PHYSICAL REVIEW B **76**, 094423 (2007)

Magnetoelastic nature of the solid oxygen ε-phase structure

H. V. Gomonay and V. M. Loktev
Bogolyubov Institute for Theoretical Physics NAS of Ukraine, Metrologichna Street 14-b, 03143, Kyiv, Ukraine

(Received 10 March 2007; revised manuscript received 11 June 2007; published 28 September 2007)

For a long time the crystal structure of the high-pressure ε phase of solid oxygen was a mystery. The results of recent experiments have solved this riddle showing that the magnetic and crystal structures of this phase can be explained by strong exchange interactions of antiferromagnetic nature. The singlet state implemented on quaters of O_2 molecules has 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 $4(O_2)$ rhombuses into almost regular quadrates. The antiferromagnetic character of exchange interactions stabilizes the distortion of the crystal lattice in the ε phase and impedes such a distortion in the long-range α and δ phases.

DOI: 10.1103/PhysRevB.76.094423 PACS number(s): 75.80.+q, 61.50.Ks, 64.70.Kb, 71.70.Gm

I. INTRODUCTION

Solid oxygen is known to occupy a particular place in the family of cryocrystals.[1] The steady interest in oxygen for almost 50 years is due to the magnetic properties of O_2 molecule which posses nonzero spin $S_{O_2}=1$ in the ground electronic state. This ensures magnetism in all solid O_2 phases.

Solid oxygen has a rather complicated phase diagram, which includes three low-temperature phases stable at ambient pressure γ ($T<43.8$ K), β ($23.8\leqslant T\leqslant 43.8$ K), and α ($T\leqslant 23.8$ K), and several high pressure phases δ, ε, and ζ (see Ref. 2 which also includes a comprehensive history of the problem). All phases except ζ-O_2 are insulators. Metallization of solid O_2 takes place at 96 GPa (Refs. 3 and 4) at room temperature. Moreover, ζ-O_2 was also observed in the superconducting state.[5]

An interesting feature of all the phases (except γ-O_2) of solid oxygen is parallel alignment of the molecules which is usually explained by strong contribution of exchange interactions into the anisotropic part (i.e., depending on the mutual orientation of molecules) of intermolecular potential. The presence of stable orientation ordering enables us to substantially simplify many of the 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 $R\bar{3}m$) β phase can be thought of as a paraphase for all the magnetic phases. In particular, β-O_2 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 β-O_2 is typical for antiferromagnets (AFMs).[6] Noncollinear three-sublattice ordering in this phase (Loktev structure) was predicted in Ref. 7 and is now generally accepted. Below 23.9 K (or at high pressure) the β phase becomes unstable and transforms into a monoclinic (space group $C2/m$) α phase. The corresponding αβ-phase transition has magnetoelastic nature associated with the strong dependence of exchange interaction vs intermolecular distance, as was shown in Ref. 8. The α phase possesses a collinear (Néel) magnetic structure with the easy direction parallel to the monoclinic axis **b** of slightly distorted lattice (compared to regular hexagonal). Long-range AFM ordering, which can be described within a simple two-sublattice model, is stabilized by the "deformation-induced splitting" of intrasublattice and intersublattice exchange integrals. It should be stressed that all the in-plane exchange constants originate from a single constant $J(\mathbf{r})$ that has AFM character [i.e., $J(\mathbf{r})>0$] is isotropic and describes intermolecular spin interactions in the β phase.[9] The mutual shift of the close-packed basal planes that accompanies formation of AFM ordering also has magnetoelastic nature and originates from the space dependence of the interplane exchange integral.[10]

Hydrostatic pressure up to 6 GPa induces continuous shift of the basal planes, while the magnetic structure of α-O_2 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 O_2 transforms into the orthorhombic (space group *Fmmm*) δ phase. The type of magnetic order in α and δ phases is similar (collinear AFM structure) within the *ab* plane, but the relative orientation of spins in the neighboring planes (between the first interplane neighbors) is different—parallel in α-O_2 and antiparallel in δ-O_2.[11] Due to the crucial change of magnetic structure (from two to four sublattice) the αδ-phase transition is classified as first order.[12] Abrupt change of magnetic order at the αδ-transition point is accompanied by discontinuous shift of the close-packed planes, which also originates from space dependence of the interplane exchange integral.

Further increase of pressure up to 8 GPa produces another phase transformation into the ε phase whose elusive structure has been determined recently.[13,14] The transition is undoubtedly first order and is accompanied by a considerable (up to 5.4%) volume reduction. The crystal structure of the ε phase is layered, as is the case for α, β, and δ phases, and has monoclinic (space group $C2/m$) symmetry. Variation of the 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 the ε phase is the association of four O_2 molecules into rhomb-shaped (according to Ref. 13) or square-shaped (according to Ref. 14) $(O_2)_4$ molecular units, which are symmetry equivalent and centered on the lattice points at (0,0,0) and (0.5,0.5,0). The common spin state of the $(O_2)_4 \equiv O_8$ cluster is nonmagnetic,[15] with the total spin $S_{O_8}=0$.

The physical reasons for such an unusual behavior of the magnetic molecular crystal are not yet clearly understood. Should the ε phase be considered as a chemically new substance? What is the nature of forces that keep $(O_2)_4$ quadrates in neighboring planes locked under high pressure? What is the role of magnetic interactions? All of these questions are still open. First-principles calculations[16] demonstrate the tendency of the O_2 molecules for dimerization and formation of herringbone-type chains but failed to prove that the $(O_2)_4$ structure has the lowest energy.Taking these results into account, in the present paper we make an attempt to elucidate the role of the exchange interactions in formation of the nonmagnetic ε phase and show how the pressure-induced variation of the exchange constants may produce strong distortion of crystal lattice.

II. INTUITIVE CONSIDERATIONS

Analysis of the magnetic and structural properties of β, α, and δ phases of solid oxygen shows[2] 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 the ε phase makes no exclusion and its complicated and surprising structure is mainly due to the strong exchange intermolecule interaction that keeps quarters of O_2 molecules as the independent chemical units, equalizes intermolecular distances within these complexes, and weakens intercluster bonds to such an extent that O_8 clusters can be approximately considered as (magnetically) noninteracting units.

From the general point of view, magnetic collapse (disappearance of magnetic properties) observed in the ε phase may result from coupling of two, three, or any other number of O_2 molecules in a singlet spin state. The tendency of the O_2 molecules to form such multimolecular clusters (consisting of two, three, and four units) was ascertained long ago in the optical spectra of the α phase, where two-, three- (at higher temperature), and four-molecule dipole transition bands were directly observed and identified.[17] Why, then, is the $4O_2$ complex more favorable[18,19] than, say, dimer $2O_2$ or trimer $3O_2$?

One possible reason for such a behavior is the weakness of van der Waals intermolecular forces in comparison with exchange interaction. As long as exchange interactions are not taken into account, O_2 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[20] (see also Refs. 1 and 2). Singlet complexes concatenated by the exchange forces and decoupled from each other may also be considered as noninteracting (or weakly interacting) solids. Dimers themselves[21] are highly anisotropic, formation of the decoupled pairs should produce additional distortion of crystal lattice [see Fig. 1(a)] so, O_4 complexes seem to be unstable with respect to formation of herringbone chains. On the contrary, $3O_2$, $4O_2$, and $7O_2$ complexes may be invariant with respect to rotation around third, fourth, or, correspondingly, sixth order symmetry axis, and so are isotropic in the basal plane. In turn, a hexagonal plane can be completed by the regular triangulars [Fig. 1(b)], 60°-angled diamonds (Fig. 2), or hexagons that by appropriate deformations may be transformed into highly symmetric n-O_2 units. The lattice distortions shown in Figs. 1 and 2 by arrows could be classified (see Table I) according to the symmetry of different optical modes.[22]

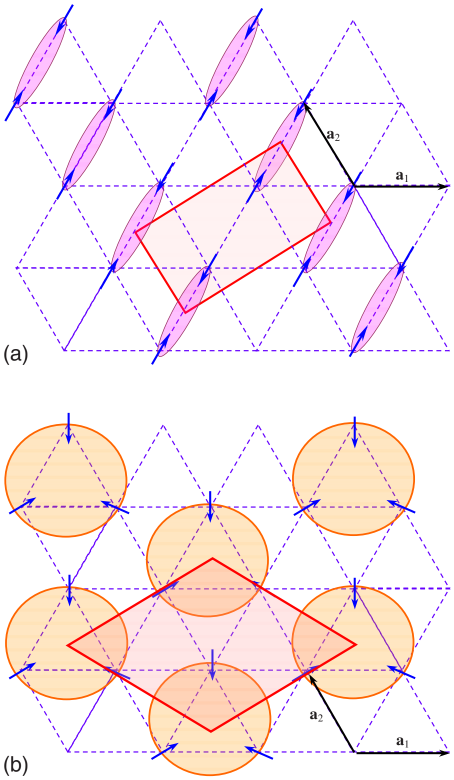


FIG. 1. (Color online) Covering of the hexagonal plane with (a) pairs and (b) triples of O_2 molecules. Arrows show directions of the molecular shift in a corresponding optical mode and the red (dark gray) parallelogram is a unit cell of the superstructure.

It is quite obvious that the 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 to anisotropic (shear) deformation of the 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 an increase of AFM exchange coupling at high pressure and the softening of the appropriate optical mode.

III. MODEL

A. Order parameter

A phenomenological description of ε-O_2 as a phase in a series of $\beta \rightarrow \alpha \rightarrow \delta \rightarrow \varepsilon$ transitions is not so straightforward

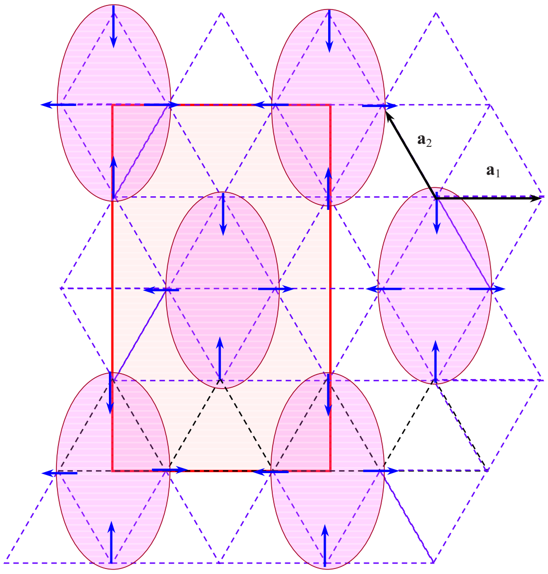
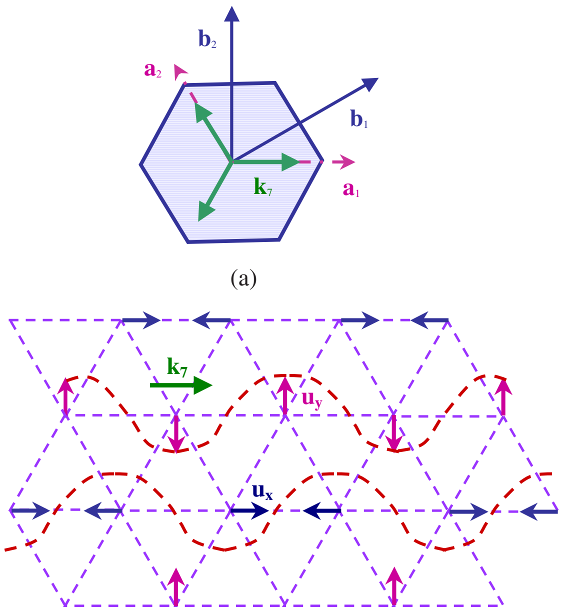


FIG. 2. (Color online) Covering of hexagonal plane with quarters (outlined with ellipses) of O_2 molecules. Arrows show directions of the molecular shift in a corresponding optical mode and the red (dark gray) rectangle is a unit cell of the superstructure.



(a)

(b)

FIG. 3. (Color online) Optical mode responsible for the pra-phase-ε-phase transition. (a) Brillouin zone in a two-dimensional reciprocal space for a hexagonal lattice. Special choice of the k_7 wave vector with $\mu=-1/4$ and corresponding rays are shown in green (thick arrows). (b) The structural order parameter is represented as a superposition of the transverse (u_y) and longitudinal (u_x) modes shifted by 1/4 period.

as that of the other magnetic phases. According to the phase diagram,[24] the 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? The three-dimensional space group of ε-O_2 coincides with that of α-O_2, though in the phase diagram both phases are separated with the high symmetry δ phase. Moreover, 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 the $\delta\varepsilon$ transition.

The easiest way to overcome these difficulties is to accept that all the magnetic phases, including ε-O_2, originate from a virtual nonmagnetic phase viewed as a stack of regular triangular planes. This assumption is based on the following facts.

(i) Crystal lattices of β, α, and δ 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 the [1100] direction.[10]

(ii) Though the O_2 lattice in ε phase is strongly distorted within the basal plane, as compared to lattice of α phase, an angle between the bonds connecting the molecules in neighboring O_8 clusters remains approximately equal to 60° in a wide interval of pressures, as seen from experiment.[14]

TABLE I. Wave vectors and polarization of optical modes coupled with different singlet states. Representatives of stars $\mathbf{k}$ are given according to Kovalev's notations (Ref. 23). Lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and reciprocal lattice vectors $\mathbf{b}_1$, $\mathbf{b}_2$ are attributed to the hexagonal pra-phase.

Number of O_2 mol.	Wave vector	Polarization vector
two-dimer	$\mathbf{k}_{12}=\mathbf{b}_1/2$	$\mathbf{a}_1+\mathbf{a}_2$
three-trimer	$\mathbf{k}_{13}=(\mathbf{b}_1+\mathbf{b}_2)/3$	$\sqrt{3}(\mathbf{a}_1+\mathbf{a}_2)+i(\mathbf{a}_1-\mathbf{a}_2)$
four-quater	$\mathbf{k}_7=\mathbf{b}_1/2-\mathbf{b}_2/4$	$u_x\sqrt{3}\mathbf{a}_1+iu_y(\mathbf{a}_1+2\mathbf{a}_2)$

From this point of view, the structural order parameter of pra-phase-ε-phase transition can be represented by the amplitudes u_x, u_y of the optical mode

$$u(\mathbf{n}) = e^{i\mathbf{b}_1\cdot\mathbf{n}/2}\left[u_x \cos\frac{\mathbf{b}_2\cdot\mathbf{n}}{4} + u_y \sin\frac{\mathbf{b}_2\cdot\mathbf{n}}{4}\right], \qquad (1)$$

where $\mathbf{n}$ denotes the position of a molecule within the basal plane.[25]

Figure 3(a) shows the position of the $k_7=\mathbf{b}_1/2+\mu\mathbf{b}_2$ vector within the first Brillouin zone in a two-dimensional reciprocal space of a hexagonal lattice. For a special value $\mu=-1/4$ both longitudinal [blue (horizontal) arrows in Fig. 3(b)] and transverse [red (vertical) arrows] k_7 modes implement the same one-dimensional irreducible representation that is compatible with the point symmetry group $(2/m)$ of the α and ε phases. The order parameter (1) can then be interpreted as a superposition of the longitudinal and transverse optical modes with the same wave vector $k_7=\mathbf{b}_1/2-\mathbf{b}_2/4$ and the mutual phase shift $\pi/2$ [see Fig. 3(b)].

A macroscopic description of the magnetic state of the ε phase may be given using spin-spin correlation functions. A 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 the [1100] direction calculated with respect to the initial nonshifted hexagonal stacking) is symmetry related to the transverse acoustic modes propagating in [0001] and [1000] directions (wave vectors parallel to $\mathbf{b}_3$ and $\mathbf{b}_1$, correspondingly).

B. Free energy and spin Hamiltonian

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

$$\begin{aligned}\Phi = {} & \frac{1}{2}\sum_j K(\mathbf{k}_j)|\mathbf{u}(\mathbf{k}_j)|^2 + \frac{c_{11}+c_{12}}{2}(u_{xx}+u_{yy})^2 \\ & + \frac{c'}{2}[(u_{xx}-u_{yy})^2 + 4u_{xy}^2] + P(u_{xx}+u_{yy}) \\ & + \sum_j \lambda_{\mathrm{ph}}^{(\mathrm{iso})}(\mathbf{k}_j)|\mathbf{u}(\mathbf{k}_j)|^2(u_{xx}+u_{yy}) \\ & + \lambda_{\mathrm{ph}}^{(\mathrm{an})}(\mathbf{k}_7)[u_x^2(\mathbf{k}_7) - u_y^2(\mathbf{k}_7)](u_{xx}-u_{yy}) + E_{\mathrm{mag}}. \qquad (2)\end{aligned}$$

Vectors $\mathbf{k}_j$ in the above expression denote different wave vectors, classified according to irreducible representations of $6/mmm$ space group, phenomenological constants $K(\mathbf{k}_j)$ describe nonmagnetic contribution into the corresponding phonon frequencies, and coefficients $\lambda_{\mathrm{ph}}(\mathbf{k}_j)$ originate from the crystal anharmonicity and describe nontrivial coupling between phonon amplitude and crystal lattice parameters. The last term in Eq. (2) accounts for the (external) hydrostatic pressure P.

While the origin of the first term in Eq. (2) is quite obvious (potential energy of the corresponding oscillations in a harmonic approximation), the form of the coupling term with $\lambda_{\mathrm{ph}}^{(\mathrm{an})}(\mathbf{k}_7)$ needs additional explanations. As was already mentioned, the special choice of the wave vector k_7 (with $\mu = -1/4$) corresponds to a mode in which rotational symmetry (point group $2/m$) coincides with the symmetry of the α and ε phases. Homogeneous elongation and contraction of crystal lattice described by the strain component $u_{xx}-u_{yy}$ has the same symmetry properties. As a result, the term with $\lambda_{\mathrm{ph}}^{(\mathrm{an})} \times (\mathbf{k}_7)$ is invariant with respect to the symmetry operations of $6/mmm$ pra-phase space group and describes deformation of crystal lattice that could be produced by the mutual shifts of O_2 molecules during transition into the ε phase.

Magnetic contribution E_{mag} is calculated as an average of spin Hamiltonian $\hat{\mathcal{H}}$ over a ground state $|\Psi\rangle$ of the crystal $E_{\mathrm{mag}} = \langle \Psi | \hat{\mathcal{H}} | \Psi \rangle$, where

$$\hat{\mathcal{H}} = \sum_{\mathbf{n},\mathbf{m}} J(\mathbf{r}_{\mathbf{n},\mathbf{m}}) \hat{\mathbf{S}}_{\mathbf{n}} \cdot \hat{\mathbf{S}}_{\mathbf{m}}, \qquad (3)$$

and summation is accomplished over the nearest and next to the nearest neighbors separated by distance $|\mathbf{r}_{\mathbf{n},\mathbf{m}}|$. Magnetoelastic part of the internal energy is derived from the expression (3) with due account of space dependence of the exchange integral $J(\mathbf{r}_{\mathbf{n},\mathbf{m}})$.

Once the ground state of the 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 was already mentioned, β and α phases posses a kind of the Néel spin ordering that can be described macroscopically by assigning an average value $\langle \mathbf{S}_{\mathbf{n}} \rangle$ to the spin vector at each site.

A ground state $|\Psi_\varepsilon\rangle$ of the ε phase is a true eigenfunction of spin-Hamiltonian (3) and is calculated within the assumption of magnetically decoupled O_8 clusters. In other words, $|\Psi_\varepsilon\rangle$ may be represented as an unentangled combination of quaters wave functions $|\psi_{\mathbf{n}}\rangle$, that satisfies equation

$$\hat{\mathcal{H}}^{(\mathrm{intra})}|\Psi_\varepsilon\rangle = E^{(\mathrm{intra})}|\Psi_\varepsilon\rangle, \quad |\Psi_\varepsilon\rangle \equiv \prod_{\mathbf{n}} |\psi_{\mathbf{n}}\rangle, \qquad (4)$$

with the Hamiltonian of intracluster interactions written as

$$\begin{aligned}\hat{\mathcal{H}}^{(\mathrm{intra})} = {} & \sum_{\mathbf{n}} \{J(\mathbf{r}_{12})[\hat{\mathbf{S}}_{1\mathbf{n}} \cdot \hat{\mathbf{S}}_{2\mathbf{n}} + \hat{\mathbf{S}}_{2\mathbf{n}} \cdot \hat{\mathbf{S}}_{3\mathbf{n}} + \hat{\mathbf{S}}_{3\mathbf{n}} \cdot \hat{\mathbf{S}}_{4\mathbf{n}} \\ & + \hat{\mathbf{S}}_{4\mathbf{n}} \cdot \hat{\mathbf{S}}_{1\mathbf{n}}] + J(\mathbf{r}_{13})\hat{\mathbf{S}}_{1\mathbf{n}} \cdot \hat{\mathbf{S}}_{3\mathbf{n}} + J(\mathbf{r}_{24})\hat{\mathbf{S}}_{2\mathbf{n}} \cdot \hat{\mathbf{S}}_{4\mathbf{n}}\}. \qquad (5)\end{aligned}$$

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. 4). The choice of the unit cell corresponds to one of three different domains of the α phase. The positions of the individual O_2 molecules (labeled with number 1, 2, 3, 4) within the cluster are defined with the basis vectors $\pm\tau_1 \equiv \pm\mathbf{a}_1$ and $\pm\tau_2 \equiv \pm\mathbf{a}_2$.

The interaction between the clusters with account of the next-to-nearest neighbors is described by operator $\mathcal{H}^{(\mathrm{inter})}$ (see Fig. 4 for notations)

$$\begin{aligned}\hat{\mathcal{H}}^{(\mathrm{inter})} = {} & \frac{1}{2}\sum_{\mathbf{n}} \{J(\mathbf{r}_{12}')[\hat{\mathbf{S}}_{1\mathbf{n}}(\hat{\mathbf{S}}_{2(\mathbf{n}-\tau_1)} + \hat{\mathbf{S}}_{4(\mathbf{n}+\tau_2)}) \\ & + \hat{\mathbf{S}}_{3\mathbf{n}}(\hat{\mathbf{S}}_{2(\mathbf{n}-\tau_2)} + \hat{\mathbf{S}}_{4(\mathbf{n}+\tau_1)}) + \hat{\mathbf{S}}_{2\mathbf{n}}(\hat{\mathbf{S}}_{1(\mathbf{n}+\tau_1)} + \hat{\mathbf{S}}_{3(\mathbf{n}+\tau_2)}) \\ & + \hat{\mathbf{S}}_{4\mathbf{n}}(\hat{\mathbf{S}}_{1(\mathbf{n}-\tau_2)} + \hat{\mathbf{S}}_{3(\mathbf{n}-\tau_1)})] \\ & + J(\mathbf{r}_{13}')(\hat{\mathbf{S}}_{1\mathbf{n}} \cdot \hat{\mathbf{S}}_{3(\mathbf{n}+\tau_1-\tau_2)} + \hat{\mathbf{S}}_{3\mathbf{n}} \cdot \hat{\mathbf{S}}_{1(\mathbf{n}-\tau_1+\tau_2)}) \\ & + J(\mathbf{r}_{24}'')[\hat{\mathbf{S}}_{1\mathbf{n}}(\hat{\mathbf{S}}_{3(\mathbf{n}+\tau_1+\tau_2)} + \hat{\mathbf{S}}_{3(\mathbf{n}-\tau_1-\tau_2)})\end{aligned}$$

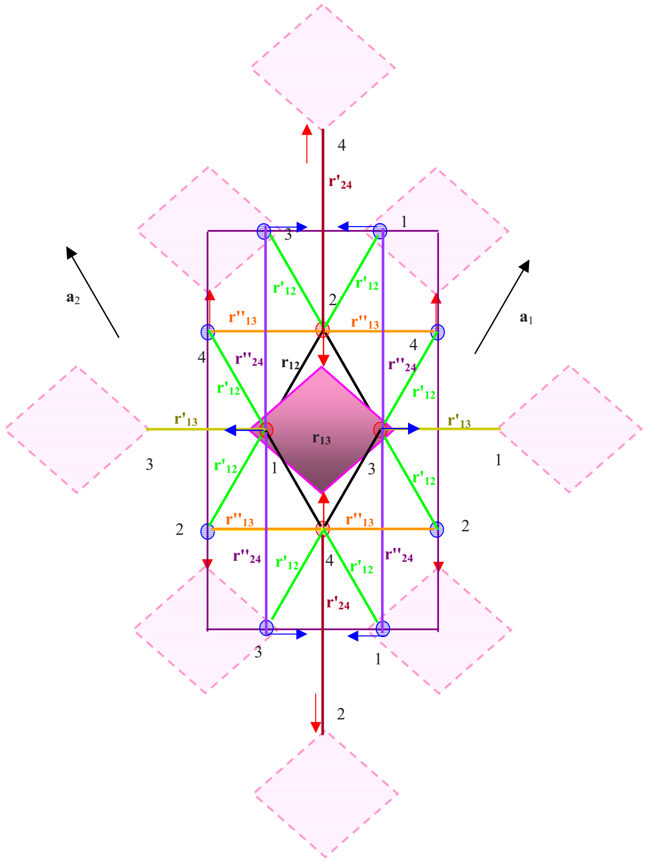


FIG. 4. (Color online) Primitive cell of the ε phase. Magnetically coupled quaters of molecules are outlined by quadrates. Red (vertical) and blue (horizontal) arrows show the shift of O_2 molecules in the course of phase transition. Vectors $\mathbf{a}_{1,2}$ are the Brave lattice vectors of the hexagonal pra-phase.

$$+\hat{\mathbf{S}}_{3\mathbf{n}}(\hat{\mathbf{S}}_{1(\mathbf{n}+\tau_1+\tau_2)}+\hat{\mathbf{S}}_{1(\mathbf{n}-\tau_1-\tau_2)})]$$

$$+J(\mathbf{r}''_{13})[\hat{\mathbf{S}}_{2\mathbf{n}}(\hat{\mathbf{S}}_{4(\mathbf{n}+\tau_1-\tau_2)}+\hat{\mathbf{S}}_{4(\mathbf{n}-\tau_1+\tau_2)})$$

$$+\hat{\mathbf{S}}_{4\mathbf{n}}(\hat{\mathbf{S}}_{2(\mathbf{n}+\tau_1-\tau_2)}+\hat{\mathbf{S}}_{2(\mathbf{n}-\tau_1+\tau_2)})]$$

$$+J(\mathbf{r}'_{24})[\ \hat{\mathbf{S}}_{2\mathbf{n}}\cdot\hat{\mathbf{S}}_{4(\mathbf{n}+\tau_1+\tau_2)}+\hat{\mathbf{S}}_{4\mathbf{n}}\cdot\hat{\mathbf{S}}_{2(\mathbf{n}-\tau_1-\tau_2)})]\}, \qquad (6)$$

so that spin Hamiltonian (3) is represented as a sum:

$$\hat{\mathcal{H}}=\hat{\mathcal{H}}^{(\mathrm{intra})}+\hat{\mathcal{H}}^{(\mathrm{inter})}. \qquad (7)$$

In the ε phase the first term in Eq. (7) is responsible for the formation of the ground state, while the second one describes the contribution that arises from excitations. In α, δ, and β phases both terms contribute equally to the magnetic energy of the crystal.

IV. ε 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 the spin state ψ of the O_8 cluster in terms of the eigenfunctions $|0\rangle$, $|\pm 1\rangle$ of spin operators $\hat{S}_j^Z$, where Z is a quantization axis.

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

$$\left(\sum_{j=1}^{4}\hat{\mathbf{S}}_j\right)^2\psi_{\mathrm{singlet}}=0, \qquad \sum_{j=1}^{4}\hat{S}_j^Z\psi_{\mathrm{singlet}}=0. \qquad (8)$$

Obviously, the ψ_{singlet} is also an eigenfunction of Hamiltonian $\hat{\mathcal{H}}^{(\mathrm{intra})}$.

Additional simplification of the problem may be achieved using the 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 eigenvalues of operators (see Table II)

$$\hat{P}_1\equiv(\hat{\mathbf{S}}_1,\hat{\mathbf{S}}_2)+(\hat{\mathbf{S}}_2,\hat{\mathbf{S}}_3)+(\hat{\mathbf{S}}_3,\hat{\mathbf{S}}_4)+(\hat{\mathbf{S}}_4,\hat{\mathbf{S}}_1),$$

$$\hat{P}_2\equiv(\hat{\mathbf{S}}_1,\hat{\mathbf{S}}_3), \quad \hat{P}_3\equiv(\hat{\mathbf{S}}_2,\hat{\mathbf{S}}_4). \qquad (9)$$

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

$$\begin{aligned}\psi_{\mathrm{gr}}^{(\mathrm{singlet})}={}&\frac{1}{\sqrt{5}}(|1\bar{1}1\bar{1}\rangle+|\bar{1}1\bar{1}1\rangle)+\frac{1}{3\sqrt{5}}\Bigg[2|0000\rangle+|010\bar{1}\rangle\\&+|10\bar{1}0\rangle+|0\bar{1}01\rangle+|\bar{1}010\rangle-\frac{3}{2}(|001\bar{1}\rangle+|01\bar{1}0\rangle\\&+|1\bar{1}00\rangle+|\bar{1}001\rangle+|00\bar{1}1\rangle+|0\bar{1}10\rangle+|\bar{1}100\rangle\\&+|100\bar{1}\rangle)+\frac{1}{2}(|11\bar{1}\bar{1}\rangle+|\bar{1}\bar{1}11\rangle+|1\bar{1}\bar{1}1\rangle+|\bar{1}11\bar{1}\rangle)\Bigg],\end{aligned} \qquad (10)$$

TABLE II. Eigenvalues of operators $\hat{P}_1$, $\hat{P}_2$, $\hat{P}_3$ in a singlet subspace, cluster energy $\langle\hat{\mathcal{H}}^{(\mathrm{intra})}\rangle/N$ per molecule for arbitrary intermolecular spacing, equilibrium angle φ between intermolecular bonds within the cluster, and corresponding equilibrium energy E_ε per molecule.

Function	$\hat{P}_1$	$\hat{P}_{2,3}$	$\langle\hat{\mathcal{H}}^{(\mathrm{intra})}\rangle/N$	φ_{eq}	E_ε
$\psi_{\mathrm{gr}}^{(\mathrm{singlet})}$	-6	1	$[J(\mathbf{r}_{13})+J(\mathbf{r}_{24})-6J(\mathbf{r}_{12})]/4$	$\pi/4$	$[J(\sqrt{2}a)-3J(a)]/2$
$\psi_{\mathrm{ex1}}^{(\mathrm{singlet})}$	-4	0	$-J(\mathbf{r}_{12})$	arb.	$-J(a)$
$\psi_{\mathrm{ex2}}^{(\mathrm{singlet})}$	0	-2	$-[J(\mathbf{r}_{13})+J(\mathbf{r}_{24})]/2$	$\pi/4$	$-J(\sqrt{2}a)$

$$\psi_{\text{ex1}}^{(\text{singlet})} = \frac{1}{2\sqrt{3}}[|1\bar{1}00\rangle + |001\bar{1}\rangle + |\bar{1}100\rangle + |00\bar{1}1\rangle + |11\bar{1}\bar{1}\rangle + |\bar{1}\bar{1}11\rangle - |1\bar{1}\bar{1}1\rangle - |\bar{1}11\bar{1}\rangle - |100\bar{1}\rangle - |01\bar{1}0\rangle - |\bar{1}001\rangle - |0\bar{1}10\rangle], \tag{11}$$

$$\psi_{\text{ex2}}^{(\text{singlet})} = \frac{1}{3}[|11\bar{1}\bar{1}\rangle + |\bar{1}\bar{1}11\rangle + |1\bar{1}\bar{1}1\rangle + |\bar{1}11\bar{1}\rangle + |0000\rangle - |010\bar{1}\rangle - |0\bar{1}01\rangle - |10\bar{1}0\rangle - |\bar{1}010\rangle]. \tag{12}$$

In order to find out what of three functions (10)–(12) describes the ground state of Hamiltonian (7), we compare corresponding eigenvalues (see Table II, fourth column). Taking into account the antiferromagnetic character of the exchange interaction $[J(\mathbf{r})>0]$, the fact that $J(\mathbf{r})$ monotonically decreases with intermolecular distance r and geometrical relation $r_{12} \leqslant r_{13} < r_{24}$, one can easily verify that

$$\langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{gr}} < \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{ex1}} < \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{ex2}}, \tag{13}$$

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

It is interesting to compare $\psi_{\text{gr}}^{(\text{singlet})}$ with the AFM Néel state observed in the α phase, where all the nearest neighbors are coupled antiferromagnetically. In terms of O_2 spin states this means that the most preferable combinations are $|1\bar{1}1\bar{1}\rangle$ and $|\bar{1}1\bar{1}1\rangle$. States $\psi_{\text{singlet}}^{(\text{ex1,2})}$ are orthogonal to a subspace spanned over the "Néel-state" vectors $|1\bar{1}1\bar{1}\rangle$ and $|\bar{1}1\bar{1}1\rangle$. On the contrary, $\psi_{\text{gr}}^{(\text{singlet})}$ belongs to this subspace with 0.4 probability.

We may also compare eigenvalues of Hamiltonian (7) in a singlet state for different clusters: hypothetical dimer, trimer, and the 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 eigenvalues of Hamiltonian (that could be found without explicit expression for wave function) are

$$\langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{dim}} = -NJ(\mathbf{r}_{12}) \text{ for dimer,}$$

$$\langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{trim}} = -N\left[\frac{2}{3}J(\mathbf{r}_{12}) + \frac{1}{3}J(\mathbf{r}_{13})\right] \text{ for trimer,} \tag{14}$$

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

$$\langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{gr}}^{(\text{singlet})} < \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{dim}} = \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{ex1}}^{(\text{singlet})} \leqslant \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{trim}} < \langle \hat{\mathcal{H}}^{(\text{intra})} \rangle_{\text{ex2}}^{(\text{singlet})}. \tag{15}$$

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 $n=4$.

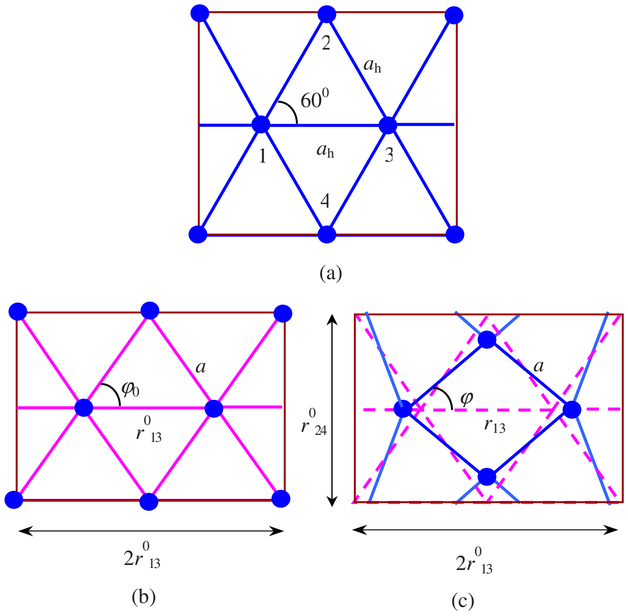


FIG. 5. (Color online) Two-step distortion of the crystal lattice of hexagonal pra-phase (a): (i) homogeneous deformation (b); (ii) inhomogeneous distortion of rhombus (c).

B. Distortion of crystal lattice

It was already mentioned that magnetic interactions in solid oxygen are so strong that they cause a large distortion of the crystal lattice. This effect was observed, e.g., in the course of $\alpha\beta$ transitions, where in-plane lattice deformation achieved nearly 5%.[26] 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.

The in-plane structure of the ε phase can be considered as a result of two-step distortion[27] of the ideal hexagonal basal plane of pra-phase (β-) with the lattice constant a_h (see Fig. 5): (i) homogeneous deformation which changes scales in X and Y directions

$$r_{13}^{(0)} = a_h(1+u_{xx}), \quad r_{24}^{(0)} = \sqrt{3}a_h(1+u_{yy}) \tag{16}$$

and (ii) inhomogeneous distortion of the 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.

The 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 φ between the directions to nearest neighbors $r_{13}=2a\cos\varphi$, $r_{24}=2a\sin\varphi$, and

$$u_x = a\cos\varphi - \frac{1}{2}r_{13}^{(0)} \equiv a(\cos\varphi - \cos\varphi_0),$$

$$u_y = \frac{1}{2}r_{24}^{(0)} - a\sin\varphi = a(\sin\varphi_0 - \sin\varphi), \tag{17}$$

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 O_2 molecules in the ε phase are then calculated by minimization of Gibbs' free energy (2) with respect to the components of deformation tensor u_{jk} and angle φ. The last term E_{mag} is the magnetic energy in the singlet ground state

$$E_{\text{mag}} = \frac{N}{4}[J(\mathbf{r}_{13}) + J(\mathbf{r}_{24}) - 6J(\mathbf{r}_{12})]. \tag{18}$$

Thus, expression (2) can be rewritten as

$$\begin{aligned}\Phi = {}& \frac{1}{2}(c_{11}+c_{12})(u_{xx}+u_{yy})^2 + \frac{1}{2}c'[(u_{xx}-u_{yy})^2 + 4u_{xy}^2] \\ & + P(u_{xx}+u_{yy}) + 2a^2\sin^2\frac{\varphi-\varphi_0}{2}[K(\mathbf{k}_7) + \lambda_{\text{ph}}^{(\text{iso})}(\mathbf{k}_7)(u_{xx} \\ & + u_{yy}) - \lambda_{\text{ph}}^{(\text{an})}(\mathbf{k}_7)\cos(\varphi+\varphi_0)(u_{xx}-u_{yy})] \\ & + \frac{N}{4}[J(2a\sin\varphi) + J(2a\cos\varphi) - 6J(a)].\end{aligned} \tag{19}$$

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 φ:

$$\frac{dJ(r_{13})}{dr}\cos\varphi + \frac{dJ(r_{24})}{dr}\sin\varphi + \frac{4K(\mathbf{k}_7)a}{N}\sin(\varphi-\varphi_0) = 0. \tag{20}$$

Constant $K(\mathbf{k}_7)$ describes the contribution into intermolecular bonds which arises from weak Van der Waals forces[28] so that $K(\mathbf{k}_7)a^2 \ll a|dJ(r)/dr|N$ and we can neglect the last term in Eq. (20). Then, Eq. (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 quadrate 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 the opposite spins and thus are attracted to each other, due to the antiferromagnetic character of the exchange forces. On the contrary, the molecules in the opposite corners (pairs 13 and 24) have parallel spins and are therefore repulsed. For a fixed value of the attraction force (and for a fixed nearest-neighbor distance) the energy of repulsion reaches its minimum at the maximal average distant between corresponding molecules. This can be achieved in a symmetrical combination similar to a quadrate. Small deflection (e.g., 96° and 84° at 17.6 GPa) from the right angle observed in the experiment[13] may be calculated from Eq. (20) with account of the contribution from the optical mode

$$\varphi = \frac{\pi}{4} - \frac{4\sqrt{2}K(\mathbf{k}_7)a\sin(\pi/4-\varphi_0)}{NJ'(r_{13})}. \tag{21}$$

A rough estimation of the $K(\mathbf{k}_7)$ value can be done on the basis of structural data for the ε phase. According to Ref. 14, $\varphi_0 \equiv \arctan(r_{24}^{(0)}/r_{13}^{(0)})=53°$. Using the most elaborated phenomenological form[29,30] of space dependence for

$$J(r) = J_0\exp[-\alpha(r-r_0) + \beta(r-r_0)^2], \quad 2.6 \leqslant r \leqslant 4.2, \tag{22}$$

with $J_0=60$ K, $\alpha=3.5$ Å^{-1}, $\beta=1.2$ Å^{-2}, $r_0=3.1854$ Å, and taking $a=2.18$ Å,[13,14] we get an upper limit for $K(\mathbf{k}_7)/N \leqslant 9.2$ K/Å^2, while an estimated value of $J'(r_{13})/a \geqslant 80$ K/Å^2. Considering K as a stiffness constant of intermolecular bonds, one obtains the characteristic frequency 16.2 cm^{-1} which is smaller than the frequencies of optical modes ($\geqslant$300 cm^{-1}) calculated in Ref. 16. On the other hand, characteristic value of the magnetoelastic constant $J'(r_{13})a \propto 370$ cm^{-1}. So, it may be assumed that the magnetoelastic interactions contribute strongly to the optical phonon modes related with the mutual shift of O_2 molecules within the quaters.

The stability condition of the "quadrate" solution

$$\frac{d^2J(r)}{dr^2} + \frac{2K(\mathbf{k}_7)}{N}\cos(\pi/4-\varphi_0) > 0 \tag{23}$$

is obviously satisfied, because according to Ref. 2 $J(r)$ is a monotonically decreasing concave function [see, e.g., Eq. (22)] of intermolecular distance, and $K(\mathbf{k}_7)>0$ (from the condition of crystal lattice stability).

So, even in magnetically neutral state the exchange interactions play a role of a motive force that crucially changes the angle φ 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:

$$u_{xx}-u_{yy} = \frac{2a^2\lambda_{\text{ph}}^{(\text{an})}(\mathbf{k}_7)}{c'}\cos(\pi/4+\varphi_0),$$

$$u_{xx}+u_{yy} = -\frac{1}{c_{11}+c_{12}}\left[P + 2\lambda_{\text{ph}}^{(\text{iso})}(\mathbf{k}_7)a^2\sin^2\frac{\pi/4-\varphi_0}{2}\right]. \tag{24}$$

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 the ε phase is due solely to anharmonicity [coupling constant $\lambda_{\text{ph}}^{(\text{an})}(\mathbf{k}_7)$] of the crystal lattice. Isotropic striction $u_{xx}+u_{yy}$ describes the relative change of the in-plane square. From the pressure dependence of lattice parameters[13] we can estimate the in-plane compressive modulus $c_{11}+c_{12}=88$ GPa. From the value of jump of isotropic striction in the $\delta\varepsilon$-transition point $\Delta(u_{xx}+u_{yy})=0.019$ we estimate isotropic anharmonicity constant $\lambda_{\text{ph}}^{(\text{iso})}(\mathbf{k}_7)=1.1\times10^5$ K/Å^2.

V. COMPARISON WITH α AND δ PHASES

In the previous section it was shown that once the singlet ground state is formed, the crystal lattice should be distorted in a described manner, due to strong exchange interactions and reduced optical phonon frequency. However, what about the inverse mechanism? Can the crystal lattice of the δ (α phase) be unstable with respect to $u(\mathbf{k}_7)$ distortions?

To answer this question, we minimize Gibb's potential (2) assuming the presence of the collinear long-range AFM order. In this case $\langle \hat{S}_n^2 \rangle = 2$, $\langle \hat{S}_n^Z \rangle = \pm 1$ at a site $\mathbf{R}_\mathbf{n}$, and spin polarization alters from 1 to -1 when shifted through the vectors $\mathbf{a}_1$, $\mathbf{a}_2$. Taking into account the locations of molecules 1–4 (see Fig. 4), it can be easily seen that

$$\langle \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2 \rangle = \langle \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_3 \rangle = \langle \hat{\mathbf{S}}_3 \cdot \hat{\mathbf{S}}_4 \rangle = \langle \hat{\mathbf{S}}_4 \cdot \hat{\mathbf{S}}_1 \rangle = -1,$$

$$\langle \hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_3 \rangle = \langle \hat{\mathbf{S}}_2 \cdot \hat{\mathbf{S}}_4 \rangle = 1. \tag{25}$$

Substituting these values into Eq. (7) we obtain an expression for the magnetic energy E_{AFM} of the AFM state:

$$E_{\mathrm{mag}} \equiv E_{\mathrm{AFM}} = E_{\mathrm{AFM}}^{\mathrm{cluster}} + E_{\mathrm{AFM}}^{\mathrm{int}} = \frac{N}{4}[J(r_{13}) + J(r_{24}) - 4J(r_{12})] + \frac{N}{4}\{J(r'_{13}) + J(r'_{24}) + 2[J(r''_{13}) + J(r'_{24})] - 4J(r'_{12})\}, \tag{26}$$

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 Eq. (17) we express all the intermolecular distances (see Fig. 4) in the expression (26) in terms of φ, a as follows:

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

$$r'_{13} = 2a(2\cos\varphi_0 - \cos\varphi),$$

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

$$r'_{24} = 2a(2\sin\varphi_0 - \sin\varphi),$$

$$r''_{24} = 2a\sqrt{\sin^2\varphi_0 + (\cos\varphi_0 - \cos\varphi)^2}. \tag{27}$$

Analysis of the expressions (2) and (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 $\varphi = \varphi_0$, $r'_{12} = r_{12}$, $r'_{13} = r''_{13} = r_{13}^{(0)}$, $r'_{24} = r''_{24} = r_{24}^{(0)}$, as can be seen from the following relations:

$$\frac{\partial\Phi}{\partial\varphi} = Na\left[J'(r'_{12})\frac{2\sin(\varphi_0 - \varphi)}{\sqrt{5 - 4\cos(\varphi - \varphi_0)}} + J'(r_{24})\frac{\sin\varphi(\cos\varphi_0 - \cos\varphi)}{\sqrt{\sin^2\varphi_0 + (\cos\varphi_0 - \cos\varphi)^2}} + J'(r_{13})\frac{\cos\varphi(\sin\varphi - \sin\varphi_0)}{\sqrt{\cos^2\varphi_0 + (\sin\varphi_0 - \sin\varphi)^2}}\right] + 2a^2K(\mathbf{k}_7)\sin(\varphi - \varphi_0) = 0, \tag{28}$$

$$\frac{\partial^2\Phi}{\partial\varphi^2} = Na[J'(r_{24})\sin\varphi_0 + J'(r_{13})\cos\varphi_0 - 2J'(r'_{12})] + 2a^2K(\mathbf{k}_7) > 0. \tag{29}$$

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 the AFM state the crystal lattice is stable with respect to distortions even in the case of vanishingly small stiffness $K(\mathbf{k}_7)$. As in the case of the ε 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 ε phase, Fig. 5), and this impedes nonsymmetrical distortion of O_8 rhombuses.

It is also instructive to compare the magnetic energies of AFM

$$E_{\mathrm{AFM}} = N[J(2a\cos\varphi_0) + J(2a\sin\varphi_0) - 2J(a)] \tag{30}$$

and ε phases

$$E_\varepsilon = \frac{N}{2}[J(\sqrt{2}a) - 3J(a)]. \tag{31}$$

It is obvious that in a nondeformed hexagonal lattice ($\phi_0 = 60°$) $E_\varepsilon < E_{\mathrm{AFM}}$ 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 was shown in Ref. 8.

VI. 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 the ε phase can be explained by strong magnetoelastic contribution into exchange energy along with the softening of $u(\mathbf{k}_7)$ 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 the $u(\mathbf{k}_7)$ mode is vanishingly small.

ACKNOWLEDGMENT

The authors would like to acknowledge H. J. Jodl for fruitful discussions and interest in their work.

[1] *Cryocrystals*, edited by B. I. Verkin and A. F. Prikhot'ko (Naukova Dumka, Kyiv, 1983).

[2] Y. A. Freiman and H. J. Jodl, Phys. Rep. **401**, 1 (2004).

[3] S. Desgreniers, Y. Vohra, and A. Ruoff, J. Phys. Chem. **94**, 1117 (1990).

[4] Y. Akahama, H. Kawamura, D. Häusermann, M. Hanfland, and O. Shimomura, Phys. Rev. Lett. **74**, 4690 (1995).

[5] K. Shimizu, K. Suhara, M. Ikumo, M. I. Eremets, and K. Amaya, Nature (London) **393**, 767 (1998).

[6] A. S. Borovik-Romanv, M. P. Orlova, and P. G. Strelkov, Dokl. Akad. Nauk SSSR **99**, 699 (1954).

[7] V. M. Loktev, Sov. J. Low Temp. Phys. **5**, 142 (1979).

[8] Y. B. Gaididei and V. M. Loktev, Sov. J. Low Temp. Phys. **7**, 1305 (1981).

[9] Y. B. Gaididei and V. M. Loktev, Sov. Phys. Solid State **16**, 2226 (1975).

[10] H. V. Gomonay and V. M. Loktev, Low Temp. Phys. **31**, 763 (2005).

[11] I. N. Goncharenko, O. L. Makarova, and L. Ulivi, Phys. Rev. Lett. **93**, 055502 (2004).

[12] In the absence of magnetic interactions the $\alpha\delta$ transition can be classified as a second order, according to Liftshits' criterium.

[13] L. F. Lundegaard, G. Weck, M. I. McMahon, S. Desgreniers, and P. Loubeyre, Nature (London) **443**, 201 (2006).

[14] H. Fujihisa, Y. Akahama, H. Kawamura, Y. Ohishi, O. Shimomura, H. Yamawaki, M. Sakashita, Y. Gotoh, S. Takeya, and K. Honda, Phys. Rev. Lett. **97**, 085503 (2006).

[15] Disappearence of the magnetic properties of solid oxygen was experimentally proved in Ref. 24.

[16] J. B. Neaton and N. W. Ashcroft, Phys. Rev. Lett. **88**, 205503 (2002).

[17] Y. Gaididei, L. Glushkov, V. Loktev, V. Pavloschuk, A. Prikhotko, and L. Shanskii, Sov. J. Low Temp. Phys. **3**, 368 (1977).

[18] In the very recent paper Ref. 19 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.

[19] R. Steudel and M. W. Wong, Angew. Chem., Int. Ed. **146**, 1768 (2007).

[20] C. A. English and J. A. Venables, Proc. R. Soc. London, Ser. A **340**, 57 (1974).

[21] F. A. Gorelli, L. Ulivi, M. Santoro, and R. Bini, Phys. Rev. B **63**, 104110 (2001).

[22] In contrast to homogeneous deformations, an optical mode removes degeneracy of the nearest-neighbor intermolecular distance.

[23] O. V. Kovalev, *Irreducible Representations and Corepresentations of the Fedorov' Groups* (Nauka, Moscow, 1986), p. 386.

[24] I. N. Goncharenko, Phys. Rev. Lett. **94**, 205701 (2005).

[25] Order parameter of pra-to-β-, α-, and δ-phase transitions is coupled with a transverse acoustic mode in [0001] direction.

[26] I. Krupskii, A. Prokhvatilov, Y. Freiman, and A. Erenburg, Sov. J. Low Temp. Phys. **5**, 130 (1979).

[27] In approximation of linear elasticity the sequence of steps is immaterial. An accepted sequence is convenient from methodological point of view.

[28] In the phases with long-range magnetic ordering (α, δ phases) the main contribution into the optical phonon frequencies arises from the exchange interactions.

[29] R. D. Etters, K. Kobashi, and J. Belak, Phys. Rev. B **32**, 4097 (1985).

[30] R. LeSar and R. D. Etters, Phys. Rev. B **37**, 5364 (1988).