitude of the magnetization density, the molecular positions are shown by filled dots. The magnetic moment per molecule corresponds to $1.52\mu_B$.

in solid O_2. The δ phase—which is well characterized and stable up to ≈ 8 GPa—is a stacking of planes where molecules are arranged in a triangular lattice, and where a strictly colinear antiferromagnetic order is stabilized by a strong planar distortion of the lattice, lifting frustration.[8,11] With increasing pressure, the b/a ratio decreases, until frustration destabilizes the colinear antiferromagnetic order when b/a approaches the ideal triangular value of $1/\sqrt{3}$. Standard mean-field arguments suggest that when frustration prevails, it is energetically more advantageous for the molecular moments to arrange themselves in a 120° spin spiral. We suggest that this kind of noncolinear rearrangement might be favored in high-pressure oxygen, before the moments are eventually killed altogether in the ultrahigh pressure ζ phase. The onset of noncolinear magnetic order could be one of the fingerprints of the $\delta \rightarrow \epsilon$ transition. Alternatively, noncolinearity could arise softly far away from the δ phase, and well inside the ϵ. We should stress that we still have too little information on the actual structure of the ϵ phase to draw definite conclusions, and our study of a simplified model for this structure only provides a qualitative physical argument in support of the noncolinear scenario.

Our results also indicate how band-overlap metallization has the effect of reducing and eventually killing the molecular moments. According to this picture, it could be possible for the ζ phase to retain some remnant of noncolinear magnetic structure at the lowest pressures (~ 1 Mbar), whereas it should definitely be nonmagnetic at high enough pressure. Whether or not there exists a pressure range between the insulating, magnetic ϵ phase and the metallic nonmagnetic phase where solid oxygen is metallic *and* magnetic is another matter which will require further investigation.

VI. CONCLUSIONS

In conclusion, in this paper we have presented the first fully unconstrained DFT calculation of the noncolinear magnetic structure occurring in a topologically frustrated molecular antiferromagnet. Our results, obtained for a model structure mimicking features of the elusive ϵ phase of solid oxygen at high pressure, suggest a possible scenario for the sequence of structural changes, driven by the interplay between in-plane lattice distortions and the magnetic structure. The validation of our conjectures will require further experimental as well as theoretical work.

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