Shift of close-packed basal planes as an order parameter of transitions between antiferromangetic phases in solid oxygen: II. Temperature/pressure dependence of sound velocities and lattice parameters

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In the present paper we generalize a phenomenological model developed by Gomonay and Loktev (*Fiz. Nizk. Temp*. **31**, 1002 (2005)) for the description of magnetostructural phase transitions and related peculiarities of elastic properties in solid oxygen under high pressure and/or temperature below 40 K. We show that variation of all the lattice parameters in the vicinity of α–β phase transition is due to both the shift of basal closed-packed planes and appearance of the long-range magnetic order. Competition between these two factors from one side and lattice compression below $T_{\alpha\beta}$ from another produces nonmonotonic temperature dependence of lattice parameter b (along monoclinic axis). Steep decrease of the sound velocities in the vicinity of $T_{\alpha\beta}$ can be explained by the softening of the lattice with respect to shift of the close-packed planes (described by the constant K_2) prior to phase transition point. We anticipate an analogous softening of sound velocities in the vicinity of α–δ phase transition and nonmonotonic pressure dependence of sound velocities in α phase.

1. Introduction

Solid oxygen that belongs to a family of cryocrystals is being studied for more than 100 years and still attracts attention of researches. This simple molecular crystal has very complicated temperature–pressure T–P phase diagram consisting of magnetic and nonmagnetic, metallic and dielectric, studied and nondiscovered phases (see, e.g., review [2] and references therein). Phase transitions and drastic change of the magnetic, electronic, elastic properties of solid O_2 can be triggered by variation of temperature, pressure, external magnetic field, etc. The thorough analysis of corresponding regularities is rather nontrivial problem because the O_2 crystal lattice is mainly hold by the weak van der Waals forces and so is very soft in comparison with ordinary solids. Besides, in contrast to other crystals, exchange magnetic interactions at low temperature prove to be of the same order as lattice energy. As a result, application of external fields (temperature, stress, magnetic) gives rise to a pronounced variation of all the lattice and magnetic parameters. In this situation precise microscopic calculations should be combined with general thermodynamic treatment.

In the 1st part of this paper [1] we made an attempt to develop a phenomenologic (Landau-type) model aimed at the description of the lattice and magnetic properties of solid oxygen in a sequence of temperature/pressure induced $\beta \rightarrow \alpha \rightarrow \delta$ transitions.

The proposed model was based on the following assumptions:

1. Magnetoelastic coupling is so strong that abrupt change of the magnetic structure leads to the noticeable variation of the crystal lattice.

2. The primary order parameter in the series of $\beta \to \alpha \to \delta$ phase transitions is a homogeneous shift of closed-packed planes. The order parameter is defined with respect to the virtual hexagonal, D_{6h}^1 pra-phase.

3. The only macroscopic parameter that controls these transitions is the specific volume. Temperature dependence of the specific volume cannot be calculated within the model and should be taken from the experiment.

As it was shown, this model gives good agreement with experimental data. However, some questions have been left beyond its scope. In particular, we have considered only two factors that define crystal structure of different phases — shift of the closed packed planes and specific volume of the crystal. More thorough analysis should account for rather strong rhombic deformations within the plane and separate contribution of interplane distance and isotropic in-plane strain into the change of specific volume.

In the present paper we try to refine the model by taking into account all the parameters that define the crystal structure of β, α, and δ phases and explain observed peculiarities of temperature/pressure dependence of lattice constants and sound velocities.

We would also like to mention with our great pleasure that the preliminary results of this paper were presented at International Conference CC-2006 (in Kharkov) devoted to the prominent Ukrainian scientist and wonderful woman Antonina Fedorovna Prihot'ko who is well known for her brilliant experiments in physics of cryocrystals. She is also famous for fundamental results in optical investigation of α and β phases in solid oxygen. With the present paper we try to pay our tribute of respect to her memory.

2. Model

It was already mentioned that the crystal structure of β, α, and δ phases can be considered as a homogeneously deformed hexagonal lattice. In general, such a deformation can be consistently described with the use of four independent variables: lattice parameters a, b, c, and angle β of monoclinic cell. Corresponding combinations that form representation of the D_{6h}^1 space symmetry group (parent pra-phase) are:

i) relative shift of closed-packed planes $\xi = (c/a)\cos\beta$;

ii) isotropic strain in the basal plane $\Delta s/s_0 = (ab - a_0 b_0)/(a_0 b_0)$;

iii) relative extension/contraction $u_{zz} = (h - h_0)/h_0$ in the direction perpendicular to closed-packed planes (Z axis), where $h \equiv c \sin\beta$;

iv) shear strain in the basal plane $u = (a - \sqrt{3}b) \times (\sqrt{3}a_0 b_0)^{-1/2}$.

The quantities with subscript «0» are attributed to a certain reference state (at zero T or P). In assumption of small variation of interplane distance (formally expressed

by inequality $u_{zz} \ll 1$) relative change of the specific volume $\Delta v/v$ can be readily expressed in a form of a simple sum $\Delta v/v = \Delta s/s_0 + u_{zz}$.

Equilibrium values of ξ, u_{zz}, u, and $\Delta s/s_0$ at a given temperature T and hydrostatic pressure P are calculated from standard conditions for minimum of Gibbs' potential Φ that is supposed to be invariant with respect to operations of the symmetry group D_{6h}^1.

Using results of symmetry analysis given in [1] (see Table 1 therein) general expression for Φ can be represented as a sum of structural Φ_{str}, magnetic Φ_{mag}, elastic Φ_{elast} contributions, and interaction term Φ_{int}:

$$\Phi = \Phi_{str} + \Phi_{mag} + \Phi_{elast} + \Phi_{int}. \tag{1}$$

The structure of the first term in (1)

$$\Phi_{str} = -K_2(s,h)[\cos 2\pi\xi_1 + \cos 2\pi\xi_2 + \cos 2\pi(\xi_1 - \xi_2)] +$$

$$+ \frac{1}{4}K_4[\cos 4\pi\xi_1 + \cos 4\pi\xi_2 + \cos 4\pi(\xi_1 - \xi_2)] + P\left(\frac{\Delta s}{s} + u_{zz}\right) \tag{2}$$

reflects the translational invariance of the crystal with respect to relative shift $\mathbf{u}$ of neighboring close-packed planes of hexagonal lattice, namely: $2\pi\xi_{1,2} \equiv \mathbf{b}_{1,2}\mathbf{u}$, where $\mathbf{b}_{1,2}$ are vectors of the reciprocal pra-phase lattice. Phenomenological constants K_2 and K_4 can be considered as coefficients in Fourier series of lattice potential.

The coefficient K_2 is supposed to be a linear function of the isotropic in-plane strain and interplane distance with corresponding phenomenological constants $\lambda_s, \lambda_h \propto \lambda_v$ (where $\lambda_v = 10$ GPa was estimated in [1]):

$$K_2(v) \equiv K_0 - \lambda_s \frac{\Delta s}{s} - \lambda_h u_{zz}.$$

Both constants $\lambda_s, \lambda_h > 0$ are supposed to be positive sign basing on general considerations (confirmed with further calculations, see below). Namely, the effective constant K_2 describes the strength of intermolecular forces that keep relative arrangement of basal planes. Increase of the average intermolecular distance should give rise to weakening of intermolecular bonds and hence to a decrease of K_2.

Magnetic contribution in (1)

$$\Phi_{mag} = -J(\mathbf{k}_{13})\sum_{j=1}^{2}(\mathbf{l}_j^{(\beta)})^2 - J(\mathbf{k}_{12})\sum_{j=1}^{3}(\mathbf{l}_j^{(\alpha)})^2 -$$

$$- J(\mathbf{k}_{14})\sum_{j=1}^{3}(\mathbf{l}_j^{(\delta)})^2 \tag{3}$$

accounts for the exchange interaction only, $J(\mathbf{k}_j) > 0$ are Fourier components of exchange integrals labeled according to stars $\mathbf{k}_j$ ($j = 12, 13, 14$) of irreducible representations of D_{6h}^1 space group, antiferromagnetic (AFM) vectors $\mathbf{l}^{(\beta)}$, $\mathbf{l}^{(\alpha)}$, $\mathbf{l}^{(\delta)}$ unambiguously describe the mag-

netic ordering in β, α, and δ phases*. It should be also stressed that the magnetic ordering in β phase has short-range nature (so-called correlation ordering with three sublattice 120° Loktev structure [2,6,7]). Collinear long-range magnetic ordering characterized by one of $\mathbf{l}^{(\alpha)}$ vectors, is established in α phase. An effective Neel temperature T_N is close to the temperature $T_{\alpha\beta}$ of α–β transition ($T_{\alpha\beta} = 23.5$ K and $T_N = 40$ K at ambient pressure) [2], so, saturation magnetization M_0 and, correspondingly, $|\mathbf{l}^{(\alpha)}| = M_0$ noticeably depend on temperature in the vicinity of $T_{\alpha\beta}$.

The elastic contribution in (1)

$$\Phi_{\mathrm{elas}}(\hat{u}) = \frac{1}{2}c'[(u_{xx} - u_{yy})^2 + 4u_{xy}^2] + \frac{1}{2}c_{33}u_{zz}^2 \quad (4)$$

does not include strain tensor components u_{xz}, u_{yz}, that can be considered as small excitations over finite deformations given by the order parameter $\xi_{1,2}$. An expression (4) is valid in the limit of infinitely small strains $u_{xx} - u_{yy}$, u_{zz}. In such an approximation operations of plane shift and deformation commute, hence, all the parameters of the model can be referred to the same «zero» state. Otherwise, one should specify the succession of lattice transformations, use different reference frames at each stage and work within nonlinear elasticity approach.

Interaction energy includes terms that describe different crossover effects. Here we are concentrated on several of them. First, variation of interatomic distances gives rise to the change of intra- (characterized with interaction constants Λ_{intra}, $\Lambda_\perp$), and inter- (constants Λ_{inter}, $\Lambda_\parallel$) plane exchange integrals**. This effect has magnetoelastic origin and can be formally described by two expressions. The first one is responsible for isotropic

$$\Phi_{\mathrm{mag\text{-}el}}^{(\mathrm{iso})} = \left(\Lambda_{\mathrm{intra}}^{(\beta)}\frac{\Delta s}{s} + \Lambda_{\mathrm{inter}}^{(\beta)}u_{zz}\right)\sum_{j=1}^{2}(\mathbf{l}_j^{(\beta)})^2 + \left(\Lambda_{\mathrm{intra}}^{(\alpha)}\frac{\Delta s}{s} + \Lambda_{\mathrm{inter}}^{(\alpha)}u_{zz}\right)\sum_{j=1}^{3}(\mathbf{l}_j^{(\alpha)})^2 + \left(\Lambda_{\mathrm{intra}}^{(\delta)}\frac{\Delta s}{s} + \Lambda_{\mathrm{inter}}^{(\delta)}u_{zz}\right)\sum_{j=1}^{3}(\mathbf{l}_j^{(\delta)})^2,$$

$$(5)$$

and another one for anisotropic effects

$$\Phi_{\mathrm{mag\text{-}el}}^{(\mathrm{an})} = -\Lambda_\parallel^{(\alpha)}[(\mathbf{l}_1^{(\alpha)})^2\cos 2\pi\xi_1 + (\mathbf{l}_2^{(\alpha)})^2\cos 2\pi\xi_2 + (\mathbf{l}_3^{(\alpha)})^2\cos 2\pi(\xi_1 - \xi_2)] -$$

$$- \Lambda_\parallel^{(\delta)}[(\mathbf{l}_1^{(\delta)})^2\cos 2\pi\xi_1 + (\mathbf{l}_2^{(\delta)})^2\cos 2\pi\xi_2 + (\mathbf{l}_3^{(\delta)})^2\cos 2\pi(\xi_1 - \xi_2)] -$$

$$- \Lambda_\perp^{(\alpha)}\{(u_{xx} - u_{yy})(\mathbf{l}_1^{(\alpha)})^2 + 2u_{xy}[(\mathbf{l}_2^{(\alpha)})^2 - (\mathbf{l}_3^{(\alpha)})^2]\} - \Lambda_\perp^{(\delta)}\{(u_{xx} - u_{yy})(\mathbf{l}_1^{(\delta)})^2 + 2u_{xy}[(\mathbf{l}_2^{(\delta)})^2 - (\mathbf{l}_3^{(\delta)})^2]\}. \quad (6)$$

Another coupling effect originates from strong anharmonicity which is a peculiar feature of molecular crystals. Corresponding contribution into thermodynamic potential has a form

$$\Phi_{\mathrm{anhar}} = -\lambda_e\{(u_{xx} - u_{yy})\cos 2\pi\xi_1 +$$

$$+ 2u_{xy}[\cos 2\pi\xi_2 - \cos 2\pi(\xi_1 - \xi_2)]\} - \lambda_\perp\frac{\Delta s}{s}u_{zz}, \quad (7)$$

where the coupling constants λ_e, $\lambda_\perp$ are of the same nature as λ_s, λ_h but from the general point of view should be much smaller in value (see Table 1). Really, λ_s, λ_h describe variation of average interatomic distances that result from reconstruction of crystal lattice in the course of phase transition. These constants are proportional to Grünaisen parameter which is very high. At the same time λ_e and $\lambda_\perp$ are responsible for a «differential» effect, namely, variation of anisotropy of the crystal lattice in the course of phase transition.

Table 1. Phenomenological coefficients

Coefficient	Value	Comments
χ_s	$0.31 \cdot 10^{-12}$ cm^2/dyne $3.2 \cdot 10^{-12}$ cm^2/dyne	at amb. P, at $T = 19$ K, $P = 1$–10 GPa
$\beta_P(T)$	$1.6 \cdot 10^{-4}$ 1 / K $1.7 \cdot 10^{-3}$ 1 / K	$T < 23.5$ K $T > 23.5$ K
K_{eff}	3 GPa	calc. at amb. P
K_4	5 GPa	calc. at amb. P
λ_s	13 GPa 0.2 GPa	at amb. P, at $T = 19$ K, $P = 1$–10 GPa
λ_h	10 GPa	in assumption that $c_{33} = 10$ GPa
$\lambda_\perp = c_{13}$	1 GPa	in assumption that $c_{33} = 10$ GPa
λ_e	0.06 GPa	in assumption that $c' = 1$ GPa
$\Lambda_\parallel^{(\alpha)}M_0^2$	–0.04 GPa	
$\Lambda_\perp^{(\alpha)}M_0^2$	–0.02 GPa	
$\Lambda_{\mathrm{inter}}M_0^2$	$\propto 0.06$ GPa	in all phases

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*   We assume that the series (3) may also include a wave vector corresponding to 4-sublattice structure of recently decoded ε phase [3–5]. Detailed analysis of this phase is out of scope of that paper.

**   We keep superscripts (β), (α), and (δ) in the constants of magnetic nature only, in order to emphasize a step-like change of magnetic structure in the phase transition point. Variation of other phenomenologic coefficients is not so crucial.

Standard minimization procedure enables to obtain the value of lattice parameters and stability conditions of β, α and δ phases.

3. Temperature/pressure dependence of lattice parameters

Equations for order parameter and stability regions were derived and discussed in details in [1]. The refinement of the model (splitting of in- and out-of-plane contribution into specific volume) gives rise to no qualitative changes. In this section we discuss only some additional effects that can be explained and predicted in the framework of the model. As in [1] we consider a homogeneous (from crystallographic point of view) phase with $\xi \equiv \xi_1 = \xi_2 / 2$. An effective macroscopic order parameter that vanishes in β phase is introduced as $\eta \equiv 1 + 2\cos 2\pi\xi$. Magnetic ordering in α and δ phases is described by a single AFM vector $\mathbf{l}_1^{(\alpha)}$ and $\mathbf{l}_1^{(\delta)}$, correspondingly.

3.1. Order parameter and isomorphic in-plane strain

In the «more symmetrical» β and δ phases an order parameter takes the limiting values $\eta = 0$ (β phase) and $\eta = -1$ (δ phase). Saturation magnetization M_0 (or correlation parameter in β phase) are constant. Pressure and temperature dependence of the isomorphic in-plane strain $\Delta s / s$ in these cases cannot be calculated from general thermodynamic considerations and is determined experimentally as

$$\frac{\Delta s}{s} = \int_0^T \beta_s(T'; P)dT' - \chi_s(T)P + [\underbrace{\Lambda_{\text{intra}}^{(\beta)}}_{\beta-\text{ph}} + \underbrace{\Lambda_{\text{intra}}^{(\delta)}}_{\delta-\text{ph}}]M_0^2 ,$$

(8)

where the in-plane thermal expansion coefficient $\beta_s(T; P)$ and isothermal $\chi_s(T)$ compressibility vary in a wide range with pressure and temperature (for example, Abramson et al. observed 10% change of compressibility per 1 GPa in β phase at room temperature [8]).

In α phase the temperature/pressure dependence of η and $\Delta s / s$ can be calculated from the system

$$\left[K_0 - K_4 + \Lambda_{\parallel}^{(\alpha)} M_0^2 - \lambda_s \frac{\Delta s}{s} - \lambda_h u_{zz} \right]\eta +$$
$$+ \frac{1}{2}K_4(3\eta^2 - \eta^3) - \Lambda_{\parallel}^{(\alpha)} M_0^2 = 0 ,$$
$$\frac{\Delta s}{s} = \int_0^T \beta_s(T'; P)\, dT' - \chi_s P + \frac{\chi_s \lambda_s}{2}(\eta^2 - 3) - \chi_s \Lambda_{\text{intra}}^{(\alpha)} M_0^2(T) .$$

(9)

(The behavior of interplane deformation u_{zz} will be discussed in the next section.) The values of phenomenological constants derived from fitting of functions $\eta(T, P)$, $\Delta s / s(T, P)$ to experimental data [9,10] with due to account of $M_0(T)$ temperature dependence [11,12] are given in Table 1. It can be seen from the Table 1 that

$K_{\text{eff}} = K_0 - K_4 + \Lambda_{\parallel}^{(\alpha)} M_0^2$ and K_4 are comparable in order of value with the shear modulus of the material [13]. The value of χ_s which we associate with the «seed» compressibility is much smaller compared with experimetally observed values [2]. This means that the main contribution into compressibility arises from shifts of close-packed planes and magnetic interactions.

3.2. Interplane distance

Distance h between the close-packed planes can be calculated from equations

$$u_{zz} = -\frac{\lambda_\perp}{c_{33}}\frac{\Delta s}{s} - \frac{\Lambda_{\text{inter}}^{(\beta)}}{c_{33}}M_0^2 \qquad \text{for } \beta \text{ phase} ,$$
$$= -\frac{\lambda_\perp}{c_{33}}\frac{\Delta s}{s} - \frac{\lambda_h}{2c_{33}}\eta^2 - \frac{\Lambda_{\text{inter}}^{(\alpha)}}{c_{33}}M_0^2(T) \quad \text{for } \alpha \text{ phase} ,$$
$$= -\frac{\lambda_\perp}{c_{33}}\frac{\Delta s}{s} - \frac{\lambda_h}{2c_{33}} - \frac{\Lambda_{\text{inter}}^{(\delta)}}{c_{33}}M_0^2 \qquad \text{for } \delta \text{ phase} ,$$

(10)

once the dependencies $\eta(T, P)$ and $\Delta s / s(T, P)$ are known. Analysis of equations (10) shows that in the β phase temperature/pressure dependence of u_{zz} (and hence interplane distance) is related with lattice compression within the close-packed plane. Thus, constant $\lambda_\perp$ coincides with the elastic modulus c_{13}. Estimated ratios $c_{13} / c_{33} = 0.1$ at ambient pressure and $c_{13} / c_{33} = 0.24$ at $T = 19$ K, $P = 1-7$ GPa and also the positive sign of $c_{13} > 0$ are in agreement with observations made by Abramson et al. [8].

Figure 1 shows temperature dependence of interplane distance experimentally measured (squares) and calculated from (10) (fitting parameters calculated in assumption that $c_{33} = 10$ GPa are given in Table 1). Below $T_{\alpha\beta}$ an interplane distance abruptly diminishes and then its temperature derivative changes sign. This fact may be ex-
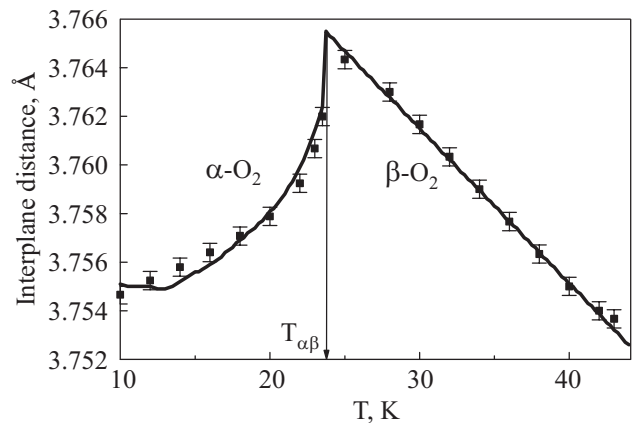

Fig. 1. Temperature dependence of interplane distance: (squares) calculated according to experimental data [9]. Theoretical curve (solid line) is calculated from Eq. (10). Arrow indicates the point of α–β transition.
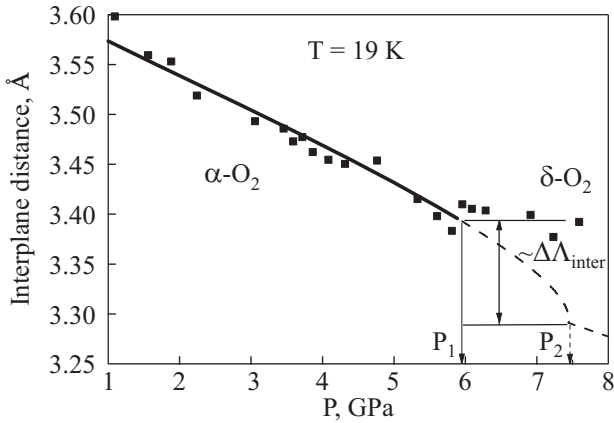
Fig. 2. Pressure dependence of interplane distance at $T = 19$ K: (squares) calculated according to experimental data [10]. Theoretical curve (solid line) is calculated from Eq. (10). Arrow indicates the point of the real, P_1, and hypothetical, P_2, α–δ transition.

Fig. 3. Pressure dependence of in-plane rhombic strain $u_{xx} - u_{yy}$ (solid line) calculated from Eq. (11). Squares: experimental data [10].

plained by the combined influence of the magnetic ordering (characterized by difference $\Lambda_{inter}^{(\beta)} - \Lambda_{inter}^{(\alpha)}$) and shift of basal planes (corresponding interaction constant λ_h). In β phase each O_2 molecule is situated over the center of underlying triangle. In-plane compression (that arises due to cooling or application of pressure) pushes out the overlaying molecules in vertical direction, so interplane distance increases. In α phase hexagonal planes are not only shifted from an ideal «close-packed» (with respect to underlying layer) position but can also «slip» under compression. Appearance of an additional degree of freedom allows lattice compression not only in-plane but also in perpendicular direction. Formally this means that constant λ_h is positive, in agreement with monotonic decrease of interplane distance under pressure-induced compression (see Fig. 2).

Contribution of magnetic interactions into interplane distance is important not only at α–β, but also at α–δ transition as can be seen from Fig. 2. If we assume that α and δ phases have the same magnetic structure, then pressure dependence of interplane distance according to (10) should be continuous up to (hypothetical) 2nd order transition point at $P_2 = 7.5$ GPa (dashed line in Fig. 2). Change of magnetic structure that originates from interplane exchange interactions induces 1st order phase transition at $P_1 = 6$ GPa $< P_2$ followed by abrupt change of the order parameter η and all the related parameters including u_{zz}. So, difference between the observed and hypothetical u_{zz} value above P_1 (see Fig. 2 and Eq. (10)) is proportional to $\Lambda_{inter}^{(\delta)} - \Lambda_{inter}^{(\alpha)}$ and is of magnetic nature.

3.3. In-plane deformation: parameters a, b

It is quite obvious from symmetry considerations that establishment of long-range magnetic order in α phase is followed by in-plane deformation described by
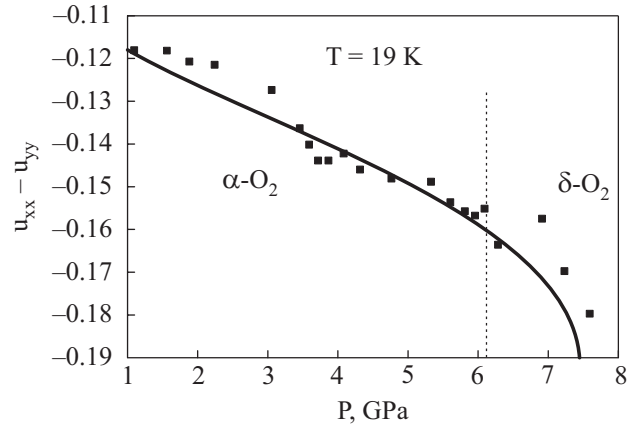
$u_{xx} - u_{yy} \equiv u$. Analysis of the expressions (6), (7) shows that the same effect can be produced by the shift of basal planes (term with λ_e) as seen from the following equation:

$$u = \frac{\lambda_e}{c'}(\eta^2 - 3\eta) + \frac{\Lambda_{\perp}^{(\alpha)} M_0^2(T)}{c'} . \qquad (11)$$

Pressure dependence of $u_{xx} - u_{yy}$ calculated from Eq. (11) along with experimental data is given in Fig. 3. It is clearly seen that in α-phase lattice anisotropy $u_{xx} - u_{yy}$ monotonically increases in absolute value with pressure. This effect can be explained from very simple considerations. Pressure produces compression in all directions in the basal plane but relative shift of planes can induce an effective tension in b direction as seen from Fig. 4 (O_2 molecules move apart in b direction when overlaying molecule moves toward the edge). As a result, deformation in basal plane is essentially anisotropic and aniso-
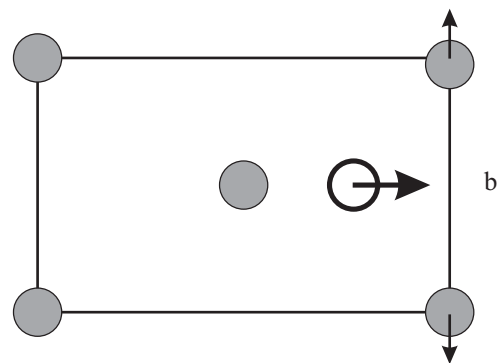

Fig. 4. In-plane displacements (arrows) of O_2 molecules induced by relative shift of the overlaying (open circle) plane.
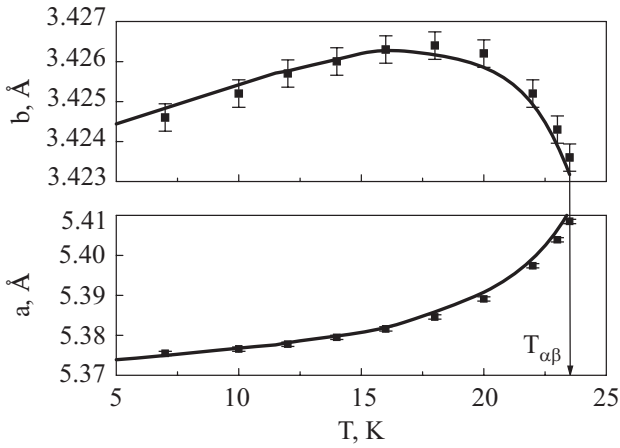
Fig. 5. Temperature dependence of lattice parameters *a* and *b* (solid lines) calculated from Eqs. (9), (11). Squares: experimental data [9].

tropy is more pronounced at smaller interatomic distances (i.e., at higher pressure).

The same effect takes place during cooling α phase at ambient pressure. Figure 5 shows temperature dependence of *a* and *b* lattice parameters below $T_{\alpha\beta}$. Intermolecular lattice distance *a* decreases monotonically because of cooling-induced compression. In contrast, temperature dependence of the parameter *b* is nonmonotonic. Increase of *b* during cooling from 23.5 to 18 K means that tension in this direction is stronger than cooling-induced compression. In particular, Eq. (11) demonstrates that two mechanisms may be responsible for this behavior: repulsion of ferromagnetically ordered neighbors [2] (described by the term $\Lambda_{\perp}^{(\alpha)}M_0^2(T)$, M_0^2 increases with temperature decrease) and already mentioned shift of basal planes.

Comparison of the above theoretical dependences with experimental data obtained by different groups using different technique makes it possible to estimate the values and range of phenomenological constants (see Table 1). All the coefficients could be grouped in three categories: i) large ($\propto 10$ GPa) constants responsible for anharmonicity effects ($\lambda_{s,h}$); ii) intermediate ($\propto 1$ GPa) constants ($K_{\text{eff}}, K_4, c_{13}$) that characterize elastic properties of crystal and iii) small (below 0.1 GPa) constants that describe magnetic interactions and anisotropy effects (rest of the constants). Though small in value the magnetic interactions reveal themselves in the case of competition between different structural interactions like pressure induced compression and repulsion that arises due the shift

of basal planes. Strong anharmonicity is quite natural phenomena for molecular crystals. It is remarkable that at ambient pressure both coefficients λ_s and λ_h are of the same order and the main contribution into effective structural constant K_2 arises from isomorphic in-plane strain* $\Delta s / s$.

4. Peculiarities of sound velocities in the vicinity of phase transition points

Experimental study of sound velocity in solid oxygen provides information about interactions that play the leading role in phase transitions. High-pressure measurements in β phase [8] show monotonic increase with pressure of all the elastic constants except shear modulus c_{44}, the value of which abruptly decreases in the vicinity of β–δ-transition point (approximately 8 GPa at 295 K). Low-temperature curves [13,14] have a pronounced minima at $T_{\alpha\beta}$.

Critical behavior of sound velocities can be quite naturally explained in the framework of the developed model using the concept of Goldstone mode. Really, the 2nd (or weak 1st**) order phase transitions are usually accompanied with softening of a certain bond responsible for appearance of the order parameter. So, characteristic frequency of the corresponding excitations (symmetry related to the order parameter) should vanish or at least noticeably diminish in the vicinity of the phase transition point (Goldstone mode). In the case of $\beta \to \alpha \to \delta$ transitions an order parameter (shift of basal planes) is symmetry related with strain tensor component u_{zx} (see Table 2 in [1]) and, as a result, with the transverse acoustic modes propagating in [0001] and [1000] directions. Thus, these modes should have peculiarity in phase transition points.

Sound velocities of the «soft» transverse, v_t, and longitudinal, v_l, acoustic waves propagating in [1000] direction are expressed through the elastic moduli in a standard way

$$v_t^2 = \frac{1}{2\rho}[c_{11} + c_{55} - \sqrt{(c_{11} - c_{55})^2 + 4c_{15}^2}],$$

$$v_l^2 = \frac{1}{2\rho}[c_{11} + c_{55} + \sqrt{(c_{11} - c_{55})^2 + 4c_{15}^2}], \qquad (12)$$

where ρ is crystal density.

Elastic moduli that equal to the 2nd derivatives of thermodynamic potential Φ (see Eq. (1)) with respect to strain tensor components are calculated at equilibrium values of lattice parameters:

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* We are grateful to Prof. Yu.A. Freiman who has drawn our attention to this fact.

** In other words, 1st order phase transition between the phases that are in subgroup relation, i.e., 1st order close to 2nd one.

$$c_{11} = \left.\frac{\partial^2 \Phi}{\partial(\Delta s / s)^2}\right|_0 , \quad c_{55} = \left(\frac{c\sin\beta}{a}\right)^2 \left.\frac{\partial^2 \Phi}{\partial\xi^2}\right|_0 ,$$

$$c_{15} = \frac{c\sin\beta}{a} \left.\frac{\partial^2 \Phi}{\partial\xi\partial(\Delta s / s)}\right|_0 , \quad du_{xz} = \left(\frac{c\sin\beta}{a}\right) d\xi . \tag{13}$$

Factor $(c/a)\sin\beta$ in (13) is deduced from geometrical considerations.

Then, omitting some terms immaterial for further discussion we obtain that in all three phases $c_{11} = \chi_s^{-1}$, $c_{15} = 0$ in β and δ phases and

$$c_{55} = \left(\frac{4\pi c\sin\beta}{a}\right)^2 \left[\lambda_s(\beta_s T - \chi_s P) - \frac{3}{2}K_{\text{eff}}\right] \tag{14}$$

in β phase,

$$c_{55} = \left(\frac{4\pi c\sin\beta}{a}\right)^2 \times$$
$$\times [\lambda_s(\chi_s P - \beta_s T) + K_{\text{eff}} - K_4 + 2\Lambda_\parallel^{(\alpha)} M_0^2] \tag{15}$$

in δ phase, and

$$c_{55} = \left(\frac{4\pi c\sin\beta}{a}\right)^2 \times$$
$$\times \left[\lambda_s(\chi_s P - \beta_s T) - K_{\text{eff}} - 3K_4\eta\left(1-\frac{\eta}{2}\right)\right]\sin^2 2\pi\xi ,$$
$$c_{15} = \frac{4\pi c\sin\beta}{a}\lambda_s \sin 2\pi\xi \tag{16}$$

in α phase.

It can be easily seen from (14) that in β phase shear modulus increases with temperature and decreases with pressure, at least in the vicinity of transition point, in consistency with observations [8].

More interesting is comparison of experimental and theoretical temperature dependencies* $c_{t,l} = \rho v_{t,l}^2$ shown in Fig. 6. Anomalous softening of c_t agrees well with theoretical predictions and thus may be explained by high compliance of O_2 crystal lattice with respect to shift of the closed-packed molecular planes. Softening of c_l is not so obvious from general point of view but in the case of molecular crystal may originate from strong anharmonicity.

An analogous softening of elastic moduli and corresponding sound velocities is also expected in the vicinity of α–δ transition. Figure 7 shows hypotetical pressure dependence of the moduli product** $c_t c_l$ calculated on the basis of equations (12)–(16) with characteristic values of
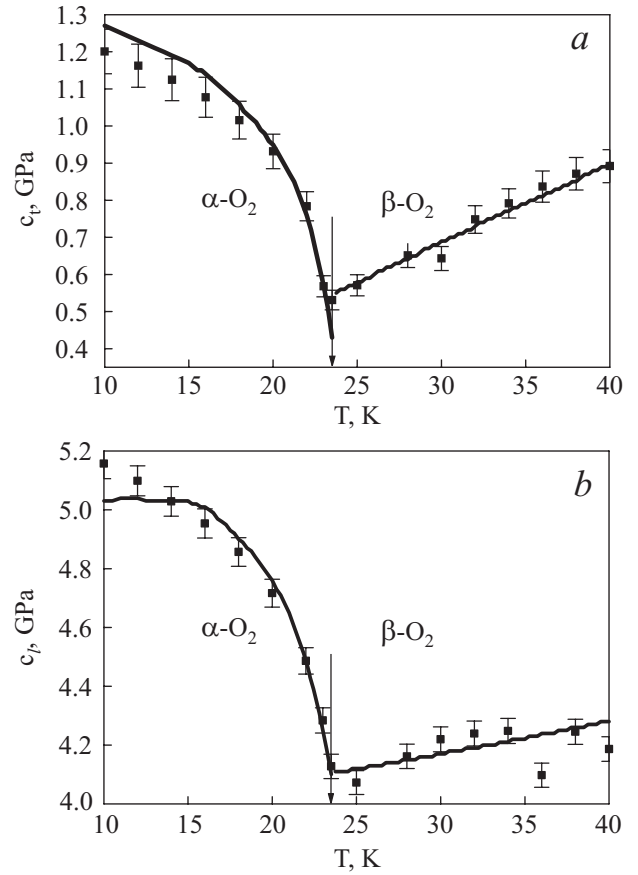

Fig. 6. Temperature dependences of shear modulus c_t (*a*) and compression modulus c_l (*b*) calculated from (12)–(16) (solid line). Squares: experimental data [13].

phenomenologic parameters (see Table 1). It is clear that this dependence should be nonmonotonic, with notice-
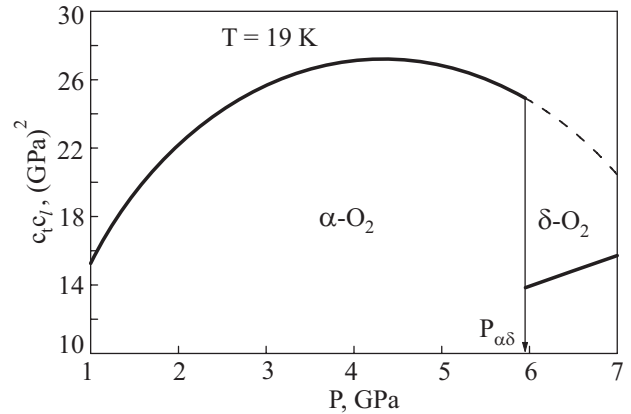

Fig. 7. Pressure dependence of the product of $c_t c_l$ calculated from (12)–(16) (solid line).

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* Temperature dependence of $c_{11} = \chi_s^{-1}$ is taken from fitting the data in β phase.

** The lack of experimental data makes it impossible to separate c_t and c_l contributions.

able decrease of moduli while approaching to $\alpha\beta$- and $\alpha\delta$-phase boundaries.

5. Conclusions

In summary, we have calculated temperature and pressure dependence of all the crystal lattice parameters of solid oxygen in the magnetic α, β, δ phases. The above phenomenological model ascribes the leading role in structural changes to the shift of close-packed basal planes in satisfactory agreement with the experiment.

In particular, shift of the planes is responsible for nonmonotonic temperature dependence of lattice parameter b in α phase (effective repulsion), change of the effective thermal coefficient in c direction in α–β transition (nonmonotonic t dependence of interplane distance), softening of shear modulus and corresponding velocities in the vicinity of $T_{\alpha\beta}$.

We assume that with certain stipulation the developed model may be applied to interpretation of IR spectra [15,16] which pressure dependence looks similar to pressure dependence of the order parameter. In particular, we predict nonmonotonic pressure dependence of elastic moduli in α phase and critical behavior in α–δ-transition point. At the same time some of the problems are still being outside the theoretical treatment. First of all it concerns magnetocrystalline structure of ε phase, metallization of highly compressed oxygen along with corresponding mechanism of superconductivity, optical properties of high-pressure phases, etc. These and other problems are the subject of future investigations.

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