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Structure of 'Orange' $^{18}O_2$ at 9·6 GPa and 297 K*

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(*Received* 3 *May* 1982; *accepted* 21 *September* 1982)

Abstract

A single crystal of 'orange' $^{18}O_2$ at 9·6 (3) GPa and 297 (1) K was produced in a Merrill–Bassett diamond-anvil high-pressure cell and examined by X-ray diffraction. Pressure was determined with the ruby-fluorescence method. The unit cell is orthorhombic, space group *Fmmm*, lattice constants $a = 4{\cdot}2151$ (6), $b = 2{\cdot}9567$ (4), $c = 6{\cdot}6897$ (17) Å, molar volume = $12{\cdot}56 \times 10^{-6}$ m^3 mol^{-1} with four molecules per unit cell. The charge densities of the molecules overlap or distort to a considerable degree. Generalized scattering factors were used in an aspherical-atom least-squares refinement. For five refined parameters and 24 observations the final R_w is 0·056. A correction is made to our previous work on β-O_2 at 5·5 GPa and 299 K.

Introduction

Diamond-cell technology has made possible the detailed study of solidified gases at ultrahigh pressure. Recently Nicol, Hirsch & Holzapfel (1979) carried out optical observations on solid O_2 in a diamond cell over the range $248 < T < 323$ K and $5{\cdot}0 < P < 18{\cdot}0$ GPa (1 GPa = 10 kbar) that show a surprisingly complex behavior. At 298 K they found that oxygen freezes at 5·9 GPa and then at 9·6 and 9·9 GPa undergoes transitions marked by dramatic color changes.

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* Work performed under the auspices of the US Department of Energy.

0567-7408/83/020153-05$01.50

It is not completely clear how the high-temperature high-pressure phases of oxygen relate to the known low-temperature low-pressure phases which, in order of increasing temperature, are: monoclinic α-O_2 ($C2/m$), rhombohedral β-O_2 ($R\bar{3}m$), and cubic γ-O_2 ($Pm3n$) (Donohue, 1974; Cox, Samuelsen & Beckurts, 1973; Mills & Schuch, 1970, unpublished results). At low P and T, γ-O_2 adjoins the melting curve. Near room temperature, however, Schiferl, Cromer & Mills (1981) determined from a single crystal grown at 5·5 GPa and 299 K that β-O_2 is the stable form at the melting point. d'Amour, Holzapfel & Nicol (1981) found the structure of O_2 at 6·8 GPa also to be that of β-O_2, but with numerous stacking faults. These authors gave a tentative phase diagram and suggested that β-O_2 transforms to α-O_2 at 9·6 GPa and that a new form, ε-O_2, not found at low T, occurs above 9·9 GPa at room temperature. The boundaries of these phases meet at a triple point near 10 GPa and 320 K. d'Amour (1981, unpublished results) also reported that at 8·0 GPa β-O_2 transforms into a structure in which the c axis is doubled.

As a continuation of X-ray studies on condensed gases (Schuch & Mills, 1970; Schiferl, Cromer & Mills, 1978; Schwalbe, Schiferl, Mills, Jones, Ekberg, Cromer, LeSar & Shaner, 1980; Cromer, Mills, Schiferl & Schwalbe, 1981; Schiferl *et al.*, 1981), we made X-ray diffraction measurements on a single crystal of $^{18}O_2$ at 9·6 (3) GPa and 297 (1) K. The present work confirms that a color change does indeed take place near 9·3 GPa, but it signals a transition to a new orthorhombic structure rather than the proposed monoclinic α-O_2 form. These two structures, however, are closely related and transformation from one to the other may be second order.

Experimental

A Merrill–Bassett diamond-anvil cell (Merrill & Bassett, 1974), modified to utilize stronger beryllium pieces (Schiferl, 1977) and to provide uniform X-ray absorption and better optical access (Keller & Holzapfel, 1977), was loaded by condensing isotopically enriched (96·4%) $^{18}O_2$ gas into it using the indium-dam technique (Liebenberg, 1979; Mills, Liebenberg, Bronson & Schmidt, 1980). Care was taken to prevent any material other than $^{18}O_2$ and ruby powder from entering the sample chamber. $^{18}O_2$ was used instead of normal oxygen gas, which is almost entirely $^{16}O_2$, in the hope that the transition pressures would be lowered a few kilobars by the mass-isotope effect. This was an important consideration because the transitions reported by Nicol *et al.* (1979) occur barely within the pressure capability of our Merrill–Bassett cells.

Pressures were determined by the ruby-fluorescence method, assuming the R_1 line shift to be given by the linear relation, $\Delta\lambda/\Delta p = 3{\cdot}65$ Å GPa^{-1} (Forman, Piermarini, Barnett & Block, 1972; Barnett, Block & Piermarini, 1973). The calibration of our Spex Model 1403 spectrometer was carefully checked and the fluorescence of ruby powder from the same boule at ambient pressure was used as a zero-pressure reference.

In the course of preparing a single crystal for X-ray studies, we observed several interesting phenomena. Our first intention was to determine the Raman spectra, color changes, structures, and compression of $^{18}O_2$ up to 10 GPa in steps of about 1·5 GPa. Above 6·0 (1) GPa, however, we were unable to produce single crystals for X-ray studies by our usual procedures at room temperature. An attempt to anneal the sample by heating the diamond cell to 381 K caused the pressure to increase to 7·2 GPa. Under these conditions the sample turned opaque, but no single crystal was formed. On cooling to room temperature, the sample again became clear and colorless and the pressure returned to 6·0 (1) GPa, where we initiated optical measurements.

Raman studies of the vibrational (stretching mode) frequency of the $^{18}O_2$ molecule up to 9 GPa showed a single peak near 1495 cm^{-1}. After a subsequent pressure increase to 9·6 GPa, the color changed* and three stretching-mode peaks were observed at 1490, 1492, and 1495 cm^{-1}. The relative intensities were somewhat different in different parts of the sample area and varied with time as the pressure changed due to relaxation of components in the high-pressure cell. Apparently three solid phases which coexist at a triple point near 320 K and 10 GPa were present in our sample.

The single crystal used in our X-ray studies was grown by finally allowing the 9·6 GPa sample to anneal for 150 days. During this time the pressure relaxed to 9·3 GPa, but the structure did not revert to β-O_2. The X-ray studies were carried out at 297 (1) K with initial and final pressures of 9·3 and 9·9 GPa, respectively, giving an average pressure of 9·6 (3) GPa. The sample was placed on an automated Picker diffractometer and the unit cell was shown to be face-centered orthorhombic with space group $F222$, $Fmm2$, or $Fmmm$. The lattice constants $a = 4{\cdot}2151\ (6)$, $b = 2{\cdot}9567\ (4)$, and $c = 6{\cdot}6897\ (17)$ Å [$\lambda(\text{Mo}\ K\alpha_1) = 0{\cdot}70930$ Å] were determined from a least-squares refinement of eight reflections, each measured by the eight-position Hamilton (1974) technique and each with $27 < 2\theta < 40°$.

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* The most common description of this color was orange, but observers taking turns at the microscope described the same sample variously as orange, pink, magenta, purple and yellow! The absorption spectrum is similar to that reported by Nicol *et al.* (1979) and shows a rather broad (*ca* 100 nm FWHM) peak centered at about 510 nm and skewed toward the short-wavelength region. The extreme variation in the color perceived probably results from different relative sensitivities of the eyes of various observers to different parts of the spectrum.

Intensity data were collected and processed in the manner described by Cromer & Larson (1977). All reflections not shadowed by the pressure cell were measured out to $2\theta = 70°$ with graphite-monochromated Mo $K\alpha_1$ radiation. There were 102 non-space-group-extinguished reflections which were reduced to 32 non-equivalent reflections. Of these, 24 reflections were observed according to the criterion $I > 3\sigma(I)$. No absorption corrections were judged necessary. A comparison of equivalent reflections yielded $R_F = 0{\cdot}025$ (Cromer & Larson, 1977).

After the X-ray run, the single-crystal portion of the sample was examined by Raman spectroscopy and the stretching-mode peak at 1492 cm^{-1} was found to be very strong, while the other two peaks were quite weak. Where the laser beam (514·5 nm, 60 mW, 20 µm diam.) was focused on the single crystal, a spot approximately 60 µm diam. was turned polycrystalline. Despite this damage, the peak at 1492 cm^{-1} remained dominant, indicating that our phase was the same one identified by Nicol and coworkers as stable between 9·6 and 9·9 GPa.

Structure refinement

With the assignment of four molecules per unit cell, we calculated a molar volume of $V = 12{\cdot}56 \times 10^{-6}$ m^3 mol^{-1} for 'orange' $^{18}O_2$ at 9·6 GPa and 297 K. This V is consistent with the value $12{\cdot}66 \times 10^{-6}$ m^3 mol^{-1}, which is obtained from a straight-line extrapolation to 9·6 GPa of room-temperature X-ray data (d'Amour *et al.*, 1981) for β-$^{16}O_2$ at 5·9 and 6·8 GPa. It is reasonable to assume that the molar volumes of $^{16}O_2$ and $^{18}O_2$ are comparable, and that the volume change on transition from β-O_2 to 'orange' O_2 in the neighborhood of 9 GPa is not large.

The unit-cell dimensions and a calculated Patterson map were consistent with eight atoms in position 8(*i*), $\pm[0,0,z]$ of space group *Fmmm*, forming a close-packed arrangement of roughly ellipsoidal O_2 molecules. Subsequent least-squares refinements confirmed this structure. Extinction corrections were found to be unnecessary.

A standard refinement with anisotropic thermal parameters led to the results given in Table 1. The interatomic distance, uncorrected for thermal motion, is $d_0 = 1{\cdot}165$ (9) Å. If a torsional motion about the center of mass is assumed, the corrected value is

$$d = 2[d_0/2 + (U_{11}^2 + U_{22}^2)/(2d_0/2)] = 1{\cdot}252 \text{ Å}$$

(Busing & Levy, 1964). This corrected value is unreasonably large because the gas-phase value is 1·207 Å (Sutton, 1958).

The oxygen form factor used in the above refinement was for a spherically averaged free atom. An oxygen atom in the molecule should have at least two pronounced distortions: one a dipole due to the σ bond and directed toward the molecular midpoint; the other a quadrupole caused by the formation of π bonds. The quadrupole distortion might easily be perceived as thermal motion normal to these bonds.

Accordingly, a refinement with generalized scattering factors (GSF) was attempted (Stewart, 1969; Cromer, Larson & Stewart, 1976). Because of correlations and the paucity of data, it was not possible to refine all parameters. Anisotropic thermal parameters were highly correlated with the GSF parameters; consequently an isotropic thermal parameter was used. The dipole d_z correlated strongly with the atomic z-position parameter and thus d_z was held at zero. The free parameters (totalling five, as in the previous refinement) were: the scale factor, z, B, q_1, and q_5. The other quadrupole parameters q_2, q_3, q_4 and the d_x and d_y dipoles are identically zero because of the *mm*2 site symmetry. The results are also given in Table 1. The q_1

Table 1. *Least-squares refinements of solid oxygen*

	'Orange' $^{18}O_2$ ($P = 9{\cdot}6$ GPa, $T = 297$ K)		β-$^{16}O_2$ ($P = 5{\cdot}5$ GPa, $T = 299$ K)[a]
	Anisotropic model	GSF model	GSF model
z	0·0871 (10)	0·0878 (10)	0·0579 (3)
β_{11}	0·0357 (21)	–	0·1011 (44)
β_{22}	0·0420 (38)	–	–
β_{33}	0·0000 (36)[b]	–	0·0031 (3)
u_{11}^2 (Å^2)	0·0322	–	0·0311
u_{22}^2 (Å^2)	0·0186	–	–
u_{33}^2 (Å^2)	0·0000	–	0·0166
B (Å^2)	–	0·22 (16)	–
d_z	–	–	−0·21 (26)
q_1	–	1·74 (36)	–
q_5	–	−6·8 (22)	−2·4 (10)
R	0·049	0·049	0·043
R_w	0·057	0·056	0·026

(*a*) Refinement of our earlier structure for β-$^{16}O_2$ (Schiferl *et al.*, 1981).

(*b*) β_{33} tended toward a negative value of about one-tenth its standard deviation, but was constrained to be zero.

Table 2. *Comparison of observed and calculated structure factors for 'orange'* $^{18}O_2$ *at* 9·6 GPa *and* 297 K *in order of increasing Bragg angle*

h k l	F_o	F_c	*h k l*	F_o	F_c
2 0 0	600	608	5 1 1	89	90
1 1 1	572	590	3 3 1	105	108
0 2 0	411	418	4 2 4	74	72
0 2 2	170	169	3 3 3	<22	10
3 1 1	243	231	5 1 3	<27	9
2 2 0	286	278	0 4 0	112	122
2 2 2	110	116	0 4 2	77	54
3 1 3	<30	20	6 0 0	70	86
4 0 0	177	175	2 4 0	97	110
4 0 2	83	76	0 4 4	75	69
2 2 4	130	126	6 0 2	<35	39
1 3 1	159	157	2 4 2	73	49
4 0 4	90	90	5 3 1	66	77
1 3 3	<25	14	2 4 4	<25	63
4 2 0	118	127	6 0 4	<35	53
4 2 2	62	56	6 2 2	<36	38

term adds electron density along the x and y axes (in the plane z = 0·087), and the density is correspondingly reduced along the diagonals in this plane. The q_5 term adds density in a torus about the z axis and removes density in lobes along the z axis on either side of the atom. The uncorrected bond length is now d_0 = 1·175 (9) Å and, because the thermal motion is much reduced, the correction is small. The corrected value is d = 1·184 Å. The observed structure factors and those calculated with the parameters in Table 1 are given in Table 2.

Discussion

If ellipsoidal O_2 molecules are taken to have the dimensions defined by their 0·002 electron-density contours in units of 6·749 e $Å^{-3}$ (major axis S_1 = 4·18 Å and minor axis S_2 = 3·18 Å) (Bader, Henneker & Cade, 1967), then they cannot be packed into the unit cell. The charge densities of the molecules must either overlap strongly or be severely distorted in order to fit into the small orthorhombic cell. Raich & Mills (1971) used a shaped, hard core to calculate the repulsive part of a pair potential for nitrogen. They found that the high-pressure transition between α- and γ-N_2 could be explained on the basis of a core 0·7 times the size of the undistorted (gas) molecule and roughly bounded by the 0·04 electron-density contour. In the case of O_2, multipole interactions may allow the molecules to distort and pack in face-centered-orthorhombic unit cells.

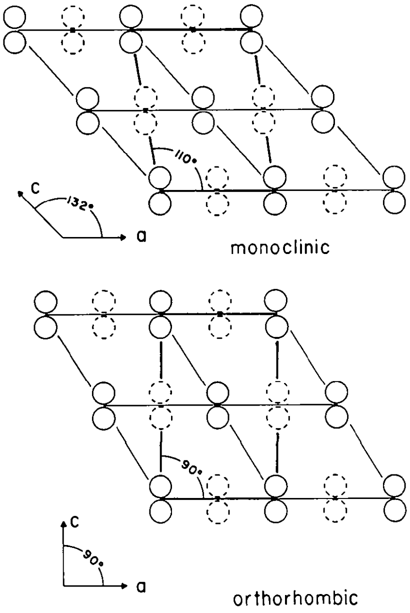

Fig. 1. Schematic representation of the relation between the monoclinic $C2/m$ structure of α-O_2 and the orthorhombic $Fmmm$ structure of 'orange' oxygen. The b axes out of the plane of the paper are equivalent. Dotted circles indicate atoms at $y = \frac{1}{2}$; full circles indicate atoms at $y = 0$.

It is not possible to say whether use of the heavy isotope $^{18}O_2$ significantly lowered any of the transition pressures, because the structure changes were too sluggish. For naturally occurring O_2, Nicol and coworkers identified a triple point near 10·0 GPa and 300 K where the phases β-O_2, ε-O_2, and one which they tentatively called α-O_2 coexist. Our Raman work indicates that for heavy oxygen three phases can indeed coexist in varying proportions over the pressure range $9·3 < P < 9·9$ GPa at 297 K. We believe, however, that the orthorhombic crystal structure reported here corresponds to the phase that Nicol and coworkers found between 9·6 and 9·9 GPa and identified as 'α-O_2'. Both the pressure range and Raman spectra are seen to be the same.

The present structure is, nevertheless, closely related to that of α-O_2, as shown in Fig. 1. Only a small change in the monoclinic angle β and, perhaps, a very slight change in the orientation of the molecules to make them truly normal to the a axis of the monoclinic cell, is necessary to bring the structures into coincidence. The transition between the present $Fmmm$ structure and the $C2/m$ of α-O_2 may occur elsewhere in the phase diagram and be of second order. Boccara (1968) discusses the conditions necessary for a second-order phase transition characterized by deformation of the unit cell. Specifically, he shows that a structure with point group mmm can transform into one with point symmetry $2/m$ *via* a second-order transition. Of course, this is not a guarantee that the transition will be second order. The fact that α-O_2 is antiferromagnetically ordered at low temperatures suggests that transition to the orthorhombic structure might be associated with a magnetic order–disorder transition. If so, the transition temperature should be near the value of the exchange integral divided by the Boltzmann constant, J/k. Meier, Schinkel & de Visser (1981) found an empirical relation that shows the exchange parameter for solid O_2 varies as the −14 power of the intermolecular distance r. Using their value J/k = 36 K and the Barrett, Meyer & Wasserman (1967) value r = 3·20 Å for α-O_2 at zero pressure near 20 K, and taking r = 2·96 Å from the present work, we calculate an exchange parameter J/k of 107 K at high pressure. Boccara (1968) points out that magnetic ordering complicates his symmetry arguments. It does not, however, change the possibility of a second-order transition in O_2.

Comments on our 5·5 GPa β-O_2 paper

J. Donohue pointed out to us that an error was made in the thermal-motion correction to the bond length in our previous paper on the 5·5 GPa β-O_2 structure (Schiferl *et al.*, 1981). Subsequent discussions with W. R. Busing led to the following analysis: the uncorrected distance is d_0 = 1·180 Å; from Table 2 of the previous paper, u_{11}^2

$= u_{22}^2 = 0{\cdot}0507$ Å^2 and $u_{33}^2 = 0{\cdot}0291$ Å^2; the corrected distance using the torsion model with fixed center of mass is thus 1·352 Å, much larger than we reported. If it is assumed that the center of mass has isotropic motion equal to u_{33}^2, we can then subtract this motion from components perpendicular to the bond. This assumption leads to a corrected value of d = 1·253 Å, still an unreasonably large value.

We therefore attempted to refine the β-O_2 structure once more, using an aspherical model with GSF's. The site symmetry is such that there is only one non-zero dipole and one non-zero quadrupole. Refinement was stable using these GSF parameters as well as anisotropic thermal parameters. The dipole is a positive distortion directed to the bond midpoint and the quadrupole is as described earlier. The results are shown in the last column of Table 1.

The uncorrected bond length is d_0 = 1·184 Å. Making the assumption that the u_{33}^2 motion refers to the center of mass, leads to a corrected value of d = 1·233 Å, a still unreasonably large bond length. Our β-O_2 crystal showed an enormous extinction effect; it is possible that this effect was improperly accounted for, perhaps because the crystal was anisotropically strained, and caused the thermal motion to be overestimated.

B. B. McInteer and M. Goldblatt of Los Alamos kindly prepared the $^{18}O_2$ gas sample. The crystallographic computations were performed on a CDC 7600 using the Los Alamos system of crystallographic programs developed primarily by A. C. Larson. We thank W. R. Busing, J. Donohue, R. D. Etters, and M. Nicol for useful discussions.

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