Magnetic structures of $\delta$-O$_2$ resulting from competition of interplane exchange interactions

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Abstract

Solid oxygen is a unique molecular crystal whose phase diagram is mostly imposed by magnetic ordering, i.e., each crystal phase has a specific magnetic structure. However, recent experiments showed that high-pressure $\delta$-phase is implemented in different magnetic structures. In the present paper we study the role of interplane exchange interactions in formation of the magnetic structures with different stacking sequences of the close-packed planes. We show that temperature-induced variation of 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 $\delta$-O$_2$. Variation of the magnetic ordering is, in turn, accompanied by the step-wise variation of interplane distance governed by space and angular dependence of interplane exchange constants. PACS numbers: 75.50.Ee; 61.50.Ks; 81.40 Vw
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 ultra-cold 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 (\(\alpha, \beta, \delta,\) and \(\varepsilon\), see Fig.1). Exchange magnetic interactions between O\(_2\) molecules at low temperature prove to be of the same order as lattice energy. As a result, the phase diagram of the solid oxygen is completely imposed by the magnetic structures, i.e., the crystal structure is being “spin controlled”\(^4\). However, recent experiments by Klotz et al\(^5\) revealed the different types of magnetic ordering within the high-pressure \(\delta\)-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 \(\delta\)-phase results from variation of the inter- and intra-plane exchange magnetic coupling. We show that competition between the different interplane exchange constants induced by the 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 \(\delta\)-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 atomic \(ab\)-planes\(^7\), as shown in Fig. 2(b). As it as already mentioned, each O\(_2\) molecule has a spin \(S_{O_2} = 1\) in its ground state that determines magnetic properties of solid oxygen. The magnetic ordering within \(ab\)-plane corresponds to collinear antiferromagnet (AFM) and is described by two magnetic sublattices\(^4\), \(S_1\) and \(S_2\) (see Fig. 2a). It is worth noting that the in-plane ordering is similar in \(\alpha\)- and \(\delta\)-phases with the magnetic
Figure 1. (Color online) Phase diagram of oxygen. Solid lines show the generally accepted phase boundaries\textsuperscript{5}. Points indicate the experimental data used for calculations of intermolecular distances shown in Fig. 3: isobaric trajectories are represented by up triangles\textsuperscript{5} ($P \approx 7.3$ GPa, \(\delta\)-phase) and down triangles\textsuperscript{6} (ambient pressure, \(\alpha\)-phase), isotherms are represented by diamonds\textsuperscript{7} ($T = 19$ K, \(\alpha\)-phase) and circles\textsuperscript{8} (RT, \(\delta\)-phase). HTC, ITC and LTC denote, correspondingly, high, intermediate and low temperature commensurate magnetic structures\textsuperscript{5}.

moments directed nearly along the \(b\)-axis. In what follows we suppose the in-plane AFM configuration unchangeable, in accordance with the experimental data\textsuperscript{4}. The 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 \(\delta\)-O\(_2\) could be explained from the analysis of the magnetic energy of the crystal (per unit volume) which in the mean-field approximation takes a form

\[
w_{\text{mag}} = \frac{1}{N} \sum_{p} \left[ 2J_b(r_b) \left( S_{1p}^2 + S_{2p}^2 \right) + 4J_{ab}(r_{ab})S_{1p}S_{2p} \right. \\
+ J_{bc}(r_{bc}) \left( S_{1p}S_{1p+1} + S_{2p}S_{2p+1} \right) + J_{ac}(r_{ac}) \left( S_{1p}S_{2p+1} + S_{2p}S_{1p+1} \right) \\
+ J_{c}(r_c) \left( S_{1p}S_{1p+2} + S_{2p}S_{2p+2} \right) \right].
\]

Here the vectors \(S_{\alpha p}(\alpha = 1, 2)\) are the spins averaged over the \(p\)-th \(ab\)-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. 2b),

$$
\begin{align*}
    r_b &= b, \quad r_{ab} = \sqrt{a^2 + b^2}/2, \quad r_{bc} = \sqrt{b^2 + c^2}/2, \\
    r_{ac} &= \sqrt{a^2 + c^2}/2, \quad r_c = c,
\end{align*}
$$

vectors $a, b,$ and $c$ define the orthorhombic unit cell. All the spins have the same value $|S_{\alpha p}| = M_0(T)$ which is supposed to be temperature dependent.

We assume that the 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, in addition, the functions of angle $\theta$ between the molecular axes and intermolecular vector $r$ (see, e.g., Refs. 9–11).

According to experimental data$^5$, variation of lattice parameters $a$, $b$ and $c$ within the 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:

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

(2)

where $a_0, b_0, c_0$ are the lattice parameters at $T \to 0$ (for a fixed pressure value), and coordinate axes $x, y, z$ 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 $D_{2h}^2$: $i)$ relative variation of the specific volume $\delta v/v \equiv u_{xx} + u_{yy} + u_{zz}$; $ii)$ rhombic deformation of in-plane unit cell $u_{rh} \equiv u_{xx} - u_{yy}$; $iii)$ variation of interplane distance $u_{zz}$.

Elastic energy written in these notations takes a form

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

(3)

where $c_{rh}$, $c_{33}$ are elastic modula, $T$ and $P$ are temperature and external pressure correspondingly, $f(\delta v/v; T)$ 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 (1) by expansion of the exchange parameters $J(r)$ in series over small strains $u_{jj}$ as it was done, e.g., in Ref.12 (see below).
III. QUALITATIVE CONSIDERATIONS

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

2. Magnetic phase diagram of $\delta$-O\textsubscript{2} includes three phases with different stacking sequences of \textit{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. 2b). It is evident that mutual orientation of NN spins depends upon the sign of the difference $J_{bc} - J_{ac}$. If $J_{bc} < J_{ac}$, the configuration with $S_{1p} \uparrow \uparrow S_{2p+1}$ (labeled in Ref.\textsuperscript{5} as HTC phase\textsuperscript{13}) is energetically favorable. In the opposite case $J_{bc} > J_{ac}$ the configuration $S_{1p} \uparrow \uparrow S_{1p+1}$ (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 $S_{1p}$ and $S_{1p+2}$ spins (ITC phase). It should be noticed that the idea that “the interactions between the third interplane neighbours can stabilize the ferromagnetic coupling of O\textsubscript{2} planes even if all the exchange constants are ... antiferromagnetic” was advanced by Goncharenko et al\textsuperscript{4}, before the magnetic structure of \textit{delta}-phase was ultimately established.

3. Both $\alpha$- and $\delta$-phases have the same magnetic ordering within \textit{ab}-plane. However, $\delta$-O\textsubscript{2} shows a variety of the magnetic structures with different stacking sequences of \textit{ab}-planes, while $\alpha$-O\textsubscript{2} shows only one stacking sequence (corresponding to HTC $\delta$-O\textsubscript{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 the intermolecular distances $r_{ac}$ and $r_{bc}$ as the functions of average intermolecular distances represented by the volume $v$ of the crystal unit cell (see Fig. 3). The distances $r_{ac}$ and $r_{bc}$ were calculated using the results of measurement of temperature\textsuperscript{5,6} and pressure\textsuperscript{7,8} dependencies taken in different regions of solid O\textsubscript{2}.
phase diagram including $\alpha$- and $\delta$-phases\(^{14}\). It can be clearly seen that in the $\alpha$-O$_2$ the distance $r_{ac} > r_{bc}$ and the difference between these values is of the order of 20\%. Taking into account the character of space 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 step-like decrease. Correspondingly, the relative difference between $r_{ac}$ and $r_{bc}$ diminishes down to $\alpha$ 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.

Figure 3. (Color online) Volume dependence of intermolecular distances $r_{bc}$, $r_{ac}$. Experimental data are taken from Refs.5 (up triangles), 6 (down triangles), 7 (diamonds), 8 (circles), see also Fig.1. Lines show linear approximation calculated for $\alpha$-phase.

In the next sections we will substantiate these qualitative considerations with the phenomenological analysis of the magnetic and crystal structure of $\delta$-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 free energy $w = w_{\text{mag}} + w_{\text{el}}$ (see Eqs. (1) and (3)) with respect to parameters $\delta v/v$, $u_{\text{rh}}$ and $u_{\text{zz}}$. In the first approximation we neglect small contribution of interplane exchange $^{5}$, $J_{ac}(\propto J_{bc})/J_{ab} < 1/30$. Intraplane exchange constants depend on the deformations implicitly, through the intermolecular distances $r(\delta v/v, u_{\text{rh}}, u_{\text{zz}})$, see e.g. Ref.12. We further assume that the thermal-expansion coefficient $^{15}$, $\beta_v$, and isothermal compliance $\chi_T$ are constant in the considered part of phase diagram, so, the function $f$ in equation (3) can be written as$^{16}$:

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

(4)

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

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

(5)

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

(6)

and

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

(7)

Superscript “$\perp$” in Eq. (7) indicates intraplane exchange contribution into $u_{\text{zz}}$.

Temperature dependence of the values $\delta v/v$, $u_{\text{zz}}$ and $u_{\text{rh}}$ can be unambiguously defined if we take into account the following facts: $i$) decreasing and exponential character of $J(r)$ function; $ii$) relations between intermolecular distances at $T = 0$: $r_b^{(0)} \equiv b_0 > r_{ab}^{(0)} \equiv \sqrt{a_0^2 + b_0^2}/2$ and $a_0 > b_0$; $iii$) temperature dependence of sublattice magnetization $M_0(T)$ predicted by the mean-field theory and supported by neutron diffraction measurements$^{17}$ (see inset in Fig. 4):

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

(8)

Here $T_N$ is the Néel temperature and $T_{\text{sat}}$ (usually $\propto 0.5T_N$) is the temperature at which $M_0$ attains its saturation value.
As a result, cell volume, $\delta v/v$, and in-plane orthorhombic deformation, $u_{rh}$, are increasing functions of temperature (because $dJ_b(r_b^{(0)})/dr < dJ_{ab}(r_{ab}^{(0)})/dr < 0$), while interplane distance (and corresponding deformation $u_{zz}$) is decreasing function of temperature. All the dependencies could be approximated with the function

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

where the constant $A$ (1/K) depends upon the values $dJ/dr$.

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

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

It can be clearly seen that temperature variation of the in-plane deformation $u_{rh}$ 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 mention, in-plane exchange forces cause strong contraction along $r_{ab}$ direction which gives dominant contribution into orthorhombic deformation and volume effect. An analogous mechanism is responsible for the anisotropic lattice compressibility within the $ab$-plane in a wide range of pressure values, as was pointed out in Ref. 18.

However, interplane deformation $u_{zz}$ deflects from the dependence (9) in the transition points between the magnetic phases with different stacking sequences of 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 the formation of equilibrium magnetic structures of $\delta$-O$_2$ we reduce minimization of the magnetic energy (1) to the well-known (see, e.g., review Ref. 19) 1-dimensional ANNNI (Axial Next-Nearest Neighbor Ising) problem. In assumption of the fixed in-plane spin ordering, the 3-dimensional magnetic
structure is uniquely described by the set of Ising variables ("pseudospins") $\sigma_p = \pm 1$ defined as follows (see also Fig. 5):

$$M_0^2 \sigma_p \equiv S_{1p}S_{1p+1} = S_{2p}S_{2p+1} = -S_{2p}S_{1p+1} = -S_{1p}S_{2p+1}. \quad (11)$$
Parameters $\sigma_p$ in fact define “ferromagnetic” (if $\sigma_p = 1$) or “antiferromagnetic” (if $\sigma_p = -1$) in two neighboring ($p$-th 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., $S_{1p} S_{1p+2} = (S_{1p} S_{1p+1})(S_{1p+1} S_{1p+2})/M_0^2 = M_0^2 \sigma_p \sigma_{p+1}$, etc. (see Fig. 5).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Fig5.png}
\caption{(Color online) Three types of magnetic ordering in $\delta$-phase. Left panel – “ferromagnetic ordering” with the order parameter $\sigma_p \equiv S_{1p} \cdot S_{1p+1}/M_0^2 = -1$ (HTC, upper panel) or $\sigma_p = 1$ (LTC, bottom panel). Right panel – “antiferromagnetic” ordering with the order parameter $\sigma_p$ alternating between $\pm1$ from layer to layer (ITC).}
\end{figure}

Thus, the magnetic energy (1) in mean-field approximation can be adequately presented
in a form of 1-dimensional Ising model for the effective “pseudospins” $\sigma_p$:

$$w_{\text{mag}} = \frac{2M_0^2}{N} \sum_p \left[ \Delta J_c \sigma_p + J_c \sigma_p \sigma_{p+1} \right].$$ \hspace{1cm} (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 an LTC ($\sigma_p = 1, \Delta J_c < 0$) or HTC ($\sigma_p = -1, \Delta J > 0$) magnetic structure (see Fig. 5). In turn, the exchange coupling between NNN, $J_c$, is responsible for interaction between the neighboring “pseudospins”. If $J_c < 0$ (ferromagnetic exchange between the “real” spins), “ferromagnetic” coupling is still preferable (LTC or HTC structures). However, if 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 corresponding energies:

$$w_{\text{mag}}^{\text{LTC}} = (-\Delta J_c + J_c) M_0^2, \quad w_{\text{mag}}^{\text{ITC}} = -J_c M_0^2, \quad w_{\text{mag}}^{\text{HTC}} = (\Delta J_c + J_c) M_0^2. \hspace{1cm} (13)$$

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 of 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 of the relation between the NN and NNN exchange constants in $\delta$-O$_2$?”. We suppose that temperature variation of interplane exchange constants is due to a strong and nontrivial angular dependence of the exchange coupling. In particular, \textit{ab initio} calculations of the exchange interactions between an isolated pair of O$_2$ molecules\textsuperscript{9,10} revealed the following facts: \textit{i)} exchange coupling parameters $J(r, \theta)$ show nonmonotonic, strongly oscillating behaviour as a function of angle $\theta$; \textit{ii)} the values $\theta$ at which $J(r, \theta)$ attains its minimal and maximal values are very sensitive to intermolecular distance $r$; \textit{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 $J(r,90^\circ)$ (molecular axes are perpendicular to the intermolecular vector); \textit{iv)} $J(r, \theta)$ is oscillating around zero value for intermediate values of angles, $\theta \propto 20 \div 40^\circ$. On the other hand, experiment\textsuperscript{5} gives $\theta_{bc} = 24.06^\circ$, $\theta_{bc}$ varies from $32.17^\circ$ in LTC to $32.55^\circ$ in HTC structures and obviously $\theta_c = 0$. Thus, we conclude that \textit{i)} $\Delta J_c$ can change 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 oscillation around zero value of both $J_{bc}$ and $J_{ac}$; ii) the value of NNN coupling $J_c$ may be comparable with $|\Delta J_c|$ because space relaxation of the exchange constants for $\theta_c = 0$ is compensated by the enhancement due to angular dependence.

The hypothesis of strong space 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): $u_{zz}^{\text{LTC}} - u_{zz}^{\text{ITC}} = u_{zz}^{\text{ITC}} - u_{zz}^{\text{HTC}} \approx 2.9 \cdot 10^{-4}$. Really, with account of interplane exchange contribution the temperature dependence (7) of $u_{zz}$ can be refined as follows:

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

where

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

$$\lambda_2 \equiv \frac{\partial J_c}{\partial r} \bigg|_0,$$

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

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

$$\left| \frac{u_{zz}^{\text{LTC}} - u_{zz}^{\text{ITC}}}{u_{zz}^{\perp}} \right| \approx \left| \frac{dJ_{ac}/dr - dJ_{bc}/dr}{dJ_b/dr - dJ_{ab}/dr} \right| \propto 0.1.$$  (16)

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

Fig. 6 shows the pressure dependence of $u_{zz}$ calculated from experimental data Ref. 7 (points) along with the linear approximation according to formula

$$u_{zz} = -1.13 \cdot 10^{-2} P + \begin{cases} 0.38 \cdot 10^{-2}, & \text{for } \alpha - \text{O}_2, \\ 1.45 \cdot 10^{-2}, & \text{for } \delta - \text{O}_2. \end{cases}$$  (17)
Assuming that pressure dependence $u_{zz}(P)$ results from the space dependence of in-plane exchange constants (in analogy with $u_{zz}(T)$) we get the same as (16) estimation for the in- and inter-plane exchange constants:

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

![Figure 6. (Color online) Pressure dependence of $u_{zz}$. Points correspond to experimental data\textsuperscript{7} (see also Fig. 1), solid lines are the best linear fit (see formula (17)).](image)

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 $\delta$-$O_2$. 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 the strong in-plane but also on relatively small interplane exchange coupling. As a result, abrupt change of the magnetic structure (HTC-ITC-LTC transition) is followed by the step-wise variation of 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 the competition between different, relatively small interplane exchange integrals. Interpretation proposed in Ref. 5 rests upon assumption on strong temperature dependence of only one interplane exchange constant \(J_{bc}\) (\(J_3\) in notations of Ref. 5) induced by the libron excitations. We argue that due to the strong angular and space dependence of the exchange coupling the exchange forces between NN and NNN in the \(c\)-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 all the 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. 5 from the librational fluctuations can be explained by the magnetic contribution into librons parameters observed in Ref. 20.

We supposed that the values of the exchange constants in solid oxygen strongly depend upon the relative positions and orientation of axes of \(O_2\)-molecules. We proceeded from the calculations\(^9\),\(^10\) 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 \(\pi\)-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 of the crystal lattice parameters, interplane exchange constants, and, as a result, series of transitions between 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 \(\alpha-\delta\)-transition line.

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