Magnetoelastic nature of the solid oxygen $\varepsilon$-phase structure

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For a long time a crystal structure of the high-pressure $\varepsilon$-phase of solid oxygen was a mystery. Basing on the results of recent experiments that have solved this riddle it is shown that the magnetic and crystal structure of this phase can be explained by strong exchange interactions of antiferromagnetic nature. The singlet state implemented on quaters of O2 molecules has the minimal exchange energy if compared to other possible singlet states (dimers, trimers). Magnetoelastic forces that arise from the space dependence of the exchange integral give rise to transformation of 4(O2) rhombuses into the almost regular quadrates. Antiferromagnetic character of exchange interactions stabilizes the distortion of crystal lattice in $\varepsilon$-phase and impedes such a distortion in the long-range $\alpha$- and $\delta$-phases.

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Solid oxygen is known to occupy a particular place in the family of cryocystals. Steady interest to oxygen during almost 50 years is due to the magnetic properties of O2 molecule which posses nonzero spin $S_{O2} = 1$ in the ground electronic state. This ensures magnetism of all the solid O2 phases.

Solid oxygen has a rather complicated phase diagram, which includes three low temperature phases stable at ambient pressure: $\gamma$ ($T < 43.8$ K), $\beta$ ($23.8 \leq T \leq 43.8$ K) and $\alpha$ ($T \leq 23.8$ K), and several high pressure phases: $\delta$, $\varepsilon$ and $\zeta$ (see review which includes also a comprehensive history of a problem). All these phases except $\zeta$-O2 are insulators. Metallization of solid O2 takes place at 96 GPa at room temperature. Moreover, $\zeta$-O2 was also observed in a superconducting state.

An interesting feature of all (except $\gamma$-O2) the phases of solid oxygen is parallel alignment of the molecules which is usually explained by strong contribution of exchange interactions into anisotropic (i.e. depending on the mutual orientation of molecules) part of intermolecular potential. Presence of stable orientation ordering enables to simplify substantially many of theoretical models and, in particular, makes it possible to describe the structural phase transitions in solid oxygen disregarding orientational dynamics of molecules.

In the absence of the orientational degrees of freedom, the low-temperature rhombohedral (space group $R\overline{3}m$) $\beta$-phase can be thought of as a para-phase for all the magnetic phases. In particular, $\beta$-O2 has a planar structure, consisting of close packing of parallel oxygen molecules with centers of mass in the apexes of regular triangles, and with orientation perpendicular to the basal planes. The temperature dependence of magnetic susceptibility of $\beta$-O2 is typical for antiferromagnets (AFM). Noncollinear 3-sublattice ordering in this phase (Loktev structure) was predicted in and now is generally accepted. Below 23.9 K (or at high pressure) $\beta$-phase becomes unstable and transforms into monoclinic (space group C2/m) $\alpha$-phase. Corresponding $\alpha\beta$-phase transition has magnetoelastic nature associated with strong dependence of exchange interaction vs intermolecular distance, as it was shown in. The $\alpha$-phase possesses the collinear (Néel) magnetic structure with the easy direction parallel to the monoclinic axis $b$ of slightly distorted (compared to regular hexagonal) lattice. Long-range AFM ordering, which can be described within a simple 2-sublattice model, is stabilized by the “deformation-induced splitting” of intra- and inter-sublattice exchange integrals. It should be stressed that all the in-plane exchange constants originate from a single constant $J(r)$ that has AFM character (i.e., $J(r) > 0$), is isotropic and describes intermolecular spin interactions in $\beta$-phase.

Mutual shift of the close-packed basal planes that accompanies formation of AFM ordering also has magnetoelastic nature and originates from space dependence of inter-plane exchange integral.

Hydrostatic pressure up to 4÷6 GPa induces continuous shift of the basal planes, while the magnetic structure of $\alpha$-O2 and orientation of molecules remain invariable. At approximately 6.5 GPa the mutual shift of neighboring planes attains 1/2 of an in-plane intermolecular distance and solid O2 transforms into orthorhombic (space group Fmmm) $\delta$-phase. The type of magnetic order in $\alpha$- and $\delta$-phases is similar (collinear AFM structure) within $ab$-plane, but relative orientation of spins in the neighboring planes (between the first interplane neighbors) is different – parallel in $\alpha$-O2 and antiparallel in $\delta$-O2. Due to crucial change of magnetic structure (from 2 to 4-sublattice) $\alpha\delta$-phase transition is classified as the 1st order. Abrupt change of magnetic order at the $\alpha\delta$-transition point is accompanied by discontinuous shift of the close-packed planes, which also originates from space dependence of the inter-plane exchange integral.

Further increase of pressure up to 8 GPa produces another phase transformation into $\varepsilon$-phase which elusive structure has been determined recently. The transition is undoubtedly of the 1st order and is accompanied by a considerable
(up to 5.4%) volume reduction. Crystal structure of ε-phase is layered, as it is the case for α-, β-, and δ-phases, and has monoclinic (space group C2/m) symmetry. Variation of interplane distance (equal ≈ 3.4 Å at the transition point) with pressure is very small. So, the volume change is mainly due to the variation of intermolecular distances within the basal plane. The peculiar feature of ε-phase is association of four O₂ molecules into rhomb-shaped (according to Ref.12) or square-shaped (according to Ref.13) (O₂)₄ molecular units, which are symmetry equivalent and centered on the lattice points at (0,0,0) and (0.5,0.5,0). Common spin-state of the (O₂)₄ ≡ O₈ cluster is nonmagnetic²⁵, with the total spin S₀₈ = 0.

Physical reasons of such an unusual behavior of the magnetic molecular crystal are not yet clearly understood. Should ε-phase be considered as a chemically new substance, what is the nature of forces that keep (O₂)₄ quadrates in neighboring planes locked under high pressure, what is the role of magnetic interactions – all these questions are still open. First-principles calculations demonstrate the tendency of the O₂ molecules for dimerization and formation of herringbone-type chains but failed to prove that the (O₂)₄ structure has the lowest energy.

With the account of these results, in the present paper we make an attempt to elucidate the role of exchange interactions in formation of nonmagnetic ε-phase and show how the pressure-induced variation of the exchange constants may produce strong distortion of crystal lattice.

I. INTUITIVE CONSIDERATIONS

Analysis of the magnetic and structural properties of β-, α- and δ-phases of solid oxygen shows that exchange interactions in this crystal are so strong that they are responsible not only for variation of magnetic order but also produce rather noticeable deformations of the crystal lattice. So, it seems reasonable to assume that ε-phase makes no exclusion and its complicated and surprising structure is mainly due to strong exchange intermolecule interaction that keeps quarters of O₂ molecules as the independent chemical units, equals intermolecular distances within these complexes and weakens intercluster bonds to so extent that O₈ clusters can be approximately considered as (magnetically) noninteracting units.

From general point of view, magnetic collapse (disappearance of magnetic properties) observed in ε-phase may result from coupling of 2, 3, or any other number of O₂ molecules in a singlet spin state. The tendency of the O₂ molecules to form such multimolecular clusters (consisting of 2, 3, 4 units) was ascertained long ago in the optical spectra of α-phase, where two-, three- (at higher temperature) and four-molecule dipole transition bands were directly observed and identified. Why, then, 4O₂ complex is more favorable than, say, dimer, 2O₂, or trimer, 3O₂?

One of the possible reason for such a behavior is a weakness of van der Waals intermolecular forces in comparison with exchange interaction. As long as exchange interactions are not taken into account, O₂ molecules in α-, β-, δ- and ε-phases can be considered as noninteracting solid spheres packed in the most compact way, i.e. in a regular triangular lattice, within the basal plane (see also Refs.12). Singlet complexes concatenated by the exchange forces and decoupled from each other may also be considered as noninteracting (or weakly interacting) solids. Dimers themselves are highly anisotropic, formation of the decoupled pairs should produce additional distortion of crystal lattice (see Fig.1a), so, O₄ complexes seem to be unstable with respect to formation of herringbone chains. In contrary, 3O₂, 4O₂ and 7O₂ complexes may be invariant with respect to rotation around 3-rd, 4-th, or, correspondingly, 6th order symmetry axis, and so are isotropic in the basal plane. In turn, a hexagonal plane can be completed by the regular triangles (Fig.1b), 60°-angled diamonds (Fig.2), or hexagons that by appropriate deformations may be transformed into highly symmetric n-O₂ units. Lattice distortions shown in Figs.1 and 2 by arrows could be classified (see Tab.1) according to symmetry of different optical modes.

It is quite obvious that formation of trimers and sestets should be accompanied by isotropic contraction of interatomic distances within the complex, while formation of quaters (see below) is related with anisotropic (shear) deformation of corresponding rhombus. The second process seems to be energetically more favorable because shear modes are usually much more soft compared to isomorphic striction.

So, formation of quaters may be induced by increase of AFM exchange coupling at high pressure and softening of appropriate optical mode.

II. MODEL

A. Order parameter

Phenomenological description of ε-O₂ as a phase in a series of β → α → δ → ε transition is not so straightforward as of the other magnetic phases. According to phase diagram, ε-phase may be obtained from both δ- and β-phases whose Brave lattices belong to the different space groups, so, what phase should be considered as a parent phase?
Three-dimensional space group of ε-O₂ coincides with that of α-O₂, though in the phase diagram both phases are separated with the high symmetry δ-phase. What is more, α-, δ- and ε-phases are described by the same symmetry group within the basal plane. This fact makes questionable the choice of the components of deformation tensor as an order parameter of δε-transition.

The easiest way to overcome these difficulties is to accept that all the magnetic phases, including ε-O₂, originate from a virtual nonmagnetic phase viewed as a stack of regular triangular planes. This assumption is based on the following facts.
Table I: Wave vectors and polarization of optical modes coupled with different singlet states. Representatives of stars \( k \) are
given according to Kovalev’s notations.\(^{19}\) Lattice vectors \( a_1, a_2 \) and reciprocal lattice vectors \( b_1, b_2 \) are assigned to the
hexagonal pra-phase.

| Number of \( \text{O}_2 \) mol. | Wave vector | Polarization vector |
|-------------------------------|-------------|---------------------|
| 2-dimer \( b_1/2 \)          | \( a_1 + a_2 \) |
| 3-trimer \( (b_1 + b_2)/3 \) | \( \sqrt{3}(a_1 + a_2) + i(a_1 - a_2) \) |
| 4-quater \( b_1/2 - b_2/4 \) | \( u_x \sqrt{3}(a_1 + a_2) + iu_y(a_1 - a_2) \) |

i) Crystal lattices of \( \beta-, \alpha- \) and \( \delta- \) phases can be thought of as the different modifications of the same hexagonal
(space group \( 6/mmm \)) pra-phase in which the neighboring close-packed planes are shifted in \([1100]\) direction.\(^{20}\)

ii) Though the \( \text{O}_2 \) lattice in \( \varepsilon \)-phase is strongly distorted within the basal plane, as compared to lattice of \( \alpha \)-phase, an angle between the bonds connecting the molecules in neighboring \( \text{O}_8 \) clusters remains approximately equal to \( 60^\circ \) in a wide interval of pressures, as seen from the experiment.\(^{21}\)

From this point of view, the structural order parameter of pra-phase – \( \varepsilon \)-phase transition can be represented by the
amplitudes \( u_x, u_y \) of the optical mode

\[
u(n) = e^{ib_1n/2} \left[ u_x \cos \frac{b_2n}{4} + u_y \sin \frac{b_2n}{4} \right],
\]

where vector \( n \) denotes position of a molecule within the basal plane.\(^{22}\) Macroscopic description of the magnetic state of
\( \varepsilon \)-phase may be done with the use of spin-spin correlation functions. Discussion of this question is beyond the scope
of the present paper.

It is interesting to note that the structural order parameter in the sequence of \( \beta \rightarrow \alpha \rightarrow \delta \)-phase transitions (i.e. a function of mutual shift of the neighboring close-packed planes in \([1100]\) direction calculated with respect to the initial non-shifted hexagonal stacking) is symmetry related to the transverse acoustic modes propagating in \([0001]\) and \([1000]\) directions (wave vectors parallel to \( b_3 \) and \( b_1 \), correspondingly).

### B. Free energy and spin hamiltonian

Different phases of solid oxygen and inter-phase transitions are described on the basis of phenomenological expression for free energy of the crystal. Substantial simplification of the model may be achieved by neglection of interplane interactions. This assumption is justified by noticeable difference in the variation of in-plane and interplane distances in the course of pressure-induced phase transitions.

As it was mentioned above, the magnetic and crystal structure of \( \alpha- \) and \( \delta- \) phases is indistinguishable within the
\( ab \)-plane, so, herewith we consider the series of \( \beta \rightarrow \alpha \rightarrow \varepsilon \)-transition. Gibbs free energy \( \Phi \) of the crystal is modeled as a function of (two-dimensional) phonon amplitude \( u(k) \), strain tensor components \( u_{jk} \), invariant with respect to the symmetry group of hexagonal pra-phase, plus magnetic contribution into internal energy \( E_{\text{mag}} \):

\[
\Phi = \frac{1}{2} \sum_j K(k_j) |u(k_j)|^2 + \frac{c_{11} + c_{12}}{2} (u_{xx} + u_{yy})^2 + \frac{c'}{2} [(u_{xx} - u_{yy})^2 + 4u_{xy}^2] + P(u_{xx} + u_{yy})
+ \sum_j \lambda_{ph}^{(iso)}(k_j) |u(k_j)|^2 (u_{xx} + u_{yy}) + \lambda_{ph}^{(an)}(k_7) |u_x|^2 (k_7) - u_y^2 (k_7) |(u_{xx} - u_{yy}) + E_{\text{mag}}.
\]

Vectors \( k_j \) in the above expression denote different wave vectors, classified according to irreducible representations of
\( 6/mmm \) space group, phenomenological constants \( K(k_j) \) are proportional to the corresponding phonon frequencies, coefficients \( \lambda_{ph}(k_j) \) originate from the crystal anharmonicity and describe nontrivial coupling between phonon amplitude and crystal lattice parameters. Last term in \( \Phi \) accounts for the (external) hydrostatic pressure \( P \).

Magnetic contribution \( E_{\text{mag}} \) is calculated as an average of spin-hamiltonian \( H \) over a ground state \( |\Psi\rangle \) of the crystal:

\[
E_{\text{mag}} = \langle \Psi | \hat{H} | \Psi \rangle = \sum_{nm} J(r_{nm}) \hat{S}_n \hat{S}_m.
\]

\( \hat{S}_n \) and \( \hat{S}_m \) are Pauli matrices.
and summation is accomplished over the nearest and next to the nearest neighbors separated by distance $|\mathbf{r}_{nm}|$. Magnetoelastic part of the internal energy is derived from the expression (3) with due account of space dependence of the exchange integral $J(\mathbf{r}_{nm})$.

Once the ground state of magnetic subsystem is calculated, structure and stability conditions of a phase can be determined by minimization of free energy (2) with respect to phonon amplitudes and deformation tensor components.

As it was already mentioned, $\beta$- and $\alpha$-phases posses a kind of the Néel spin ordering, that can be described macroscopically by assigning an average value $\langle \mathbf{S}_n \rangle$ to the spin vector at each site.

![Figure 3: Primitive cell of $\epsilon$-phase. Magnetically coupled quaters of molecules are outlined by quadrates. Red and blue arrows show the shift of O$_2$ molecules in the course of phase transition. Vectors $\mathbf{a}_{1,2}$ are the Brave lattice vectors of the hexagonal pra-phase.](image)

A ground state $|\Psi_\epsilon\rangle$ of $\epsilon$-phase is a true eigen function of spin-hamiltonian (3) and is calculated within an assumption of magnetically decoupled O$_8$ clusters. In other words, $|\Psi_\epsilon\rangle$ may be represented as unentangled combination of quaters
wave functions $|\psi_n\rangle$, that satisfies equation

$$\hat{H}^{\text{(intra)}}|\psi_\varepsilon\rangle = E^{\text{(intra)}}|\psi_\varepsilon\rangle, \quad |\psi_\varepsilon\rangle \equiv \prod_n |\psi_n\rangle,$$

(4)

with the hamiltonian of intra-cluster interactions written as follows

$$\hat{H}^{\text{(intra)}} = \sum_n \left\{ J(r_{12})[S_{1n}\hat{S}_{2n} + \hat{S}_{2n}\hat{S}_{3n} + \hat{S}_{3n}\hat{S}_{4n} + \hat{S}_{4n}\hat{S}_{1n}] + J(r_{13})\hat{S}_{1n}\hat{S}_{3n} + J(r_{24})\hat{S}_{2n}\hat{S}_{4n} \right\}.$$

(5)

Here the vectors $\mathbf{n}$ define the positions of O$_8$ cluster in a superstructure with lattice vectors $\mathbf{a}_1 = 2\mathbf{a}_1$ and $\mathbf{a}_2 = 2\mathbf{a}_2$. For the sake of simplicity we use the rectangular “unit cell” which contains two clusters (see Fig.3). Choice of the unit cell corresponds to one of three different domains of $\alpha$-phase. The positions of the individual O$_2$ molecules (labelled with number 1, 2, 3, 4) within the cluster are defined with the basis vectors $\pm \tau_1 \equiv \pm \mathbf{a}_1$ and $\pm \tau_2 \equiv \pm \mathbf{a}_2$.

Interaction between the clusters with account of the next-to nearest neighbors is described by operator $\hat{H}^{\text{(inter)}}$ (see Fig.3 for notations)

$$\hat{H}^{\text{(inter)}} = \frac{1}{2} \sum_{\mathbf{n}} \left\{ J'(r_{12}')[S_{1n}\hat{S}_{2(n-\tau_1)} + \hat{S}_{2n}\hat{S}_{3(n-\tau_2)} + \hat{S}_{3n}\hat{S}_{4(n-\tau_2)} + \hat{S}_{4n}\hat{S}_{1(n-\tau_1)}] + J'(r_{13}')[\hat{S}_{1n}\hat{S}_{3(n+\tau_1-\tau_2)} + \hat{S}_{3n}\hat{S}_{1(n+\tau_1-\tau_2)} + \hat{S}_{1n}\hat{S}_{3(n+\tau_1+\tau_2)} + \hat{S}_{3n}\hat{S}_{1(n+\tau_1+\tau_2)}] + J'(r_{24}')[\hat{S}_{2n}\hat{S}_{4(n+\tau_1-\tau_2)} + \hat{S}_{4n}\hat{S}_{2(n+\tau_1-\tau_2)} + \hat{S}_{2n}\hat{S}_{4(n+\tau_1+\tau_2)} + \hat{S}_{4n}\hat{S}_{2(n+\tau_1+\tau_2)}] \right\},$$

(6)

so that spin-hamiltonian (5) is represented as a sum:

$$\hat{H} = \hat{H}^{\text{(intra)}} + \hat{H}^{\text{(inter)}}.$$

(7)

In the $\varepsilon$-phase the first term in (6) is responsible for formation of the ground state, while the second one describes contribution that arises from excitations. In $\alpha$-, $\delta$ and $\beta$-phases both terms contribute equally into magnetic energy of the crystal.

III. $\varepsilon$-PHASE

A. Magnetic structure

It was already mentioned that according to experimental data, the units O$_8$ form a common singlet state, while each O$_2$ molecule possesses spin $S_j = 1, j = 1-4$. So, it is convenient to express spin-state $\psi$ of O$_8$ cluster in terms of the eigen functions $|0\rangle, |\pm 1\rangle$ of spin operators $\hat{S}_j^Z$, where $Z$ is a quantization axis.

According to general theorem of quantum mechanics, singlet state in such a system has 3 representations (among 81 basic vectors) with the spin wave functions that could be easily found from the conditions

$$\left( \sum_{j=1}^{4} S_j \right)^2 \psi_{\text{singlet}} = 0, \quad \sum_{j=1}^{4} \hat{S}_j^Z \psi_{\text{singlet}} = 0.$$

(8)

Obviously, $\psi_{\text{singlet}}$ is also an eigen function of hamiltonian $\hat{H}^{\text{(intra)}}$.

Additional simplification of the problem may be achieved by account of permutation symmetry group. All three singlet states should have different symmetry with respect to permutations of molecules within the cluster and hence, correspond to the different eigen values of operators (see Table II)

$$\hat{P}_1 \equiv (\hat{S}_1, \hat{S}_2) + (\hat{S}_2, \hat{S}_3) + (\hat{S}_3, \hat{S}_4) + (\hat{S}_4, \hat{S}_1)$$
Table II: Eigen values of operators $\hat{P}_1$, $\hat{P}_2$, $\hat{P}_3$ in a singlet subspace, cluster energy $\langle \hat{H}^{(\text{intra})} \rangle / N$ per molecule for arbitrary intermolecular spacing, equilibrium angle $\psi$ between intermolecular bonds within the cluster and corresponding equilibrium energy $E_e$ per molecule.

| Function | $\hat{P}_1$ | $\hat{P}_2$ | $\hat{P}_3$ | $\langle \hat{H}^{(\text{intra})} \rangle / N$ | $\psi_{\text{eq}}$ | $E_e$ |
|----------|-------------|-------------|-------------|----------------------------------|----------------|-------|
| $\psi^{\text{(singlet)}}_{\text{gr}}$ | -6 | 1 | -2 | $[J(r_{13}) + J(r_{24}) - 6J(r_{12})]/4\pi/4$ | $\langle J(\sqrt{2}a) - 3J(a) \rangle / 2$ | - |
| $\psi^{\text{(singlet)}}_{\text{ex1}}$ | -4 | 0 | -2 | $-J(r_{12})$ | $\text{arb.}$ | $-J(a)$ |
| $\psi^{\text{(singlet)}}_{\text{ex2}}$ | 0 | -2 | 1 | $-J(r_{13}) + J(r_{24})/2\pi/4$ | $-J(\sqrt{2}a)$ |

Finally, the singlet wave functions may be written in the following form:

$$\psi^{\text{(singlet)}}_{\text{gr}} = \frac{1}{\sqrt{5}} ([11\bar{T}\bar{T}] + [\bar{T}1\bar{T}1]) + \frac{1}{3\sqrt{5}} [2|0000\rangle + |010\bar{T}\rangle + |10\bar{T}0\rangle]$$

$$|0\bar{T}01\rangle + |\bar{T}010\rangle - \frac{3}{2}([001\bar{T}] + |01\bar{T}0\rangle + |1\bar{T}00\rangle + |00\bar{T}1\rangle + |0\bar{T}10\rangle$$

$$+ |\bar{T}100\rangle + |10\bar{T}0\rangle) + \frac{1}{2} ([11\bar{T}1\rangle + |\bar{T}111\rangle + |1\bar{T}1\rangle + |\bar{T}11\rangle].$$

(10)

$$\psi^{\text{(singlet)}}_{\text{ex1}} = \frac{1}{2\sqrt{3}} ([1\bar{T}00\rangle + |001\bar{T}\rangle + |1\bar{T}00\rangle + |00\bar{T}1\rangle + |1\bar{T}1\rangle + |\bar{T}11\rangle$$

$$- |1\bar{T}1\rangle - |\bar{T}1\rangle 1) - |0\bar{T}0\rangle - |01\bar{T}0\rangle - |\bar{T}001\rangle - |\bar{T}010\rangle].$$

(11)

$$\psi^{\text{(singlet)}}_{\text{ex2}} = \frac{1}{3} ([11\bar{T}1\rangle + |\bar{T}11\rangle + |1\bar{T}1\rangle + |\bar{T}11\rangle + |00\bar{T}1\rangle$$

$$- |010\bar{T}\rangle - |0\bar{T}01\rangle - |10\bar{T}0\rangle - |\bar{T}010\rangle].$$

(12)

In order to find out what of three functions (10)-(12) describes the ground state of hamiltonian (7), we compare corresponding eigen values (see Table II, the 4th column). Taking into account ferromagnetic character of the exchange interaction ($J(r) > 0$), the fact, that $J(r)$ monotonically decreases with intermolecular distance $r$, and geometrical relation $r_{13} \leq r_{13} < r_{24}$, one can easily verify that

$$\langle \hat{H}^{(\text{intra})} \rangle_{\text{gr}} < \langle \hat{H}^{(\text{intra})} \rangle_{\text{ex1}} < \langle \hat{H}^{(\text{intra})} \rangle_{\text{ex2}},$$

and the required ground state is $\psi^{\text{(singlet)}}_{\text{gr}}$ (see eq. (10)). We have also implicitly taken into account an obvious fact that an average value of $\langle \hat{H}^{(\text{inter})} \rangle$ in any singlet state is exactly zero.

It is interesting to compare $\psi^{\text{(singlet)}}_{\text{gr}}$ with the AFM Néel state observed in $\alpha$-phase, where all the nearest neighbors are coupled antiferromagnetically. In terms of $O_2$ spin states it means, that the most preferable combinations are $|1\bar{T}1\rangle$ and $|\bar{T}1\rangle$. States $\psi^{\text{(singlet)}}_{\text{gr}}$ are orthogonal to a subspace spanned over the “Néel-state” vectors $|1\bar{T}1\rangle$ and $|\bar{T}1\rangle$. In contrary, $\psi^{\text{(singlet)}}_{\text{gr}}$ belongs to this subspace with 0.4 probability.

We may also compare eigen values of hamiltonian (7) in a singlet state for different clusters: hypothetical dimer, trimer and already described quater. It is obvious that for $2O_2$ and $3O_2$ complexes the singlet state is kept by the nearest neighbor interactions only, corresponding eigen values of hamiltonian (that could be found without explicit expression for wave function) are

$$\langle \hat{H}^{(\text{intra})} \rangle_{\text{dim}} = -NJ(r_{12}), \text{ for dimer;}$$

$$\langle \hat{H}^{(\text{intra})} \rangle_{\text{trim}} = -N\left[\frac{2}{3}J(r_{12}) + \frac{1}{3}J(r_{13})\right], \text{ for trimer.}$$

(14)

where $N$ is the number of $O_2$ molecules. In the case of monotonically decreasing AFM exchange and fixed $r_{12} \leq r_{13} < r_{24}$ values

$$\langle \hat{H}^{(\text{intra})} \rangle^{\text{(singlet)}}_{\text{gr}} < \langle \hat{H}^{(\text{intra})} \rangle^{\text{(singlet)}}_{\text{ex1}} \leq \langle \hat{H}^{(\text{intra})} \rangle^{\text{(singlet)}}_{\text{ex2}},$$

(15)

So, the magnetic energy of the crystal in the state with $S = 0$ takes on its minimum value when the number of $O_2$ molecules in a singlet group is at least $n = 4$. 
B. Distortion of crystal lattice

It was already mentioned that magnetic interactions in solid oxygen are so strong that they cause large distortion of crystal lattice. This effect was observed, e.g., in the course of αβ-transitions where in-plane lattice deformation achieved nearly 5%. In the ε-phase the effect of magnetoelastic interactions is even more pronounced, though very unusual, because in this case lattice distortion is produced by magnetic collapse, not by magnetic ordering.

In-plane structure of ε-phase can be considered as a result of two-step distortion of the ideal hexagonal basal plane of prα-phase (β-) with the lattice constant \( a_h \) (see Fig. 4): i) homogeneous deformation which changes scales in \( X \) and \( Y \) direction:

\[
\begin{align*}
r_{13}^{(0)} &= a_h (1 + u_{xx}), & r_{24}^{(0)} &= \sqrt{3} a_h (1 + u_{yy});
\end{align*}
\]

and ii) inhomogeneous distortion of rhombus formed by the in-cluster molecules 1, 2, 3, 4. In fact, this means that the virtual intermediate state (after step i)) has an α-type lattice.

![Diagram of two-step distortion of the crystal lattice](image)

Figure 4: Two-step distortion of the crystal lattice of hexagonal prα-phase (a): i) homogeneous deformation (b); ii) inhomogeneous distortion of rhombus (c).

Symmetry condition that the distances \( r_{jk} \) between the pairs of molecules \( jk = 12, 23, 34, \) and 41 within the cluster are equal, \( r_{jk} = a \), makes it possible to introduce very convenient and obvious parametrization using an angle \( \varphi \) between the directions to nearest neighbors: \( r_{13} = 2a \cos \varphi \), \( r_{24} = 2a \sin \varphi \), and

\[
\begin{align*}
u_x &= a \cos \varphi - \frac{1}{2} r_{13}^{(0)} \equiv a (\cos \varphi - \cos \varphi_0), & u_y &= \frac{1}{2} r_{24}^{(0)} - a \sin \varphi = a (\sin \varphi_0 - \sin \varphi),
\end{align*}
\]

where \( r_{13}^{(0)} = 2a \cos \varphi_0 \), \( r_{24}^{(0)} = 2a \sin \varphi_0 \) are interatomic distances in the reference frame.

The positions of O₂ molecules in ε-phase are then calculated by minimization of Gibbs’ free energy (2) with respect to the components of deformation tensor \( u_{jk} \) and angle \( \varphi \). Last term, \( E_{\text{mag}} \), is the magnetic energy in the singlet
ground state,
\[ E_{\text{mag}} = \frac{N}{4} [J(r_{13}) + J(r_{24}) - 6J(r_{12})]. \]  

(18)

Thus, expression (12) can be rewritten as
\[ \Phi = \frac{1}{2} (c_{11} + c_{12})(u_{xx} + u_{yy})^2 + \frac{1}{2} c'[(u_{xx} - u_{yy})^2 + 4u_{xy}^2] + P(u_{xx} + u_{yy}) \]
\[ + 2a^2 \sin^2 \frac{\varphi - \varphi_0}{2} \left[ K(k_7) + \lambda^{(\text{iso})}_{\text{ph}}(k_7)(u_{xx} + u_{yy}) - \lambda^{(\text{an})}_{\text{ph}}(k_7)\cos(\varphi + \varphi_0)(u_{xx} - u_{yy}) \right] \]
\[ + \frac{N}{4} [J(2a \cos \varphi) + J(2a \cos \varphi) - 6J(a)] . \]

Minimization conditions \( \partial \Phi / \partial \xi_j = 0, |\partial^2 \Phi / \partial \xi_j \partial \xi_k| > 0, \xi_j = \varphi, u_{xx}, u_{yy} \) give rise to the following equation for \( \varphi \):
\[ \frac{dJ(r_{13})}{dr} \cos \varphi + \frac{dJ(r_{24})}{dr} \sin \varphi + \frac{4K(k_7)a}{N} \sin(\varphi - \varphi_0) = 0 \]

(20)

Assuming the softening of the optical mode \( k_7 \) in the vicinity of phase transition point, so that \( K(k_7)a^2 \ll a[dJ(r)/dr]/N, \) we can neglect last term in (20). Then, equation (20) has an obvious solution \( \varphi_{\text{eq}} = \pi/4 \) (and automatically, \( r_{13} = r_{24} \)). This means that the four molecules in the ground singlet state are situated in the corners of quadrates and it is the exchange interaction within the cluster that keeps the molecules in that state. Such a symmetric arrangement of molecules seems to be quite natural in the case when the exchange forces are the strongest interactions in the system. Really, in the ground state (10) the molecules in the neighboring corners (12, 23, 34, and 41) with high probability have opposite spins and thus are attracted to each other, due to antiferromagnetic character of exchange forces. In the contrary, the molecules in the opposite corners (pairs 13 and 24) have parallel spins and are therefore repulsed. The energy of repulsion is minimized when the average distance between corresponding molecules is as much as possible, this can be achieved in a symmetrical combination like quadrate. Small deflection (e.g., 96° and 84° at 17.6 GPa) from the right angle observed in the experiment\textsuperscript{11,12} may be calculated from (20) with account of contribution from the optical mode:
\[ \varphi = \frac{\pi}{4} - \frac{4\sqrt{2}K(k_7)a \sin(\pi/4 - \varphi_0)}{N'J'(r_{13})} . \]

(21)

According to Ref.\textsuperscript{13}, \( \varphi_0 = \arctan(r_{24}(0)/r_{13}(0)) = 53^\circ \). Using the most elaborated phenomenological form\textsuperscript{21,22} of space dependence for
\[ J(r) = J_0 \exp[-\alpha(r - r_0) + \beta(r - r_0)^2], \quad 2.6 \leq r \leq 4.2, \]

(22)

with \( J_0 = 60 \text{ K}, \alpha = 3.5 \text{ Å}^{-1}, \beta = 1.2 \text{ Å}^{-2}, r_0 = 3.1854 \text{ Å}, \) and taking \( a = 2.18\text{Å}^{\text{12,13}} \), we get an upper limit for \( K(k_7)/N \leq 9.2 \text{ K}/\text{Å}^2 \), while estimated value of \( J'(r_{13})/a \geq 80 \text{ K}/\text{Å}^2 \). Considering \( K \) as a stiffness constant of intermolecular bonds, one obtains the characteristic frequency 16.2 cm\textsuperscript{-1} which is much smaller than the frequencies of optical modes (\( \geq 300 \text{ cm}^{-1} \)) calculated in Ref.\textsuperscript{14} and the frequency 1,38 cm\textsuperscript{-1} of Raman mode corresponding to the antisymmetric stretching motion of the four O\textsubscript{2} molecules, coupled in diagonal pairs\textsuperscript{12}.

Stability condition of the “quadrate” solution
\[ \frac{d^2J(r)}{dr^2} + \frac{2K(k_7)}{N} \cos(\pi/4 - \varphi_0) > 0 \]

(23)

is obviously satisfied, because according to Ref.\textsuperscript{12} \( J(r) \) is a monotonically decreasing concave function (see e.g. (22)) of intermolecular distance, and \( K(k_7) > 0 \) (from the condition of crystal lattice stability).

So, even in magnetically neutral state the exchange interactions play a role of a motive force that changes crucially an angle \( \varphi \) between intermolecular bonds.

Analysis of the expression (19) makes it possible to calculate shear deformation \( u_{xx} - u_{yy} \) and isotropic striction \( u_{xx} + u_{yy} \) within the plane:
\[ u_{xx} - u_{yy} = \frac{2a^2 \lambda^{(\text{an})}_{\text{ph}}(k_7)}{c'} \cos(\pi/4 + \varphi_0), \]
\[ u_{xx} + u_{yy} = -\frac{1}{c_1 + c_{12}} [P + 2\lambda^{(\text{iso})}_{\text{ph}}(k_7)a^2 \sin^2 \frac{\pi/4 - \varphi_0}{2}]. \]

(24)
Space dependence of the exchange constant $J(r)$ does not contribute into macroscopic deformation, because O$_8$ clusters are supposed to be decoupled from each other. So, shear deformation of $\varepsilon$-phase is due solely to anharmonicity (coupling constant $\lambda_{\text{ph}}(k_T)$) of crystal lattice. Isotropic striction $u_{xx} + u_{yy}$ describes relative change of the in-plane square. From the pressure dependence of lattice parameters we can estimate the in-plane compressive modulus $c_{11} + c_{12} = 88$ GPa. From the value of jump of isotropic striction in the $\varepsilon$-transition point, $\Delta(u_{xx} + u_{yy}) = 0.019$ we estimate isotropic anharmonicity constant $\lambda_{\text{ph}}^{\text{iso}}(k_T) = 1.1 \cdot 10^5$ K/A$^2$.

**IV. COMPARISON WITH $\alpha$- AND $\delta$-PHASES**

In the previous section it was shown that once the singlet ground state is formed, crystal lattice should be distorted in a described manner, due to strong exchange interactions and reduced optical phonon frequency. But what about the inverse mechanism, can the crystal lattice of $\delta$-(\(\alpha\)-phase) be unstable with respect to $u(k_T)$ distortions?

To answer this question, we minimize Gibb's potential (2) assuming the presence of the collinear long-range AFM order. In this case $\langle S_n^2 \rangle = 2$, $\langle S_n^z \rangle = \pm 1$ at a site $R_n$, and spin polarization alters from 1 to -1 when shifted through the vectors $a_1$, $a_2$. Taking into account the locations of molecules 1-4 (see Fig.3), it can be easily seen that

$$
\langle S_1 S_2 \rangle = \langle S_2 S_3 \rangle = \langle S_3 S_4 \rangle = \langle S_4 S_1 \rangle = -1, \quad \langle S_1 S_3 \rangle = \langle S_2 S_4 \rangle = 1
$$

Substituting these values into (7) we obtain expression for the magnetic energy $E_{\text{AFM}}$ of AFM state:

$$
E_{\text{mag}} = E_{\text{AFM}} = E_{\text{AFM}}^{\text{cluster}} + E_{\text{AFM}}^{\text{int}} = \frac{N}{4} \left[ J(r_{13}) + J(r_{24}) - 4J(r_{12}) \right] + \frac{N}{4} \left[ J(r'_{13}) + J(r'_{24}) + 2(J(r''_{13}) + J(r''_{24})) - 4J(r'_{12}) \right],
$$

where the first term describes interactions inside the cluster and the second one is responsible for interaction energy.

Using the same parametrization of shift components $u_x, u_y$ as in (17) we express all the intermolecular distances (see Fig.3) in the expression (26) in terms of $\varphi, a$ as follows:

$$
r'_{12} = a\sqrt{(2\cos \varphi_0 - \cos \varphi)^2 + (2\sin \varphi_0 - \sin \varphi)^2},
$$

$$
r'_{13} = 2a(\cos \varphi_0 - \cos \varphi), \quad r''_{13} = 2a\sqrt{\cos^2 \varphi_0 + (\sin \varphi_0 - \sin \varphi)^2},
$$

$$
r'_{24} = 2a(\sin \varphi_0 - \sin \varphi), \quad r''_{24} = 2a\sqrt{\sin^2 \varphi_0 + (\cos \varphi_0 - \cos \varphi)^2}.
$$

Analysis of the expressions (2), (26) shows that the conditions of minimum $\partial \Phi / \partial \varphi = 0$, $\partial^2 \Phi / \partial \varphi^2 > 0$ for AFM state are satisfied for $\varphi = \varphi_0$, $r'_{12} = r_{12}$, $r'_{13} = r''_{13} = r_0$, $r'_{24} = r''_{24} = r_0$, as can be seen from the following relations

$$
\frac{\partial \Phi}{\partial \varphi} = Na \left[ J'(r_{12}) \frac{2 \sin(\varphi_0 - \varphi)}{\sqrt{5 - 4 \cos(\varphi - \varphi_0)}} + J'(r_{24}) \frac{\sin \varphi (\cos \varphi_0 - \cos \varphi)}{\sqrt{\sin^2 \varphi_0 + (\cos \varphi_0 - \cos \varphi)^2}} \right] + J'(r_{13}) \frac{\cos \varphi (\sin \varphi - \sin \varphi_0)}{\cos^2 \varphi_0 + (\sin \varphi_0 - \sin \varphi)^2} + 2a^2 K(k_T) \sin(\varphi - \varphi_0) = 0
$$

$$
\frac{\partial^2 \Phi}{\partial \varphi^2} = Na \left[ J'(r_{24}) \sin \varphi_0 + J'(r_{13}) \cos \varphi_0 - 2J'(r'_{12}) \right] + 2a^2 K(k_T) > 0.
$$

Inequality (29) is obviously satisfied due to the already mentioned fact that the exchange integral is a positive and monotonically decreasing function of intermolecular distance.

So, in AFM state the crystal lattice is stable with respect to distortions even in the case of vanishingly small stiffness $K(k_T)$. As in the case of $\varepsilon$-phase, it is the exchange forces that keep the lattice from distortion. In the phase with the long-range magnetic ordering the values of the “exchange bonds” pulling the O$_2$ molecules in opposite directions are equal (compare with $\varepsilon$-phase, Fig.4), and this impedes nonsymmetrical distortion of O$_8$-rhombuses.

It is also instructive to compare the magnetic energies of AFM

$$
E_{\text{AFM}} = N [J(2a \cos \varphi_0) + J(2a \sin \varphi_0) - 2J(a)],
$$

(30)
and ε-phases

\[ E_\varepsilon = \frac{N}{2}[J(\sqrt{3}a) - 3J(a)]. \]  

(31)

It is obvious that in a nondeformed hexagonal lattice (φ = 60°) \( E_\varepsilon < E_{AFM} \) for any value of \( a \). This means that the AFM state of α and δ-phases is stabilized by the long-range elastic forces that produce homogeneous deformation (striction) of crystal lattice, as it was shown in Ref. 8.

V. CONCLUSIONS

In summary, we have calculated the wave functions of singlet state implemented on the 4(O\(_2\)) cluster and found that the exchange energy of the ground state (10) is lower than that in another singlet states implemented on dimers, trimers and quaters. Interactions between next-to-nearest neighbors (i.e., between \( O_2 \) molecules located in the opposite corners of rhombuses) plays an important role in stabilization of the magnetic and crystal structure in the ground state.

We have shown that the observed distortion of crystal lattice and formation of 4(O\(_2\)) quadrates in ε-phase can be explained by strong magnetoelastic contribution into exchange energy along with the softening of \( u(k_7) \) optical phonon mode. Stability of the distorted lattice in ε-phase is then due to antiferromagnetic character of exchange interaction in solid oxygen.

The same magnetoelastic forces ensure stability of the AFM long-range phases (α, δ) with respect to inhomogeneous distortion of crystal lattice even in the case when stiffness constant of \( u(k_7) \)-mode is vanishingly small.

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24. In the absence of magnetic interactions αδ-transition can be classified as a IInd order, according to Lifshits’ criterium.
25. Disappearance of the magnetic properties of solid oxygen was experimentally proved in Ref. [19].
26. In the very recent paper Ref. [23] the authors claim that according to their quantum chemical calculations a “rhomboid O\(_8\) structure of D\(_2h\) symmetry is a stable species, that is, a local energy minimum” and point out that the ground state of a rhomboid should be a singlet spin state. On the basis of density functional calculations the authors also predict stability of the trimer structure S\(_6\) as corresponding to a local energy minimum on the potential hypersurface.
27. In contrast to homogeneous deformations, an optical mode removes degeneracy of the nearest neighbors intermolecular distance.
28. Order parameter of pra-to-β-, α- and δ- phase transitions is coupled with a transverse acoustic mode in [0001] direction.
29. In approximation of linear elasticity the sequence of steps is immaterial. An accepted sequence is convenient from methodological point of view.