Acta Cryst. (1981). B**37**, 1329–1332

Structure of O_2 at 5·5 GPa and 299 K*

By David Schiferl, Don T. Cromer and Robert L. Mills

University of California, Los Alamos Scientific Laboratory, Los Alamos, New Mexico 87545, *USA*

(*Received* 24 *November* 1980; *accepted* 20 *January* 1981)

Abstract

An exceptionally good single crystal of O_2 was produced at 5·5 GPa and 299 K through laser annealing in a Merrill–Bassett diamond-anvil high-pressure cell. Pressure was determined with the ruby fluorescence method. X-ray diffraction studies showed the unit cell to be rhombohedral with space group $R\bar{3}m$, lattice constants $a = 2{\cdot}8467$ (2) and $c = 10{\cdot}2249$ (8) Å, and three molecules per unit cell. The structure is the same as that of β-O_2 found at low temperature. It was refined to $R_w = 0{\cdot}050$ for 39 observed intensities.

Introduction

When cooled under its own vapor pressure, liquid oxygen solidifies as cubic γ-O_2 (space group $Pm3n$) at a triple-point temperature of 55 K. On further cooling, the solid transforms into rhombohedral β-O_2 ($R\bar{3}m$) at 45 K. A final transition to monoclinic α-O_2 ($C2/m$) takes place at 24 K. Crystal structure determinations of O_2 at low temperatures and pressures have been made by numerous workers and are critically evaluated by Donohue (1974). Reported separately is a structure study of single-crystal γ-O_2 by neutron diffraction (Cox, Samuelsen & Beckurts, 1973). The only previous high-pressure X-ray studies of oxygen were made at 0·4 GPa by Mills & Schuch (1970, unpublished) on α-O_2 near 20 K, β-O_2 near 40 K, and γ-O_2 near 80 K.

Recently Nicol, Hirsch & Holzapfel (1979) published optical studies of O_2 in a diamond cell from 248 to 323 K and 5·0 to 18·0 GPa. At 298 K they observed that oxygen freezes at 5·9 GPa and then undergoes crystal structure transitions at 9·6 and 9·9 GPa, each being accompanied by a dramatic color change. By extrapolating the transition lines to the known phase diagram at lower pressures (Stevenson, 1957; Stewart, 1959), Nicol (1980) inferred that β-O_2 rather than γ-O_2 adjoins the melting curve at room temperature.

As a continuation of X-ray studies made on condensed gases (Schuch & Mills, 1970; Schiferl, Cromer & Mills, 1978; Schwalbe *et al.*, 1980; Cromer, Mills, Schiferl & Schwalbe, 1981), we made X-ray diffraction measurements on a single crystal of O_2 in a diamond cell at 5·5 ± 0·1 GPa and 299 ± 1 K. The present work confirms that the structure under these conditions is indeed β-O_2, and gives precise crystallographic data on this solid.

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 high-purity oxygen gas into it using the indium-dam technique (Liebenberg, 1979; Mills, Liebenberg, Bronson & Schmidt, 1980). Care was taken to prevent any material other than oxygen and ruby powder from entering the sample chamber. The pressure, both before and after the X-ray measurements at 299 ± 1 K, was determined to be 5·5 ± 0·1 GPa by the ruby fluorescence method, assuming the R_1 lineshift to be given by the linear relation, $d\lambda/dP = 0{\cdot}0365$ Å GPa^{-1} (Forman, Piermarini, Barnett & Block, 1972; Barnett, Block & Piermarini, 1973).

Preparation of a single crystal for X-ray studies at 5·5 GPa came about in a curious manner as a result of our determinations of the melting curve near room temperature. By heating the sample very slowly (about 0·2 K min^{-1}) while watching it under crossed polarizers with a 60× microscope, we determined that melting, as defined by the presence of equal amounts of solid and fluid, occurred at 5·6 ± 0·1 GPa and 316 ± 5 K. On cooling, the sample solidified into an almost strain-free single crystal which, however, did not survive a subsequent ruby fluorescence pressure measurement. Light from the argon laser (5145 Å at less than 10 mW incident power on the sample) caused the formation of a crystallite wherever it was focused on the sample. As the laser beam was moved across the sample, new crystals were formed, which grew rapidly at the expense of the surrounding crystals. This behavior continued for about 20 min and stopped when a single crystal was formed, which could not be destroyed but could only be

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

0567-7408/81/071329-04$01.00

strained by further illumination by the laser beam. The strain would be relieved after a wait of about 10 min with no change in the crystal orientation, as revealed by X-ray precession photographs. This crystal was then used for the X-ray structure studies.

The sample was placed on an automated Picker diffractometer and the unit cell was shown to be similar to that of rhombohedral β-O_2. The lattice constants of the hexagonal cell, a = 2·8467 (2) and c = 10·2249 (8) Å, were determined from a least-squares refinement of eight reflections, each measured by the eight-position Hamilton (1974) technique and each with $2\theta > 45°$. The reflections were exceptionally sharp (FWHM of the Mo $K\alpha_1$ line was less than 0·1° at 2θ = 47°).

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 2θ = 80° with graphite-monochromated Mo $K\alpha$ radiation. The relative intensities were similar to those found by Hörl (1962) for β-O_2, which has space group $R\bar{3}m$, and this space group was assumed for our work. There were 146 non-space-group extinct reflections which were reduced to 54 nonequivalent reflections. Of these, 46 reflections were observed according to the criterion $I \geq 3\sigma(I)$. No absorption corrections were judged necessary; a comparison of equivalent reflections yielded R_F = 0·0345 (Cromer & Larson, 1977).

Structure refinement

The unit-cell size and space group, as well as recent determinations of the phase diagram of oxygen by optical techniques (Nicol *et al.*, 1979; Nicol, 1980), indicated that the structure was almost certainly the rhombohedral β-O_2 structure found at low temperatures (Donohue, 1974). This was confirmed by subsequent least-squares refinement.

The hexagonal unit cell contains six atoms at the position 6(c) with z = 0·0577 (2). The calculated molecular volume is 2·920 (3) Å^3. The structure may be regarded as distorted f.c.c., the distortion arising because the ellipsoidal molecules are packed with their longer dimension parallel to the c axis.

Values of observed and calculated structure factors are presented in Table 1 and the crystallographic parameters are given in Table 2, where they can be compared with those for β-O_2 at 28 K and zero pressure (Hörl, 1962). Extinction corrections (Larson, 1970) were extremely large and reduced the intensity of the strongest reflections by a factor of about 10. In Table 1 we report the results for a structure refinement in which extinction corrections were made, but the structure factors of the seven strongest reflections were not used in the least-squares fit. Repeating the refinement, either with the strongest reflections included or without the extinction corrections, left the values of z and the thermal parameters essentially unchanged, but increased R_w.

Table 1. *Observed and calculated structure factors* ×10 *for* β-O_2 *at* 5·5 GPa *and* 299 K

h	k	l	F_o*	F_c	F_c†	h	k	l	F_o*	F_c	F_c†
0	0	3	−66	72	173	1	1	12	11	10	10
0	1	2	−74	86	194	2	2	0	14	14	14
1	0	4	24	23	24	0	1	14	13	11	11
0	0	6	−62	70	118	2	2	3	7	6	6
0	1	5	37	36	41	2	1	10	18	16	16
1	1	0	−60	76	127	1	3	1	13	11	11
1	1	3	44	43	52	3	1	2	12	9	9
1	0	7	−71	67	97	0	3	9	15	14	14
0	0	9	−63	71	103	0	2	13	−7	0	0
0	1	8	−64	67	94	1	3	4	−7	1	1
0	2	4	9	9	9	1	2	11	13	10	11
1	1	6	39	39	44	2	2	6	8	6	6
1	0	10	49	49	57	2	0	14	9	6	6
0	2	7	38	39	43	1	3	7	9	7	7
2	1	1	34	35	38	1	0	16	19	17	17
1	2	2	26	28	30	1	1	15	12	11	11
1	1	9	43	43	48	2	2	9	12	8	8
2	0	8	40	40	44	2	1	13	−7	0	0
2	1	4	7	4	4	0	3	12	−8	3	3
0	1	11	31	33	35	1	2	14	−8	3	3
1	2	5	8	8	8	1	3	10	8	5	5
0	2	10	27	28	30	4	0	7	6	4	4
2	1	7	22	22	22	0	2	16	14	10	10
1	2	8	23	23	23	3	2	1	8	4	4
1	0	13	−6	0	0	2	3	2	−7	3	3
2	0	11	19	18	19	0	4	8	8	4	4
0	3	6	10	11	11	3	2	4	−7	0	0

* Negative sign indicates value not used for least-squares structure refinement.

† F_c without extinction correction.

Table 2. *Structure parameters for* β-O_2

		This work	Hörl (1962)
Pressure	P (GPa)	5·5 (1)	0
Temperature	T (K)	299 (1)	28
Lattice constant	a (Å)	2·8467 (2)	3·307
	c (Å)	10·2249 (8)	11·256
Ratio	c/a	3·5918 (3)	3·404
Volume	V (10^3 mm^3 mol^{-1})	14·406 (2)	21·40
Atom parameter	z	0·0577 (2)	0·0536
Thermal parameter	$\beta_{11} = \beta_{22} = 2\beta_{12}$	0·1647 (7)	–
	$\beta_{13} = \beta_{23}$	0	–
	β_{33}	0·0055 (3)	–
Thermal ellipsoid	$(W_\perp^2)^{1/2}$	0·225 (5)	–
	$(W_\parallel^2)^{1/2}$	0·170 (5)	–
Internuclear distance	S (Å)	1·202 (2)	1·20741 (2)*
R factor	R_w	0·050	–

* Value in gas phase (Sutton, 1958).

The apparent O—O internuclear distance S_0 = 1·181 (2) Å must be corrected for the large thermal motion of the molecules. We applied the Busing & Levy (1964) corrections for a rigid molecule with the atoms 'riding' on the center of mass. The mean internuclear distance S is given by

$$S = S_0 + \tfrac{1}{2}W_\perp^2/S_0, \tag{1}$$

where $W_\perp^2$ is the mean-square displacement of either nucleus normal to the molecular axis. When this correction is applied, we find $S = 1{\cdot}202\ (2)$ Å, which is not significantly different from the gas-phase value of $S = 1{\cdot}20741\ (2)$ Å (Sutton, 1958).

Discussion

Our structure determination of β-O_2 at 5·5 GPa was made at a temperature 17 K below the melting temperature at that pressure. Although we observed unusual recrystallization during laser heating of the solid sample in this P–T region, we assume that β-O_2 extends to the melting curve at room temperature. At zero pressure and 55 K, however, γ-O_2 adjoins the liquid phase (Donohue, 1974), and β-O_2 exists only at temperatures from 10 to 30 K below the melting point. Since the γ–β transition line extends up to at least 0·4 GPa (Stewart, 1959; Mills & Schuch, 1970, unpublished), somewhere between a melting pressure P_m = 0·4 GPa (T_m = 91 K) and P_m = 5·6 GPa (T_m = 316 K) there is a triple point on the melting curve where γ-O_2, β-O_2, and fluid oxygen are all in equilibrium. We conclude that the γ-O_2 ($Pm3n$) phase is confined to a limited P–T region along the lower portion of the melting curve. It seems highly unlikely that there is any temperature where this phase is stable over a range of tens of GPa as seems to be the case for the isostructural $Pm3n$ cubic form of N_2 (Cromer *et al.*, 1981; Schwalbe *et al.*, 1980).

We find nearly perfect agreement at P_m = 5·6 GPa (T_m = 316 K) with an extrapolation of the melting curve measured to 0·4 GPa by Mills & Grilly (1955). Although probably fortuitous, the agreement may indicate that the change in slope of the melting curve at the β–γ-fluid-O_2 triple point is small. The melting curve of Nicol *et al.* (1979), however, appears to lie 25 K below ours, which would place our crystal-structure sample in their liquid phase. The discrepancy may have arisen because of impurities in their sample taken from an open container of liquid O_2, whereas our sample was condensed from pure gas in a vacuum-tight system. Mills & Grilly (1955) observed that impurities of a few-tenths per cent caused a shift of several per cent in the oxygen melting pressure. They also pointed out that O_2 is prone to 'super-pressuring', and an apparent freezing pressure can be 10% higher than the equilibrium pressure.

Stewart (1959) measured the compressibility of solid oxygen at 51 K from 0·11 to 0·77 GPa in the β phase and from 0·77 to 18·6 GPa in the α phase. The volume change at the β–α transition is very small and we were able to fit all of Stewart's data to the empirical equation,

$$V(T = 51\,\mathrm{K}) = 26{\cdot}08(P + 3)^{-0{\cdot}1493}, \qquad (2)$$

where $V(T = 51\ \mathrm{K})$ is the volume in cm^3 mol^{-1} of solid O_2 at 51 K and P is the pressure in kbar (1 kbar ≡ 0·1 GPa). The average deviation in $V(T = 51\ \mathrm{K})$ is $\pm\frac{1}{4}$%, which is less than the experimental error. Extrapolation of equation (2) to 5·5 GPa at 51 K gives $V = 14{\cdot}22 \times 10^3$ mm^3 mol^{-1} compared with the X-ray value from Table 2 of $V = 14{\cdot}41 \times 10^3$ mm^3 mol^{-1} at 5·5 GPa and 299 K. These values imply an average isobaric thermal expansion coefficient of 5×10^{-5} K^{-1}. Obviously this calculation does not take into account any volume changes that occur on transitions between the I, II, and III phases reported in this region by Nicol *et al.* (1979) and Nicol (1980).

It is not completely clear why good crystals of O_2 can be grown in a diamond-anvil cell by laser annealing. Nicol *et al.* (1979) and Nicol (1980) point out several double-molecule double-quantum transitions in O_2, such as the green vibronic bands of the $({}^1\Delta_g + {}^1\Delta_g \leftarrow {}^3\Sigma_g + {}^3\Sigma_g)$ system, which could provide the absorption required for local heating by the 5145 Å line of the argon laser.

Hazen (1980) has suggested the possibility that a condensed gas might serve both as a medium with nearly hydrostatic pressures and, through the known variation of its lattice constants with pressure, as an internal pressure standard. Oxygen seems to be a candidate, although it remains to be seen whether O_2 retains its desirable characteristics well away from the melting curve.

We thank L. C. Schmidt for constructing the indium dam, and L.A. Schwalbe for help in loading the sample. One of us (DS) also acknowledges useful discussions with M. Nicol and R. M. Hazen.

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Acta Cryst. (1981). B**37**, 1332–1336

Paraelectric–Paraelastic $Rb_2KMoO_3F_3$ Structure at 343 and 473 K

BY S. C. ABRAHAMS AND J. L. BERNSTEIN

Bell Laboratories, Murray Hill, New Jersey 07974, *USA*

AND J. RAVEZ

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 33405 *Talence CEDEX, France*

(*Received* 27 *October* 1980; *accepted* 22 *January* 1981)

Abstract

$Rb_2KMoO_3F_3$, FW 410·975, is cubic above T_c = 328 K with space group $Fm3m$ and $a(T_c)$ = 8·945 (5) Å, $V(T_c)$ = 715·72 Å^3; D_m(298 K) = 3·81 (4), $D_x(T_c)$ = 3·814 Mg m^{-3}, $Z = 4$, μ(Mo $K\alpha$) = 15·7 mm^{-1}, F(000) = 744. The linear thermal expansion coefficient, α, is 30 (3) × 10^{-6} K^{-1}. All allowed reflections within a hemisphere (or quadrant) of reciprocal space with $(\sin\theta)/\lambda \leq 1·15$ Å^{-1} were measured at 343 K (or 473 K) using a CAD-4 diffractometer, resulting in 97 independent structure factors at 343 K, 81 at 473 K. Least-squares refinement gave R = 0·032 at 343 K, 0·056 at 473 K. The O and F atoms randomly occupy the same equivalent 24(e) positions, with anisotropic thermal vibrations that increase significantly between 343 and 473 K. Diffuse scattering is not observed above T_c. The crystal becomes ferroelastic and ferroelectric below T_c. The Mo–O/F distance in the regular $Mo(O/F)_6^{3-}$ octahedron, on correction for thermal motion, is 1·900 (6) Å at 343 K, 1·926 (10) Å at 473 K.

0567-7408/81/071332-05$01.00

Introduction

The atomic arrangement in crystals with chemical formula R_3MX_6 or R_2MX_6, which are also isostructural with $(NH_4)_3FeF_6$ (Pauling, 1924) or K_2PtCl_6 (Williams, Dillin & Milligan, 1973), may undergo slight distortions from cubic symmetry at a lower temperature and may thereby acquire interesting physical properties. One such family with composition $A_2BMO_3F_3$ has ten members in which A, B = K, Rb, Cs and M = Mo, W, each of which exhibits at least one phase transition above 78 K (Ravez, Peraudeau, Arend, Abrahams & Hagenmuller, 1980). The transition at T_c = 328 K for $Rb_2KMoO_3F_3$ is from rhombohedral to cubic symmetry: a dielectric anomaly is associated with the transition and the spontaneous polarization decreases to zero above 328 K. The crystal becomes ferroelastically twinned in the rhombohedral phase (Abrahams, Bernstein & Ravez, 1981). The structure in the cubic phase has been studied at two temperatures to give accurate prototype parameters preparatory to an investigation of a single-domain