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Magnetic structures of δ-O_2 resulting from competition of interplane exchange interactions

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Solid oxygen is a unique molecular crystal whose phase diagram is mostly imposed by the magnetic ordering, i.e., each crystal phase (except γ-O_2) has a specific magnetic structure. However, recent experiments showed that high-pressure δ phase is realized in different magnetic structures. In the present paper we study the role of interplane exchange interactions in formation of the magnetic structures with the different stacking sequences of the close-packed planes. We show that the temperature-induced variation in intermolecular distances can give rise to compensation of the exchange coupling between the nearest close-packed planes and result in the phase transition between different magnetic structures within δ-O_2. Variation in the magnetic ordering is, in turn, accompanied by stepwise variation in interplane distance governed by spatial and angular dependence of the interplane exchange constants.

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I. INTRODUCTION

Solid oxygen is known to occupy a particular place in the large family of cryocrystals. First, it is the only molecular crystal that shows magnetic ordering in a wide range of temperatures and pressures.[1] On the other hand, some magnetic modifications of solid O_2 have recently found a practical application as converters for the production of ultracold neutrons.[2,3]

Due to magnetic properties of O_2 molecule that possesses nonzero spin $S_{O_2}=1$ in the ground state, solid oxygen shows rich and nontrivial phase diagram that includes, among others, different magnetic phases (long-ordered α and δ, short-ordered β, and singlet ε, see Fig. 1). Exchange magnetic interactions between O_2 molecules at low temperature prove to be of the same order as the lattice energy. As a result, phase diagram of the solid oxygen is mostly imposed by the magnetic structures, i.e., the crystal structure is being "spin controlled."[8] However, recent experiments by Klotz *et al.*[4] revealed the different types of magnetic ordering within high-pressure δ phase, nontrivial temperature behavior of the lattice constants, and put into doubt the dominant role of magnetic interactions.

In the present paper we try to corroborate the idea of spin-controlled crystal structure of solid oxygen. We argue that temperature dependence of lattice parameters in δ-phase results from variation in the interplane and intraplane exchange magnetic coupling. We show that competition between the different interplane exchange constants induced by lattice deformation can generate a variety of the magnetic structures with different stacking sequence of the close-packed *ab* planes.

II. MODEL

Crystal structure of δ-O_2 is described by orthorhombic symmetry group[1] D_{2h}^{23}. The oxygen molecules can all be considered to be oriented parallel to each other and perpendicular to the close-packed molecular *ab* planes[6] [see Fig. 2(b)]. As it was already mentioned, each O_2 molecule has a spin $S_{O_2}=1$ in its ground state that determines magnetic properties of solid oxygen. Magnetic ordering within *ab* plane corresponds to collinear antiferromagnet (AFM) and is described by two magnetic sublattices,[8] $\mathbf{S}_1$ and $\mathbf{S}_2$ [see Fig. 2(a)]. It is worth noting that in-plane ordering is similar in α and δ phases with the magnetic moments directed nearly along the **b** axis. In what follows we suppose the in-plane AFM configuration unchangeable, in accordance with the experimental data.[8] Mutual orientation of the moments in the adjacent close-packed layers is not uniquely determined and can be parallel or antiparallel, as will be shown below.

Temperature dependence of the lattice constants and magnetic phase diagram of δ-O_2 could be explained from the analysis of the magnetic and elastic energies. The former (per unit volume) in mean-field approximation takes a form

$$w_{\mathrm{mag}}=\frac{1}{N}\sum_{p}[2J_b(r_b)(\mathbf{S}_{1p}^2+\mathbf{S}_{2p}^2)+4J_{ab}(r_{ab})\mathbf{S}_{1p}\mathbf{S}_{2p}+J_{bc}(r_{bc})\times(\mathbf{S}_{1p}\mathbf{S}_{1p+1}+\mathbf{S}_{2p}\mathbf{S}_{2p+1})+J_{ac}(r_{ac})(\mathbf{S}_{1p}\mathbf{S}_{2p+1}+\mathbf{S}_{2p}\mathbf{S}_{1p+1})+J_c(r_c)(\mathbf{S}_{1p}\mathbf{S}_{1p+2}+\mathbf{S}_{2p}\mathbf{S}_{2p+2})]. \quad (1)$$

Here the vectors $\mathbf{S}_{\alpha p}(\alpha=1,2)$ describe in mean-field approximation the sublattice magnetizations within the pth *ab* plane, N is the number of *ab* planes per unit length, different constants $J(r)$ describe the in-plane and interplane exchange interactions between the nearest and next to the nearest neighbors (NN and NNN) separated by a distance r [as shown in Fig. 2(b)], $r_b=b$, $r_{ab}=\sqrt{a^2+b^2}/2$, $r_{bc}=\sqrt{b^2+c^2}/2$, $r_{ac}=\sqrt{a^2+c^2}/2$, and $r_c=c$, vectors **a**, **b**, and **c** define the orthorhombic unit cell. All the spins have the same value $|\mathbf{S}_{\alpha p}|=M_0(T)$ which is supposed to be temperature dependent.

We assume that exchange coupling between O_2 molecules has an AFM character (all the exchange constants are positive, $J>0$). Basing on the analysis made in Ref. 1 we further assume that the in-plane exchange integrals $J(r)$ are the decreasing functions of intermolecular distances r, so, $dJ(r)/dr<0$. The interplane exchange integrals $J(r,\theta)$ are,

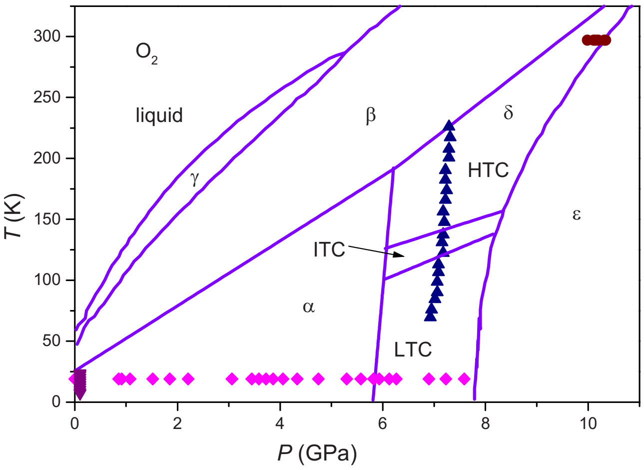

FIG. 1. (Color online) Phase diagram of oxygen. Solid lines show the generally accepted phase boundaries (Ref. 4). Points indicate the experimental data used for calculations of intermolecular distances shown in Fig. 3: isobaric trajectories are represented by up triangles (Ref. 4) ($P\approx 7.3$ GPa, δ phase) and down triangles (Ref. 5) (ambient pressure, α phase), isotherms are represented by diamonds (Ref. 6) ($T=19$ K, α phase) and circles (Ref. 7) (RT, δ phase). HTC, ITC, and LTC denote, correspondingly, high-, intermediate-, and low-temperature commensurate magnetic structures (Ref. 4).

in addition,[9] the functions of angle θ between the molecular axes and intermolecular vector **r** (see, e.g., Refs. 10–12).

According to experimental data,[4] variation in lattice parameters a, b, and c within wide temperature range is small and thus can be described by the components $u_{jj} \ll 1$ ($j=x,y,z$) of the strain tensor as follows:

$$a = a_0(1+u_{xx}), \quad b = b_0(1+u_{yy}), \quad c = c_0(1+u_{zz}), \quad (2)$$

where a_0, b_0, and c_0 are the lattice parameters at $T\to 0$ (for a fixed pressure value) and coordinate axes x, y, and z are parallel to the axes of the orthorhombic crystal unit cell (see Fig. 2). In what follows we introduce three combinations of u_{jj} that form irreducible representations of the space group D_{2h}^{23}: (i) relative variation in the specific volume $\delta v/v = u_{xx} + u_{yy} + u_{zz}$; (ii) rhombic deformation of the in-plane unit cell $u_{\mathrm{rh}} \equiv u_{xx} - u_{yy}$; and (iii) variation in interplane distance u_{zz}.

Specific elastic energy (per unit volume) written in these notations takes a form

$$w_{\mathrm{el}}(\hat{u}) = \frac{1}{2}c_{\mathrm{rh}}u_{\mathrm{rh}}^2 + \frac{1}{2}c_{33}u_{zz}^2 + f\left(\frac{\delta v}{v};T\right) + P\frac{\delta v}{v}, \quad (3)$$

where c_{rh} and c_{33} are elastic moduli, T and P are temperature and external pressure correspondingly, and $f(\delta v/v;T)$ is a model function that takes into account temperature-induced anharmonicity of the crystal lattice.

Magnetoelastic contribution into free energy of the crystal is obtained from Eq. (1) by expansion of the exchange parameters $J(r)$ in series over small strains u_{jj} as it was done, e.g., in Ref. 13 (see below).

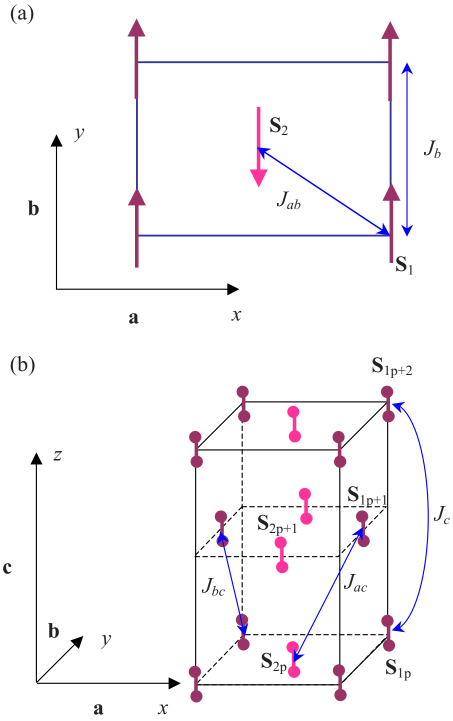

FIG. 2. (Color online) Choice of the magnetic sublattices and exchange coupling constants in δ-O$_2$: (a) $\mathbf{S}_1$ and $\mathbf{S}_2$ are spin vectors of two sublattices within ab plane directed nearly along **b** axis, J_b and J_{ab} are intrasublattice and intersublattice exchange constants, correspondingly; (b) choice of sublattices in different ab planes is arbitrary, spins $\mathbf{S}_{1p}$ and $\mathbf{S}_{1p+1}$ could be either parallel or antiparallel depending on the magnetic structure (see Fig. 5). Parameters J_{ac} and J_{bc} describe interplane exchange coupling between the nearest-neighboring ab planes, and J_c describes next-to-nearest-neighbor interplane exchange coupling along **c** direction.

III. QUALITATIVE CONSIDERATIONS

We argue that the observed temperature variation in the crystal and magnetic properties of δ-O$_2$ arises from competition of AFM exchange interactions between different sites and proceed from the following. (1) Experiments[4] demonstrate negative thermal expansion along **b** and positive thermal expansion along **a** axes. Like in α phase, this fact can be explained by competition between the in-plane exchange constants J_b and J_{ab} [see Fig. 2(a)], as it was proposed by Krupskii *et al.* in Ref. 5. The quantity J_b couples the spins with parallel orientation and thus gives rise to an increase in magnetic energy while J_{ab} couples the antiparallel spins and gives rise to energy decrease. Energy growth due to the temperature variation in $M_0(T)$ can be compensated by negative thermal expansion of r_b (effective repulsion) and positive thermal expansion of r_{ab} (effective attraction) that means that thermal expansion along **a** direction should be larger than contraction along **b** direction.

(2) Magnetic phase diagram of δ-O$_2$ includes three phases with the different stacking sequences of ab planes (see Fig. 5). This fact can be explained by competition of the interplane exchange interactions J_{bc}, J_{ac}, and J_c [see Fig. 2(b)]. It is evident that the mutual orientation of NN spins depends on the sign of the difference $J_{bc}-J_{ac}$. If $J_{bc}<J_{ac}$, configuration

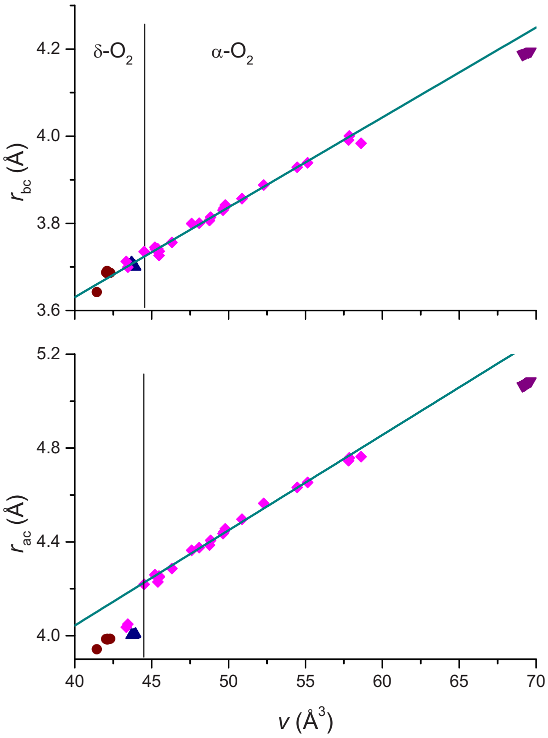

FIG. 3. (Color online) Volume dependence of the intermolecular distances r_{bc} and r_{ac}. Experimental data are taken from Ref. 4 (up triangles), Ref. 5 (down triangles), Ref. 6 (diamonds), and Ref. 7 (circles), see also Fig. 1. Lines show linear approximation calculated for α phase.

with $\mathbf{S}_{1p}\uparrow\uparrow\mathbf{S}_{2p+1}$ [labeled in Ref. 4 as high-temperature commensurate (HTC) phase[14]] is energetically favorable. In the opposite case $J_{bc}>J_{ac}$ configuration $\mathbf{S}_{1p}\uparrow\uparrow\mathbf{S}_{1p+1}$ [low-temperature commensurate (LTC) phase] is more favorable. If, for some reasons, $J_{bc}\approx J_{ac}$, an equilibrium configuration is governed only by relatively small NNN exchange interactions, i.e., by $J_c>0$, and corresponds to antiparallel coupling of $\mathbf{S}_{1p}$ and $\mathbf{S}_{1p+2}$ spins [intermediate-temperature commensurate (ITC) phase]. It should be noticed that the idea that "the interactions between the third interplane neighbors can stabilize the ferromagnetic coupling of O$_2$ planes even if all the exchange constants are… antiferromagnetic" was advanced by Goncharenko *et al.*,[8] before the magnetic structure of δ phase was ultimately established.

(3) Both α and δ phases have the same magnetic ordering within *ab* plane. However, δ-O$_2$ shows a variety of the magnetic structures with different stacking sequences of *ab* planes while α-O$_2$ shows only one stacking sequence (corresponding to HTC δ-O$_2$) in the whole range of temperature and pressure values. This fact can also be explained by competition of the interplane exchange interactions J_{bc} and J_{ac}. To clarify this point we have plotted intermolecular distances r_{ac} and r_{bc} as the functions of volume v of the crystal unit cell (see Fig. 3). Specific volume can be changed by application of both pressure and temperature, so, it can be chosen as a single thermodynamic variable that unifies an influence of the external fields and defines the state of O$_2$ within the phase diagram. The distances r_{ac} and r_{bc} were calculated using the results of measurement of temperature[4,5] and pressure[6,7] dependencies taken in the different regions of solid O$_2$ phase diagram including α and δ phases.[15] It can be clearly seen that in α-O$_2$ the distance $r_{ac}>r_{bc}$ and difference between these values is on the order of 20%. Taking into account the character of spatial and angular dependence $J(r,\theta)$, one can assume that $J_{bc}<J_{ac}$ and HTC ordering is energetically favorable. At the $\alpha\rightarrow\delta$ transition point the dependence $r_{ac}(v)$ shows steplike decrease. Correspondingly, relative difference between r_{ac} and r_{bc} diminishes down to $\propto$7.5%. Corresponding difference between J_{bc} and J_{ac} can be compensated due to strong angular dependence of $J(r,\theta)$ that becomes crucial at small intermolecular distances. Thus, the difference $J_{bc}-J_{ac}$ changes sign and ITC and LTC phases turn out to be favorable. In the next sections we will substantiate these qualitative considerations with phenomenological analysis of the magnetic and crystal structure of δ-O$_2$.

IV. INTRAPLANE EXCHANGE AND TEMPERATURE DEPENDENCE OF LATTICE PARAMETERS

Equilibrium values of lattice parameters a, b, and c at given temperature and pressure are calculated from minimization of the specific free energy $w=w_{\text{mag}}+w_{\text{el}}$ [see Eqs. (1) and (3)] with respect to parameters $\delta v/v$, u_{rh}, and u_{zz}. In the first approximation we neglect a small contribution of the interplane exchange,[4] $J_{ac}(\propto J_{bc})/J_{ab}<1/30$. The intraplane exchange constants depend on the deformations implicitly, through the intermolecular distances $r(\delta v/v, u_{\text{rh}}, u_{zz})$, see, e.g., Ref. 13. We further assume that the thermal-expansion coefficient,[16] β_v, and isothermal compliance χ_T are constant in the considered part of phase diagram, so, the function f in Eq. (3) can be written as[17]

$$f\left(\frac{\delta v}{v};T\right)=\frac{1}{2\chi_T}\left(\frac{\delta v}{v}\right)^2-\frac{\beta_v T}{\chi_T}\left(\frac{\delta v}{v}\right). \tag{4}$$

In this case the equilibrium values of deformations at a given AFM magnetic structure are the following:

$$\frac{\delta v}{v}=-\chi_T P+\beta_v T-2\chi_v M_0^2(T)\left(\left.\frac{dJ_b}{dr}\right|_{r_b^{(0)}}-\left.\frac{dJ_{ab}}{dr}\right|_{r_{ab}^{(0)}}\right), \tag{5}$$

$$u_{\text{rh}}=\frac{2M_0^2(T)}{c_{\text{rh}}}\left(\left.\frac{dJ_b}{dr}\right|_{r_b^{(0)}}+\frac{a_0^2-b_0^2}{a_0^2+b_0^2}\left.\frac{dJ_{ab}}{dr}\right|_{r_{ab}^{(0)}}\right), \tag{6}$$

and

$$u_{zz}^{\perp}=\frac{2M_0^2(T)}{c_{33}}\left(\left.\frac{dJ_b}{dr}\right|_{r_b^{(0)}}-\left.\frac{dJ_{ab}}{dr}\right|_{r_{ab}^{(0)}}\right). \tag{7}$$

Superscript "$\perp$" in Eq. (7) indicates an intraplane exchange contribution into u_{zz}.

Temperature dependence of the values $\delta v/v$, u_{zz}, and u_{rh} can be unambiguously defined if we take into account the following facts: (i) decreasing and exponential character of $J(r)$ function; (ii) relations between the intermolecular distances at $T=0$: $r_b^{(0)}\equiv b_0>r_{ab}^{(0)}\equiv\sqrt{a_0^2+b_0^2}/2$ and $a_0>b_0$; (iii)

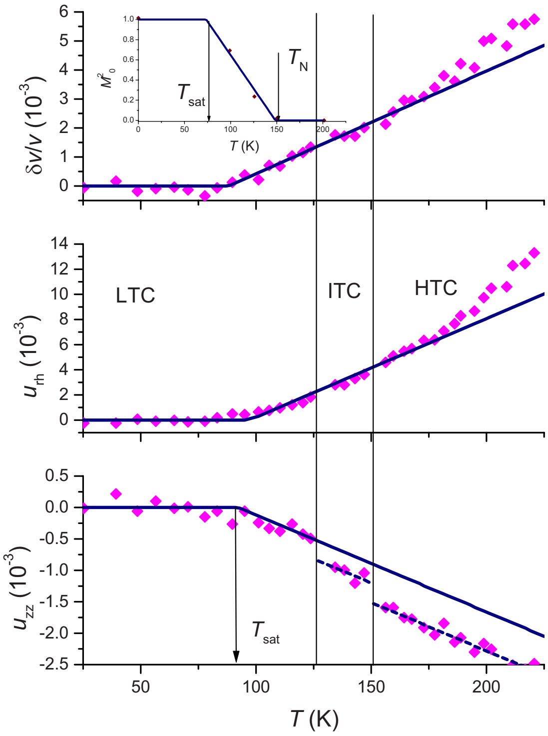

FIG. 4. (Color online) Temperature dependence of the parameters $\delta v/v$ (upper panel), $u_{\rm rh}$ (middle panel), and u_{zz} (bottom panel). Points—experimental data (Ref. 4) and solid lines—theoretical approximation according to Eq. (9). Inset shows temperature dependence of $M_0^2(T)$ (normalized to 1) taken at $P=7.6$ GPa: points—experimental data (Ref. 18) and solid line—approximation according to Eq. (8).

temperature dependence of the sublattice magnetization $M_0(T)$ predicted by the mean-field theory (in accordance with neutron diffraction measurements,[18] see inset in Fig. 4, and spectral measurements[19]),

$$M_0^2(T) \propto \begin{cases} \text{const} & T \le T_{\rm sat}, \\ (1 - T/T_N) & T_{\rm sat} \le T \le T_N. \end{cases} \tag{8}$$

Here T_N is the Néel temperature and $T_{\rm sat}$ is the temperature at which M_0 attains its saturation value.

As a result, the cell volume, $\delta v/v$, and the in-plane orthorhombic deformation, $u_{\rm rh}$, are the increasing functions of temperature [because $dJ_b(r_b^{(0)})/dr < dJ_{ab}(r_{ab}^{(0)})/dr < 0$] while the interplane distance (and corresponding deformation u_{zz}) is the decreasing function of temperature. All the dependencies could be approximated with the function

$$g(T) = \begin{cases} 0 & T \le T_{\rm sat}, \\ A(T - T_{\rm sat}) & T_{\rm sat} \le T \le T_N, \end{cases} \tag{9}$$

where the constant A (measured in 1/K) depends on the values dJ/dr.

Figure 4 shows the temperature dependencies of deformations $\delta v/v$, $u_{\rm rh}$, and u_{zz} in δ-O$_2$. Points correspond to experimental data,[4] solid lines are approximations according to Eq. (9) with $T_{\rm sat}=97$ K and

$$A = \begin{cases} 3.54 \times 10^{-5} & \text{for } \delta v/v, \\ 7.85 \times 10^{-5} & \text{for } u_{\rm rh}, \\ -1.54 \times 10^{-5} & \text{for } u_{zz}. \end{cases} \tag{10}$$

It can be clearly seen that the temperature variation in the in-plane deformation $u_{\rm rh}$ and volume $\delta v/v$ can be adequately explained by the temperature dependence of the in-plane exchange interactions and, in particular, $M_0^2(T)$ [see Eq. (8)]. As it was already mentioned, in-plane exchange forces cause strong contraction along r_{ab} direction which gives the dominant contribution into orthorhombic deformation and volume effect. An analogous mechanism is responsible for anisotropic lattice compressibility within the ab plane in a wide range of pressure values, as was pointed out in Ref. 20.

However, interplane deformation u_{zz} deflects from the dependence [Eq. (9)] in the transition points between the magnetic phases with different stacking sequences of the close-packed planes (HTC, ITC, and LTC). Full interpretation of the experimental data is possible with the account of small but important contribution of the interplane exchange interactions.

V. INTERPLANE EXCHANGE AND DIFFERENT MAGNETIC STRUCTURES

To elucidate the role of interplane exchange interactions in formation of equilibrium magnetic structures of δ-O$_2$ we reduce minimization of the magnetic energy [Eq. (1)] to the well-known (see, e.g., review Ref. 21) one-dimensional axial next-nearest-neighbor Ising problem. In assumption of the fixed in-plane spin ordering, the three-dimensional magnetic structure is uniquely described by the set of Ising variables (pseudospins) $\sigma_p = \pm 1$ defined as follows (see also Fig. 5),

$$M_0^2 \sigma_p \equiv \mathbf{S}_{1p}\mathbf{S}_{1p+1} = \mathbf{S}_{2p}\mathbf{S}_{2p+1} = -\mathbf{S}_{2p}\mathbf{S}_{1p+1} = -\mathbf{S}_{1p}\mathbf{S}_{2p+1}. \tag{11}$$

Parameters σ_p, in fact, define a "ferromagnetic" (if $\sigma_p=1$) or an "antiferromagnetic" (if $\sigma_p=-1$) coupling in the two neighboring [pth and $(p+1)$th] close-packed planes. Moreover, if all the spins are collinear, mutual orientation of the next-to-nearest-neighboring planes is also defined by the same parameters, e.g., $\mathbf{S}_{1p}\mathbf{S}_{1p+2} = (\mathbf{S}_{1p}\mathbf{S}_{1p+1})(\mathbf{S}_{1p+1}\mathbf{S}_{1p+2})/M_0^2 = M_0^2\sigma_p\sigma_{p+1}$, etc. (see Fig. 5).

Thus, the magnetic energy [Eq. (1)] in mean-field approximation can be adequately presented in a form of one-dimensional Ising model for the effective "pseudospins" σ_p,

$$w_{\rm mag} = \frac{2M_0^2}{N} \sum_p \left[\Delta J_c \sigma_p + J_c \sigma_p \sigma_{p+1}\right]. \tag{12}$$

It can be easily seen that the difference $\Delta J_c \equiv J_{bc} - J_{ac}$ plays a role of the effective field that in the absence of NNN coupling ($J_c=0$) tends to align all the pseudospins in parallel. Such a ferromagnetic ordering generates a LTC ($\sigma_p=1, \Delta J_c < 0$) or HTC ($\sigma_p=-1, \Delta J_c > 0$) magnetic structure (see Fig. 5). In turn, exchange coupling between the NNN, J_c, is responsible for interaction between the neighboring pseudospins. If $J_c < 0$ (ferromagnetic exchange between the

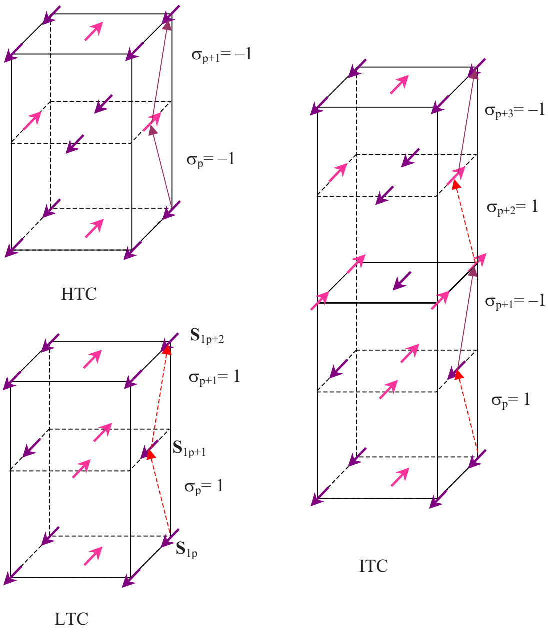

FIG. 5. (Color online) Three types of the magnetic ordering in δ phase. Left panel—"ferromagnetic ordering" with the order parameter $\sigma_p \equiv \mathbf{S}_{1p} \cdot \mathbf{S}_{1p+1}/M_0^2 = -1$ (HTC, upper panel) or $\sigma_p = 1$ (LTC, bottom panel). Right panel—antiferromagnetic ordering with the order parameter σ_p alternating between ±1 from layer to layer (ITC).

"real" spins), ferromagnetic coupling is still preferable (LTC or HTC structures). However, if the NNN exchange coupling is AFM, $J_c > 0$, then, an antiferromagnetic ordering of pseudospins ($\sigma_{2p}=1, \sigma_{2p+1}=-1$) that corresponds to ITC structure is favorable.

Stability ranges of the HTC, ITC, and LTC structures can be found from comparison of the corresponding energies,

$$w_{\rm mag}^{\rm LTC} = (-\Delta J_c + J_c) M_0^2, \quad w_{\rm mag}^{\rm ITC} = -J_c M_0^2,$$

$$w_{\rm mag}^{\rm HTC} = (\Delta J_c + J_c) M_0^2. \tag{13}$$

Thus, HTC structure is stable if $\Delta J_c \leq -2J_c$, ITC structure is stable if $-2J_c \leq \Delta J_c \leq 2J_c$, and LTC structure is stable if $2J_c \leq \Delta J_c$. So, temperature variation in the interplane exchange coupling J_{bc}, J_{ac}, and J_c may generate a series of HTC-ITC-LTC phase transitions.

Now an important question is: "what is the reason for variation in the relation between the NN and NNN exchange constants in δ-O$_2$?" We suppose that the temperature variation in interplane exchange constants is due to a strong and nontrivial angular dependence of the exchange coupling. In particular, *ab initio* calculations of the exchange interactions between an isolated pair of O$_2$ molecules[10,11] revealed the following facts: (i) exchange coupling parameters $J(r,\theta)$ show nonmonotonic, strongly oscillating behavior as a function of angle θ; (ii) the values θ at which $J(r,\theta)$ attains its minimal and maximal values are very sensitive to the intermolecular distance r; (iii) for a fixed intermolecular distance r the absolute value of $J(r,0)$ (molecular axes are parallel to the intermolecular vector) is much greater than $J(r,90°)$ (molecular axes are perpendicular to the intermolecular vector); (iv) $J(r,\theta)$ oscillates around zero value for the intermediate values of angles, $\theta \propto 20°-40°$. On the other hand, experiment[4] gives $\theta_{bc}=24.06°$, θ_{bc} varies from 32.17° in LTC to 32.55° in HTC structures and obviously $\theta_c=0$. Thus, we conclude that (i) ΔJ_c can change the sign due to the strong angular dependence of J_{ac} that equates AFM and FM exchange ($J_{ac} \approx J_{bc}$) at different ($r_{ac} > r_{bc}$) distances and/or due to oscillation around zero value of both J_{bc} and J_{ac}; and (ii) the value of the NNN coupling J_c may be comparable with $|\Delta J_c|$ because the spatial relaxation of the exchange constants for $\theta_c=0$ is compensated by the enhancement due to angular dependence.

The hypothesis of strong spatial dependence of the interplane exchange constants is also supported by the observed jumps of interplane distance in the HTC-ITC and ITC-LTC transition points (see Fig. 4, lower panel): $u_{zz}^{\rm LTC} - u_{zz}^{\rm ITC} = u_{zz}^{\rm ITC} - u_{zz}^{\rm HTC} = 2.9 \times 10^{-4}$. Really, with account of the interplane exchange contribution the temperature dependence [Eq. (7)] of u_{zz} can be refined as follows:

$$u_{zz} = u_{zz}^{\perp} + \frac{M_0^2(T)}{c_{33}} \begin{cases} (\lambda_1 - \lambda_2) & \text{for LTC}, \\ \lambda_2 & \text{for ITC}, \\ (-\lambda_1 - \lambda_2) & \text{for HTC}, \end{cases} \tag{14}$$

where

$$\lambda_1 \equiv \left[\frac{2c_0^2 - a_0^2}{8r_{ac}^{(0)}} \frac{\partial J_{ac}}{\partial r}\bigg|_0 - \frac{2c_0^2 - b_0^2}{8r_{bc}^{(0)}} \frac{\partial J_{bc}}{\partial r}\bigg|_0 \right] - \left[\frac{6r_{ac}^{(0)}}{c_0^2} \frac{\partial J_{ac}}{\partial \theta}\bigg|_0 - \frac{6r_{bc}^{(0)}}{c_0^2} \frac{\partial J_{bc}}{\partial \theta}\bigg|_0 \right],$$

$$\lambda_2 \equiv \left| \frac{\partial J_c}{\partial r} \right|_0, \tag{15}$$

and subscript "0" denotes that arguments of r and θ are taken at $T \to 0$.

Thus, if $\lambda_1 \gg \lambda_2$, then $u_{zz}^{\rm LTC} - u_{zz}^{\rm ITC} = u_{zz}^{\rm ITC} - u_{zz}^{\rm HTC} \approx M_0^2 \lambda_1 / c_{33} > 0$, in accordance with the experiment. Comparison with the experimental data makes it possible to estimate spatial dependence of the in-plane and interplane exchange constants quantitatively,

$$\left| \frac{u_{zz}^{\rm LTC} - u_{zz}^{\rm ITC}}{u_{zz}^{\perp}} \right| = \left| \frac{dJ_{ac}/dr - dJ_{bc}/dr}{dJ_b/dr - dJ_{ab}/dr} \right| \propto 0.1. \tag{16}$$

It is interesting to note that the analogous increase in interplane distances was also observed[6] during the pressure-induced transition from α to δ phase at $T=19$ K. According to phase diagram (diamonds in Fig. 1), corresponding δ-O$_2$ has a LTC structure while α-O$_2$ shows a HTC ordering, so, the interplane distance should be larger in δ-O$_2$, as it is predicted by Eq. (14).

Figure 6 shows the pressure dependence of u_{zz} calculated from experimental data Ref. 6 (points) along with the linear approximation according to formula (where P is in GPa)

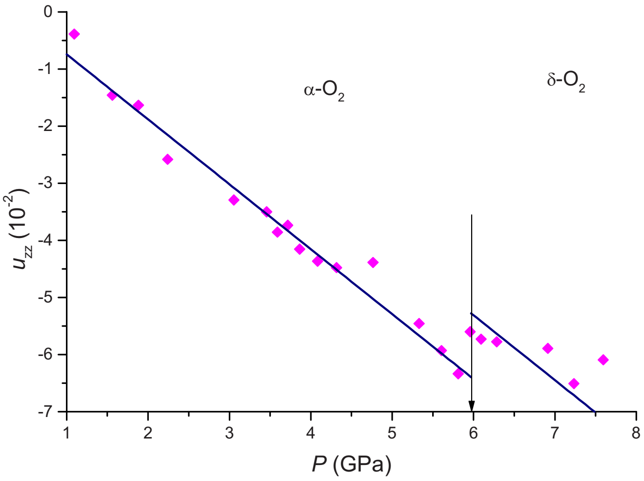

FIG. 6. (Color online) Pressure dependence of u_{zz}. Points correspond to experimental data (Ref. 6) (see also Fig. 1) and solid lines are the best linear fit [see formula (17)].

$$u_{zz} = -1.13 \times 10^{-2} P + \begin{cases} 0.38 \times 10^{-2} & \text{for } \alpha\text{-O}_2, \\ 1.45 \times 10^{-2} & \text{for } \delta\text{-O}_2. \end{cases} \quad (17)$$

Assuming that pressure dependence $u_{zz}(P)$ results from the spatial dependence of in-plane exchange constants [in analogy with $u_{zz}(T)$] we get the same as Eq. (16) estimation for the in-plane and interplane exchange constants,

$$\left| \frac{u_{zz}^{\delta} - u_{zz}^{\alpha}}{u_{zz}} \right| = \left| \frac{dJ_{ac}/dr - dJ_{bc}/dr}{dJ_b/dr - dJ_{ab}/dr} \right| \propto 0.15. \quad (18)$$

VI. CONCLUSIONS

In the present paper we have analyzed the role of interplane exchange interactions in formation of the magnetic and crystal structure of solid δ-O$_2$. We show that the crystal volume and orthorhombic deformation in *ab* plane strongly depend on the in-plane exchange forces. On the contrary, interplane distances noticeably depend not only on strong in plane but also on relatively small interplane exchange coupling. As a result, abrupt change in the magnetic structure (HTC-ITC-LTC transition) is followed by stepwise variation in the interplane distances.

We propose an interpretation of the mechanism of phase transitions between the magnetic structures with different stacking sequence of the *ab* planes based on competition between the different, relatively small interplane exchange integrals. Another interpretation proposed in Ref. 4 rests upon assumption on strong temperature dependence of only one interplane exchange constant J_{bc} (J_3 in notations of Ref. 4) induced by the libron excitations. We argue that due to the strong angular and spatial dependence of the exchange coupling the exchange forces between NN and NNN in *c* direction could be of the same order value and should be taken into account at the same foot. In this case the libron contribution into the all exchange constants should be the same while configurational (i.e., depending on the relative positions of molecules) contribution would be different. Correlation between the experimental slope of the LTC-ITC-HTC and theoretical value deduced in Ref. 4 from the librational fluctuations can be explained by the magnetic contribution into librons parameters observed in Ref. 19.

We supposed that the values of the exchange constants in solid oxygen strongly depend on the relative positions and orientation of axes of O$_2$ molecules. We proceeded from the calculations[10,11] for isolated pairs of molecules that demonstrated an oscillatory character of $J(\theta)$ function. However, accurate values of the exchange constants for certain configurations should be calculated with account of an additional parameter, namely, spatial orientation of π orbitals with respect to crystal axes. Such calculations are beyond the scope of this paper.

In this paper we considered mainly the temperature effects that cause variation in the crystal lattice parameters, interplane exchange constants, and, as a result, series of transitions between the different magnetic phases. However, analogous effects could be produced by pressure. Moreover, we assume that pressure may induce some other than the considered commensurate magnetic structures, especially in the vicinity of α-δ-transition line.

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