

## Character of the $\alpha$ - $\beta$ phase transition in solid oxygen

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Properties of the  $\alpha$  and  $\beta$  phases of solid  $O_2$  are calculated with a deformable-cell Monte Carlo method and the character of the associated phase transition is delineated. We find that the monoclinic  $\alpha$  phase is stable at temperatures  $T \lesssim 18$  K and in- and out-of-plane antiferromagnetic order is predicted that is in accord with experiment. The magnetic correlations appear to be long ranged. A phase transition into  $\beta$ - $O_2$  occurs at  $T = 17.75 \pm 0.2$  K. It is first order with a calculated volume change  $\Delta V = 0.06 \pm 0.10$  cm<sup>3</sup>/mole, and is accompanied by a magnetic transition into a highly dynamic quasi-helical state with a correlation length  $l_c = 8 \pm 1$  Å at 18 K, that decreases rapidly with increasing temperature. The results indicate that  $O_2$  behaves as a two-dimensional magnetic system. The molecular axes exhibit temperature dependent, small angle libration about an axis normal to the basal plane and there is no evidence of precession in  $\beta$ - $O_2$ . There is also no evidence of magnetic reordering in the  $\alpha$  phase as a precursor to the transition.

### I. INTRODUCTION

The  $\alpha$ - $\beta$  phase transition in solid  $O_2$  has received considerable attention because it appears to involve both structural and magnetic changes that are strongly coupled and may occur in concert. This large magnetoelastic effect is understood to be the consequence of the fact that the dominant nonmagnetic binding between the molecules is a relatively weak van der Waals interaction, which makes  $O_2$  a rather unique magnetic solid. The nature of this transition has not been previously resolved. It is therefore the purpose of this work to calculate properties of both these phases at zero external pressure, over a range of temperatures, and to elucidate the features of the transition.

The  $\alpha$  phase is known<sup>1</sup> to exist at temperatures  $0 \leq T < 23.8$  K and exhibits a monoclinic  $C2/m$  structure, where the molecules orient normal to the  $(a, b)$  basal plane as shown in Fig. 1. Neutron scattering<sup>2-4</sup> has established that the magnetic moments orient antiferromagnetically along the crystal  $b$  axis of the basal plane and, although the spin orientations on neighboring planes have not been clearly established, the measurements of Meier *et al.*<sup>4</sup> are best understood if the magnetic moments on molecules at  $(0,0,0)$  and  $(0,0,1)$  are parallel to one another and antiparallel to the spins at  $(\frac{1}{2}, \frac{1}{2}, 0)$  and  $(\frac{1}{2}, \frac{1}{2}, 1)$ , as indicated by the arrows in Fig. 1. The antiferromagnetic order is also inferred from susceptibility measurements.<sup>5-8</sup>

The  $\beta$  phase, which occurs at temperatures  $28.3 \leq T \leq 43.8$ , forms a rhombohedral  $R\bar{3}m$  structure<sup>9</sup> in which the molecular axes are collinear and orient normal to the hexagonal basal plane, as in  $\alpha$ - $O_2$ . The unit cell can be constructed by a three-layer stacking of these planes. As is shown by Krupskii *et al.*,<sup>10</sup> a monoclinic

lattice can be used to describe the structural cell of  $\beta$ - $O_2$  and, to facilitate comparisons with the  $\alpha$  phase, that representation is used in this work. The lattice parameters and reference frame are formatted as in Fig. 1. Interpretations of structural measurements have led to speculation that the molecules precess at possibly a large angle about the  $z$  axis, where the  $z$  axis is normal to the  $ab$  plane.<sup>11</sup> The magnetic character of  $\beta$ - $O_2$  has been a controversial topic because of somewhat contradictory experimental evidence. Magnetic susceptibility data<sup>5-8</sup> show more antiferromagnetic character than paramagnetic, but earlier neutron scattering and infrared results gave little evidence of antiferromagnetic order, even though there are some unexplained features in the spectra. However, the

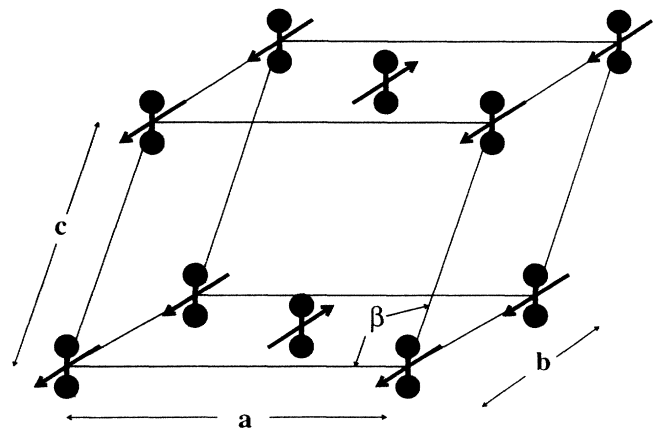


FIG. 1. Structure of  $\alpha$ - $O_2$  in the monoclinic representation used here. The arrows represent the directions of the magnetic spin vectors. The molecular axes are all perpendicular to the  $ab$  plane.

interpretation of recent neutron scattering results<sup>4,11</sup> is consistent with a quasihelical spin arrangement in which the moments of all six neighbors on the hexagonal basal plane are oriented at  $2\pi/3$  with respect to one another, and presumably lie in the  $(a,b)$  plane as shown in Fig. 2. The findings indicate that the magnetic order is probably short ranged, and a correlation length from 9 to 12 Å has been suggested.<sup>4,12</sup>

Considerable insight into the nature of the  $\alpha$ - $\beta$  transition is gained by making the following observations. The structural transformation from  $\alpha$  to  $\beta$  is accomplished by a slight distortion of the basal plane into the hexagonal plane of  $\beta$ -O<sub>2</sub>, shown in Fig. 2, accompanied by a slight shear along the  $a$  axis. As such, this can be categorized as an easy transition, as evidenced by the very small measured volume change,  $\Delta V = 0.04 \pm 0.08$  cm<sup>3</sup>/mole.<sup>10</sup> This small, perhaps nonexistent, volume change and negligible latent heat of transformation has led to speculation that the transition may be second order, and a helical magnetic structure in the  $\alpha$  phase, near the  $\alpha\beta$  transition temperature, has been proposed<sup>13,14</sup> as a precursor to the phase change. It has been suggested that the magnetic interaction plays an important part in negotiating the transition.<sup>15,16</sup> In fact, a static energy minimization procedure by English and Venables<sup>17</sup> showed that if magnetic interactions are neglected, the predicted structure of O<sub>2</sub> at temperature  $T = 0$  is that of the  $\beta$  phase. A subsequent calculation by Etters *et al.*,<sup>15</sup> confirmed this result, and further showed that the magnetic interaction is responsible for stabilizing the  $\alpha$  phase at low temperature. It was also shown that the attractive antiferromagnetic forces along the  $a$  axis are responsible for distorting the basal plane from the hexagonal symmetry of the  $\beta$  structure. It was then naturally concluded that the magnetic state of the  $\beta$  phase must preserve the hexagonal symmetry of the structure. A paramagnetic state or quasihelical order is consistent with this constraint, and both have been previously suggested. The predicted structure of both these possibilities gave the observed  $R\bar{3}m$  arrangement, and the lattice parameters were in good agreement with experiment. On the basis of energetics it was argued that the quasihelical structure is the most plausible state of  $\beta$ -O<sub>2</sub>. It was also shown<sup>15</sup> that when the thermodynamic expectation value of the magnetic Hamiltonian dimin-

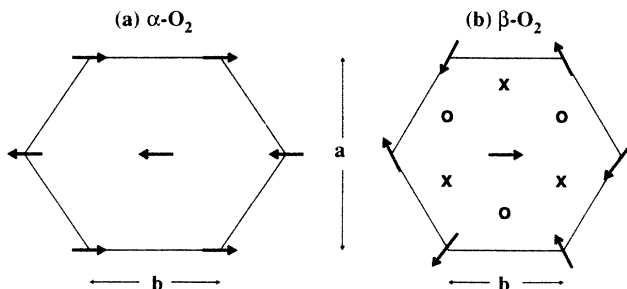


FIG. 2. Basal planes of  $\alpha$ - and  $\beta$ -O<sub>2</sub>. The arrows represent the directions of the magnetic spin vectors and the circles and crosses show the position of the molecules in the layers above and below the basal plane in  $\beta$ -O<sub>2</sub>. The molecular axes are all perpendicular to the  $ab$  plane.

ishes to less than 50% of its value for the static antiferromagnetic order at  $T = 0$ , the  $\alpha$  phase is unstable with respect to  $\beta$ -O<sub>2</sub>. The dominant sources of diminished values for that expectation value with increasing temperature are thermal fluctuations in the molecular orientations and the magnetic moments. Thermal expansion is too small to have much of an effect.<sup>10</sup> The out-of-plane contribution to the magnetic energy was determined to be nearly  $10^{-2}$  of the in-plane contribution, supporting the notation the O<sub>2</sub> is nearly a two-dimensional magnetic system. The weakness in that work was that the orientations of the magnetic moments were specified *a priori* and assumed to be static.

The purpose of the present study is to examine the  $\alpha$ - $\beta$  transition by a method that includes magnetoelastic effects and makes few assumptions with regard to structure. To that end, we have performed constant-pressure Monte Carlo calculations with variable-box shape. The magnetic spins are treated as degrees of freedom, and the magnetic interactions are approximated with a Heisenberg Hamiltonian.

## II. POTENTIAL AND METHOD

The potential between O<sub>2</sub> molecules that is used in this work has been proven to accurately represent the gas phase and the solid at zero temperature over a wide range of pressures.<sup>18</sup> The total potential energy is given by

$$U = \sum_{i < j}^N U_v(i, j) + U_{\text{EQQ}} + U_M,$$

where the site-site expression for the dispersion and overlap interaction between two molecules  $(i, j)$  is

$$U_v(i, j) = \sum_{s=1}^4 \{ A e^{-ar_s} - f(r_s) [(B_6/r_s^6) + (B_8/r_s^8) + (B_{10}/r_s^{10})] \}, \quad (1)$$

and  $A = 1.944144 \times 10^7$  K,  $\alpha = 3.8 \text{ \AA}^{-1}$ ,  $B_6 = 0.1507694 \times 10^6 \text{ K \AA}^6$ ,  $B_8 = -0.6966021 \times 10^6 \text{ K \AA}^8$ , and  $B_{10} = 0.9562391 \times 10^7 \text{ K \AA}^{10}$ .<sup>10</sup> The sum over  $s$  extends over the four distances between the two interaction sites on each molecule, placed at the atomic positions which are 1.208 Å apart at  $P = 0$ . The long-range dispersion terms are damped by the standard factor<sup>19</sup>

$$f(r_s) = \begin{cases} \exp\{ -[(1.28r_m/r_s) - 1]^2 \}, & r_s \leq 1.28r_m, \\ 1, & r_s > 1.28r_m \end{cases} \quad (2)$$

where  $r_m = 3.3 \text{ \AA}$ . The coefficients  $B_6$ ,  $B_8$ , and  $B_{10}$  are determined so that the well and long-range part of the potential agrees with a previous expression<sup>20</sup> that was found to give good agreement with experiment for the second virial coefficients and the zero-pressure structural properties<sup>10</sup> of  $\alpha$ -O<sub>2</sub>. The parameters  $A$  and  $\alpha$  were chosen to be within the range of uncertainty of expressions deduced from molecular beam scattering and recent *ab initio* data. The weak electric quadrupole-quadrupole interaction  $U_{\text{EQQ}}$  was described by placing point charges  $(-q, 2q, -q)$  along the molecular axis at  $(0.6038, 0,$

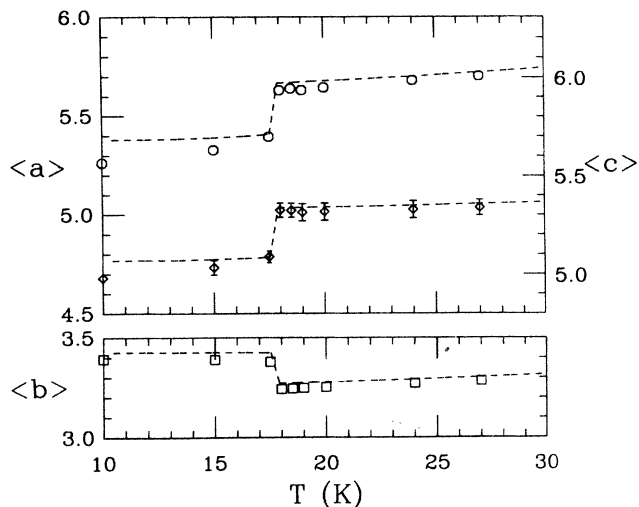


FIG. 3. Variation of calculated lattice lengths in Å with temperature. The upper part of the plot shows  $\langle a \rangle$  (circles) and  $\langle c \rangle$  (diamonds) and the lower part shows  $\langle b \rangle$  (squares). The scale for  $\langle c \rangle$  is offset by 0.3 Å from that of  $\langle a \rangle$  and is shown at the right. The error bars are calculated as described in the text and for  $\langle a \rangle$  and  $\langle b \rangle$  are smaller than the size of the symbols. The dashed lines are from the experimental data of Krupskii *et al.* (Ref. 10), with the experimental temperatures multiplied by 0.746 to give a transition temperature that can be compared to the present data.

$-0.6038$  Å), respectively, with respect to the mass center so that the calculated<sup>21</sup> quadrupole moment  $Q = -0.39 \times 10^{-26}$  esu cm<sup>2</sup> is reproduced. The potential  $U_{\text{EQQ}}$  between two molecules is then given by the Coulomb interaction between the charges on the two different molecules. All lattice sums were carried out to a cutoff of 9.5 Å. The magnetic interaction is given by

$$U_M = 2 \sum_{i < j}^N J(R_{i,j}) S_i \cdot S_j + D \sum_{i=1}^N (S_i \cdot n_i)^2, \quad (3)$$

where the first term is the dominant Heisenberg Hamil-

tonian and the second is the much smaller spin-orbit interaction that reflects the preference of the spins to align normal to the molecular axis. The unit vectors  $\hat{S}_i$  and  $\hat{n}_i$  characterize the direction of the spin and molecular axis of molecule  $i$ ,  $R_{ij}$  is the distance between mass centers of molecules  $(i, j)$ , and  $D = 5.756$  K, the gas phase value.<sup>22</sup> The exchange energy is given by

$$\begin{aligned} J(R) &= J_1 e^{-\alpha(R-R_0)}, \quad R < R_{\min} \\ &= J_2 e^{-\beta(R-R_0) + \gamma(R-R_0)^2}, \quad R_{\min} < R < R_{\max} \\ &= J_3 e^{-\delta(R-R_0)}, \quad R > R_{\max} \end{aligned}$$

where  $(J_1, J_2, J_3, \alpha, \beta, \gamma, \delta, R_0, R_{\min}, R_{\max}) = (19.855, 30.0, 17.973, 4.9, 3.5, 1.2, 1.778, 3.1854, 2.6, 4.2)$ . The first and last expressions ( $R < R_{\min}$  and  $R > R_{\max}$ ) are chosen to give smoothly converging functions at short and long  $R$ . No zero-point contributions were included in the present study.

A constant-pressure Monte Carlo procedure with continuously deformable, periodic boundary conditions is used to determine the thermodynamic averages of the physical quantities. The Monte Carlo cell is triclinic and contains 54 molecules. The number of degrees of freedom sampled are the six cell parameters  $(a, b, c, \alpha, \beta, \gamma)$  where  $a$ ,  $b$ , and  $c$  are the lengths of each side and  $\alpha$ ,  $\beta$ , and  $\gamma$  are the angles between them. What is sampled in the Monte Carlo calculations are actually the six components of the  $h$  matrix of Parrinello and Raman.<sup>23</sup> Also sampled are the nine degrees of freedom of each molecule, three translational, three rotational, and three characterizing the direction of the spin vectors. Thus, there are 486 degrees of freedom, although several constraint equations reduce the number of independent ones. For example, the sum of the squares of the direction cosines of each spin and orientation vector must be unity, reducing the total degrees of freedom to seven per molecule. Typically, averages are taken over 3000–4000 steps after the first 2000 or so steps are neglected to eliminate

TABLE I. Calculated properties of O<sub>2</sub>. The temperature  $T$  is in K, the lattice lengths  $\langle a \rangle$ ,  $\langle b \rangle$ , and  $\langle c \rangle$  are in Å,  $\langle \beta \rangle$  is in degrees, the volumes  $\langle V \rangle$  are in cm<sup>3</sup>/mol, and the configurational enthalpies  $\langle H \rangle$  (which include  $H_M$ ) and the magnetic energies  $\langle H_M \rangle$  are in K. The errors in the volumes are estimated as described in the text and are about  $\pm 0.05$  cm<sup>3</sup>/mol. Similarly, the errors in  $\langle H \rangle$  are about  $\pm 2$  K. The errors in the other quantities are shown in Figs. 3, 4, and 5.

$T$	$\langle a \rangle$	$\langle b \rangle$	$\langle c \rangle$	$\langle \beta \rangle$	$\langle V \rangle$	$\langle H \rangle$	$\langle H_M \rangle$
0	5.17	3.38	4.93	130.54	19.73	-1230	-139.7
10	5.26	3.39	4.98	131.34	20.10	-1192	-111.5
15	5.33	3.39	5.03	131.96	20.34	-1171	-93.6
17.5	5.39	3.38	5.09	132.71	20.51	-1156	-78.3
18	5.63	3.24	5.32	135.26	20.59	-1146	-60.1
18.5	5.64	3.25	5.32	135.23	20.61	-1144	-58.7
19	5.63	3.25	5.31	135.14	20.63	-1143	-58.2
20	5.64	3.25	5.31	135.13	20.68	-1138	-55.9
24	5.68	3.27	5.33	135.50	20.88	-1119	-48.9
27	5.70	3.29	5.34	135.67	21.03	-1106	-44.1

initial transients. Each step consists of sequentially sampling each of the degrees of freedom. Errors were estimated by dividing the Monte Carlo data into bins with about 200 steps per bin. Tests were made to check for trends and correlations in the data. Averages for each bin were calculated and the error was estimated as the standard deviation of those bin averages.

The application of deformable boundary condition and constant pressure ensembles has had a major impact on our ability to predict and characterize phase transitions, some in advance of experimental confirmation. The sensitivity of the method has allowed the determination of phase transitions to within a fraction of a degree temperature<sup>24</sup> and, for pressure-induced transitions, to within a fraction of a kbar.<sup>18</sup> This work is no exception. Such power is a result of allowing for volume fluctuations, which may be particularly important near a transition, and the impact of a deformable Monte Carlo cell, which obviates making *a priori* assumptions about the structure. Then the boundary conditions can deform to accommodate any new structure without bias.

### III. RESULTS

The calculated lattice parameters ( $a, b, c$ ) are displayed in Fig. 3 as circles, squares, and triangles, respectively, and are given, along with other calculated quantities, in Table I. It is clear that an abrupt change takes place at  $T_c = 17.75 \pm 0.25$  K. This, in fact, signals the  $\alpha$ - $\beta$  phase transition that is experimentally observed at  $23.8 \pm 0.3$  K.<sup>9,10</sup> The circles in Fig. 4 show  $\beta$ , the angle between the  $a$  and  $c$  crystallographic axes, which also shows an abrupt change at the same temperature. An inspection of these lattice parameters confirms that the low-temperature phase is the observed  $C2/m$  monoclinic structure and the high-temperature one is the  $R\bar{3}m$  rhombohedral struc-

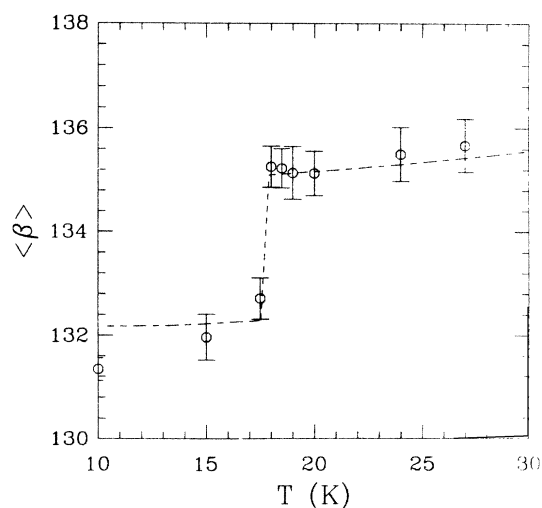


FIG. 4. Variation of the calculated angle  $\langle \beta \rangle$  between the  $a$  and  $c$  axes, in degrees. The error bars are calculated as described in the text. The dashed lines are from the experimental data of Krupskii *et al.* (Ref. 10), with the experimental temperatures multiplied by 0.746 to give a transition temperature that can be compared to the present data.

ture.<sup>9</sup> The dashed lines in Figs. 3 and 4 show the experimental results of Krupskii *et al.*,<sup>10</sup> where the experimental temperature scale has been multiplied by 0.746 to show the transition at our calculated transition temperature. Several things are apparent. First, the calculated lattice parameters ( $a, b, c, \beta$ ) agree very well with experiment both above and below the transition. Comparison of the calculated parameters with experiment at the same temperature and structure shows very good agreement, for example within 0.5% at  $T = 24$  K. The agreement at lower temperatures is less good due in part to the neglect of zero-point motion in the present study. Second, it is apparent from both theory and experiment<sup>10</sup> that the transition is first order, and that both theory and experiment give virtually identical volume change for the transition. The calculated volume change is conservatively given by  $\Delta V = 0.06 \pm 0.10$  cm<sup>3</sup>/mole. The molecular axes orient along the  $\hat{z}$  axis at all calculated temperatures in both the  $\alpha$  and  $\beta$  phases, although their root-mean-square fluctuations about this axis,  $\langle \theta^2 \rangle^{1/2}$ , increase monotonically with increasing temperature and seem to be insensitive to the phase transition. Some values in degrees are (7.7, 10.9, 11.8, 14.1) at temperatures (10, 17.5, 20, 27), respectively.

The magnetic properties also show an abrupt change at the transition temperature, as indicated by the expectation value of the magnetic Hamiltonian,  $\langle H_M \rangle$ , displayed in Fig. 5. In addition, thermal fluctuations of the spins  $\{\hat{S}_i\}$  act to reduce the magnetic energy with increasing temperature. Table II shows the calculated expectation values of the relative spin orientations  $\langle \hat{S}_i \cdot \hat{S}_j \rangle_n$  between various pairs of  $\alpha$ -O<sub>2</sub> molecules ( $i, j$ ). The index  $n = 1$  indicates that the pairs are nearest neighbors,  $n = 2$  are second nearest neighbors, etc. Values for the ideal static antiferromagnetic order of the phase are also displayed. It is noted that the first two and the sixth nearest pairs are between in-plane molecules, and the

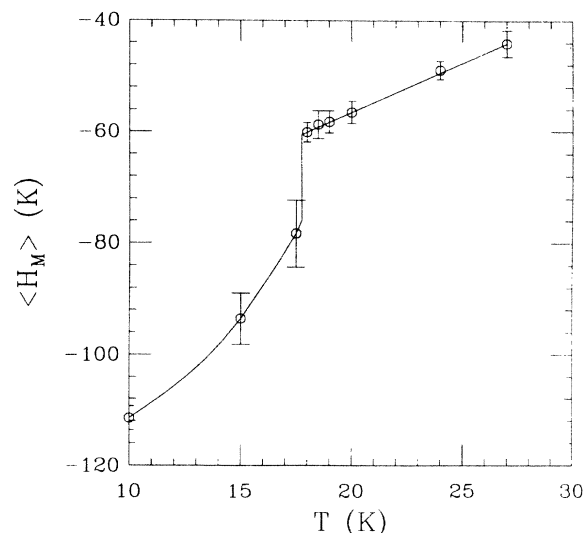


FIG. 5. Variation of the magnetic energy  $\langle H_M \rangle$  with temperature. The error bars are calculated as described in the text. The solid line is included as a guide to the reader.

TABLE II. Relativistic spin orientations for  $\alpha$ -O<sub>2</sub>. The thermodynamic expectation values of the relative spin orientations  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  vs temperature for  $\alpha$ -O<sub>2</sub>. The index  $n = i, \dots, 6$  identifies  $(i, j)$  as first- through sixth-nearest-neighbor pairs.  $n = 1, 2$ , and  $6$  are in-plane pairs and  $3-5$  are out-of-plane pairs. The first row gives values for the ideal static antiferromagnetic orientations.

$T$ (K)	$\langle \hat{S}_i \cdot \hat{S}_j \rangle_n$					
	$n = 1$	2	3	4	5	6
Ideal	-1.00	1.00	-1.00	1.00	1.00	1.00
0.0	-1.00	1.00	-1.00	1.00	1.00	1.00
10.0	-0.91	0.87	-0.81	0.81	0.81	0.90
15.0	-0.83	0.75	-0.69	0.68	0.69	0.81
17.5	-0.76	0.62	-0.52	0.54	0.54	0.73

third through the fifth are between molecules on different planes. An examination of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$ , calculated in the limit of zero temperature, show values identical to the ideal antiferromagnetic order inferred from experiment.<sup>2-4</sup> At finite temperature the calculated results for the first three in-plane neighbors,  $n = 1, 2$ , and  $6$ , indicate that the magnetic order is long ranged, although correlations can be quantitatively determined only for the neighbors shown, which are separated by distances less than one half the length of the Monte Carlo cell. Correlations with the first three out-of-plane neighbors, columns 3-5 in Table II, show similar behavior and the values of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  are surprisingly large even though these neighbors contribute only about 5% to the magnetic energy. These features persist in the  $\alpha$  phase up to the transition, although the spin-spin correlations clearly reduce from their ideal antiferromagnetic values due to increasing thermal fluctuations with increasing temperature. Most important is that the first out-of-plane nearest neighbors of any molecule are antiferromagnetically ordered, and the next two out-of-plane neighbors are ferromagnetically ordered, as seen by the signs of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  in columns 3-5 in Table II. Thus the spins are arranged as shown by the arrows in Fig. 1, and as inferred by Meier and Helmholtz<sup>4</sup> from neutron scattering. While these individual spins are relatively static at low temperatures, they become considerably more disordered near the transitions, even though the relative order between  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  remains large. This indicates that the static orientational

TABLE III. Relative spin orientations for  $\beta$ -O<sub>2</sub>. The thermodynamic expectation values of the relative spin orientations  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  vs temperature for  $\beta$ -O<sub>2</sub>. The first three columns represent the first three nearest in-plane pairs, which are first, sixth, and eighth nearest neighbors. The fourth column represents the nearest pair on adjacent planes, which are second-nearest neighbors. The first row gives values for the ideal, static quasihelical structure.

$T$ (K)	$\langle \hat{S}_i \cdot \hat{S}_j \rangle$			
Ideal	-0.50	1.00	-0.50	-0.05
18.0	-0.35	0.49	-0.22	-0.01
18.5	-0.35	0.48	-0.22	-0.01
19.0	-0.34	0.45	-0.20	-0.01
20.0	-0.33	0.43	-0.17	-0.01
24.0	-0.30	0.34	-0.13	-0.02
27.0	-0.27	0.26	-0.09	-0.02

order between spins at low temperatures gives way to a more dynamic correlation near the transition.

In the transition to the  $\beta$  phase nearly all vestiges of static magnetic order disappear. Indeed, the individual moments seem to sample all orientations almost uniformly. However, the relativistic spin orientations between neighbors take on well-defined expectation values as seen in Table III. For example, just above the transition at  $T = 18$  K the values of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  for each of the six nearest neighbors are nearly identical, with an average of  $-0.35$ . This indicates that the magnetic order is, on the average, quasihelical, with an average angle between neighboring spins of  $110^\circ$ , which is close to the value of  $120^\circ$  for the ideal case.<sup>15</sup> The dynamic nature of this order is dramatized in Fig. 6, which shows both the individual steps and the accumulated running average of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  for a typical nearest-neighbor pair in  $\beta$ -O<sub>2</sub> at  $T = 18$  K. The values at each step fluctuate greatly between the limiting values of  $\pm 1$ , but the accumulated average stabilizes into a well-defined result. The first three columns of Table III give  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  for the first three nearest neighbors of in-plane pairs of  $\beta$ -O<sub>2</sub> at various temperatures. These are overall the first-, sixth-, and eighth-nearest neighbors. The fourth column represents the nearest neighbors between a pair on adjacent planes,

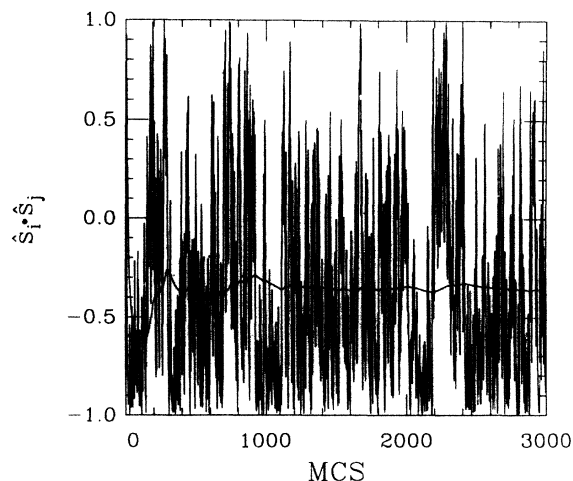


FIG. 6. Instantaneous values and cumulative averages of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  for a typical nearest-neighbor pair of molecules in  $\beta$ -O<sub>2</sub> at 18 K as a function of Monte Carlo steps (MCS's).

and are second nearest neighbors overall. There are several other important features shown in Table III. Although thermal fluctuations tend to decrease the values of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  with increasing temperature for in-plane neighbors, the effect is not large for nearest neighbors. This indicates that this dynamic magnetic order strongly persists in  $\beta$ -O<sub>2</sub> to relatively high temperatures, which is consistent with experimental evidence.<sup>12</sup> It is also noted that the in-plane spin correlations are quite short ranged, which have been quantified by calculating  $|\langle \hat{S}_i(0) \cdot \hat{S}_j(R) \rangle|$  for each of the three in-plane nearest-neighbor shells and normalizing each to its value for the ideal quasihelical arrangement. These points are then fitted to a curve of the form  $A \exp(-R/l_c)$ , where  $A$  is a constant to be evaluated at each temperature,  $R$  is the distance between spins ( $i, j$ ), and  $l_c$  is defined as the spin-spin correlation length. The results show that  $l_c = 8 \pm 1$  Å at  $T = 18.0$ , just above the transition temperature, which agrees well with values recently deduced from neutron scattering.<sup>4,12</sup> We also find that  $l_c$  decreases quite rapidly with increasing temperature, dropping to approximately 3.1 Å at  $T = 27$  K, about 9 K above the calculated transition temperature. Finally, it is apparent from Table III that the average  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  between nearest out-of-plane neighbors is extremely small, which is expected for the quasihelical structure.

#### IV. DISCUSSION AND CONCLUSION

The application of the constant-pressure ensemble with continuously deformable, periodic boundary conditions has again proven to be an enormously powerful method for calculating the properties of molecular solids. In this work, the  $C2/m$  monoclinic phase was correctly predicted for  $T < 18$  K, and Figs. 3 and 4 show that the lattice parameters are in good agreement with experiment. Moreover, as can be deduced from Table II, the system supports the antiferromagnetic order inferred from experiment. We also predict that the relative orientation of spins in the basal plane with out-of-plane neighbors is as recently inferred from the measurements of Meier and Helmholtz,<sup>4</sup> and contrary to some previous results.<sup>25,26</sup> This feature has yet to be clearly established by experiment. It is also noted from Table II that spin-spin correlations with out-of-plane neighbors appear to be surprisingly large in view of the fact that these neighbors contribute only 5% to the magnetic energy. We believe that this is because the strength of the magnetic order in each plane is great, which necessitates that  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  values between planes will also be large. This picture is consistent with the very small interplane magnetic energy, and we conclude as before, and as argued by Stephens *et al.*,<sup>12</sup> that  $\alpha$ -O<sub>2</sub> is essentially a two-dimensional magnetic system. Some arguments to the contrary<sup>4</sup> will be discussed herein. Finally, the information in Table II supports the argument that the spin correlations are long ranged at all temperatures in the  $\alpha$  phase. The fluctuation of the spins about the static antiferromagnetic ordering increases with temperature, as evidenced by the reduction in  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$ .

For  $T \geq 18$  K the system relaxes into the  $R\bar{3}m$   $\beta$ -O<sub>2</sub> structure. As with the  $\alpha$  phase, the lattice parameters

agree well with experiment and the molecular axes align normal to the basal plane with angular fluctuations about the  $z$  axis of (11°; 14°) at temperatures (18.5, 27 K), respectively. There is absolutely no evidence of large-angle precession as was suggested in an earlier work.<sup>11</sup> The magnetic order is clearly quasihelical, with all six nearest neighbors oriented at 110° with respect to one another at  $T = 18.5$  K, just above the predicted transition, and at 106° at  $T = 27$  K. This magnetic structure is highly dynamic in that the individual moments do not fluctuate about a static quasihelical order, but instead sample all orientations. Thus, all previous calculations on the magnetic character of  $\beta$ -O<sub>2</sub>, which were based upon either a static spin order or fluctuations about it, are clearly inadequate. An examination of the spin-spin correlations shows that unlike  $\alpha$ -O<sub>2</sub>, they are very short ranged with a correlation length decreasing from  $l_c = 8$  Å at 18.5 K to 3 Å at 27 K. This differs somewhat from the interpretation of Stephens *et al.*,<sup>12</sup> who obtain  $l_c \approx 9 \pm 1$  Å just above the transition temperature and conclude it remains the same up to 41 K. However, they recognize that their conclusion is subject to considerable uncertainty. Finally, it is noted from Table III that the average of  $\langle \hat{S}_i \cdot \hat{S}_j \rangle$  with all out-of-plane nearest neighbors is nearly zero. It is a consequence of the fact that this quantity is identically zero for the ideal static quasihelical structure. It is also clear that the contribution to the magnetic energy from out-of-plane neighbors is virtually zero, which means  $\beta$ -O<sub>2</sub> is even more two-dimensional magnetically than  $\alpha$ -O<sub>2</sub>.

The calculations give strong evidence that the  $\alpha$ - $\beta$  transition is first order, as shown by an abrupt change in the lattice parameters, the magnetic energy, and the magnetic order. The predicted volume change at the transition is conservatively estimated to be  $\Delta V = 0.06 \pm 0.10$  cm<sup>3</sup>/mole, in good agreement with recent experiments.<sup>10</sup> It is remarkable that the calculation clearly predicts the  $\alpha$  phase at  $T = 17.5$  K and the  $\beta$  phase at 18 K. As many as 8600 steps were taken in this region to ensure that the system was in thermodynamic equilibrium. In all cases the preferred structure formed with many fewer steps, which dramatizes the enormous sensitivity of this method. The magnetic and structural transitions occur at the same temperature and there is no evidence of any magnetic change as a precursor, as previously suggested.<sup>13,14</sup> The only change in the  $\alpha$  phase antiferromagnetic state near the transition is an increased tendency toward dynamic rather than static order. The predicted transition temperature at  $T_c = 17.75 \pm 0.25$  K is 6 K below the observed value. This is of little consequence since  $T_c$  is sensitive to small changes in characterizing the interaction potential. For example, a 15% increase in the magnitude of the exchange energy would, based upon experience with two-dimensional O<sub>2</sub> layers on graphite,<sup>24</sup> be sufficient to bring  $T_c$  into close agreement with experiment. This change in  $J(R)$  is within present uncertainty of its value. Similarity, a slight reduction of the attractive part of  $U_V$  would also create the desired effect. While such fine tuning of the potential is possible, we see no merit in doing so at this stage of understanding, especially with the small systems used in the present study.

The striking similarity between the results of this work and a previous study of O<sub>2</sub> monolayers on graphite<sup>24</sup> is further testimony to the two-dimensional character of bulk O<sub>2</sub>. The only point of divergence is that the analog to the  $\alpha$ - $\beta$  transition occurs at  $T = 11.9$  K for the layered system, a difference which has ironically been used<sup>4</sup> as an argument to conclude that out-of-plane contributions to the magnetic state of the bulk system are important. This argument is certainly incorrect. Instead, the *non-magnetic* interaction between planes is not only important in stabilizing the structure, but it also influences the stability of the magnetic order via a strong magnetoelastic coupling. This is missing in the monolayer system and is the reason for the difference in transition temperatures.

Finally, there are two other findings that help elucidate the nature of the  $\alpha$ - $\beta$  transition. In a previous parametric study<sup>15</sup> it was found that when the magnetic energy is reduced to less than 50% of its zero-temperature value, the  $\alpha$  phase becomes unstable with respect to the formation of  $\beta$ -O<sub>2</sub>. Thermal fluctuations reduce  $\langle H_M \rangle$  by this fraction when its value is  $-70$  K/molecule which, as shown in Fig. 5, occurs at almost exactly the predicted transition temperature. It is also instructive to compare the  $\alpha$ -

$\beta$  transition with the  $\alpha$ - $\delta$  transition<sup>27</sup> which occurs at low temperatures and at a pressure  $P = 28 \pm 2$  kbar. This easy transition from a monoclinic to orthorhombic structure is driven by a pressure-induced shear force along the crystallographic  $a$  axis, caused by a competition between the magnetic and nonmagnetic interactions. Analogously, the  $\alpha$ - $\beta$  transition is driven by a thermally-induced shear force also along the  $a$  axis and also caused by a competition between magnetic and nonmagnetic interactions.<sup>18,20</sup> The essential distinction between the two is that the  $\alpha$ - $\delta$  transition involves no magnetic change, whereas the  $\alpha$ - $\beta$  transition is accompanied by a change in magnetic order which eliminates the distortion of the basal plane present in  $\alpha$ -O<sub>2</sub>.

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