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Molecular Packing, Defects, and Transformations in Solid Oxygen*

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The crystal structure of α oxygen (monoclinic, $C2/m$, two molecules per cell) determined by Barrett, Meyer, and Wasserman, is consistent with O_2 molecules in contact along two rows in the (001) plane, and along two rows lying a plane that is 80.5° from (001); contact is defined as the touching of the contours at the 0.002 level of electron density of the contoured electron-density maps for O_2 computed by Bader, Henneker, and Cade. Twinning, with a twinning shear of 19° in the [100] direction on the (001) plane, should be easy; both twins and stacking faults are likely to be common and produce features in the x-ray diffraction patterns. The β-O_2 phase can be seen as closely related to the α phase: if the (001) planes shear into an ABCABC ⋯ sequence and the configuration in the (001) plane is hexagonalized, the β-type structure is obtained. In this structure, if the O-O bonds are tipped about 75° to the threefold axis and precess around it, there will be contacting molecules in three directions normal to the threefold axis and also along the triad axis of the rhombohedral cell. Calculated densities of the α and β phases are different at the transition temperature; therefore, the transformation is of first order. The order previously has been in doubt because of the sensitivity of the transformation to stress and to inhibiting factors which spread it over a temperature range.

I. INTRODUCTION

In this paper we discuss the crystal structure of α oxygen, a determination of which was reported in another paper of this series.[1] We show how the structure consists of a three-dimensional network of molecules in contact with each other along the rows of the network, using a concept of contact based on electron-density-contour calculations. We show how the structure may be twinned or faulted, how it presumably transforms to the β phase, why the transformation should be classed as of first order, and how the mechanism of the transformation accounts for the difficulties of so classifying it in the past.

Our x-ray diffraction data on α-O_2 (the form of O_2 that is stable below 23.8°K) were accounted for by a monoclinic unit cell, b axis unique, of space group $C2/m$, with two molecules per unit cell, each with O-O bonds normal, or nearly normal, to the (001) plane, and with centers at $(\frac{1}{2},\frac{1}{2},0)$ and $(0,0,0)$. A conventional-type drawing of this is given in Fig. 1. The unit cell dimensions, $a=5.403\pm0.005$ Å, $b=3.429\pm0.003$ Å, $c=5.086\pm0.005$ Å, $\beta=132.53\pm0.03°$, are a refinement of the dimensions of an equivalent cell proposed by Alikhanov.[2] We also presented the antiferromagnetic structure of α-O_2: molecules at $(0,0,0)$ have moments antiparallel to those at $(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, and presumably approximately normal to the a-b plane. This magnetic arrangement accounts for the antiferromagnetic neutron diffraction pattern of Collins.[3]

We discuss the relationship of this structure to β-O_2 (stable between 23.8 and 43.76°K) which several investigators agree is rhombohedral, $R\bar{3}m$. Hörl's electron-diffraction data yielded $a=4.210$ Å, $\alpha=46°16'$, with atoms at (u,u,u), $(\bar{u},\bar{u},\bar{u})$, where $u=0.055$.[4] The packing arguments used here are based on new Hartree-Fock calculations of the electron-density contours of the O_2 molecule by Bader, Henneker, and Cade,[5] and the discussion of the transformation characteristics follows principles that have been developed chiefly by metallurgical and mineralogical research.[6]

II. PACKING IN α-OXYGEN

The structure of α-O_2 may be considered to be composed of tightly packed rows of molecules along the two $\langle 110\rangle$ directions of the C-face-centered cell, so that each molecule touches four nearest neighbors in the a-b plane, as in Fig. 2. The center-to-center distance along these rows is 3.20 Å (see Fig. 1). It is concluded by Bader, Henneker, and Cade[5] that, in general, the equilibrium distance between molecular centers for homonuclear diatomic molecules is given by the contact of the 0.002 density levels of the computed electron-density contours. The values of the contours are given in terms of the unit 67.49 $e/\text{Å}^3$; over 95% of the molecular charge lies within the 0.002 contour. The shape of the O_2 mole-

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[1] C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys. **47**, 592 (1967).

[2] R. A. Alikhanov, in Proceedings of the 3rd Regional Conference on the Physics and Techniques of Low Temperatures, Prague, 1963, p. 127 (unpublished).

[3] M. F. Collins, Proc. Phys. Soc. (London) **89**, 415 (1966).

[4] E. M. Hörl, Acta Cryst. **15**, 845 (1962).

[5] R. F. W. Bader, W. H. Henneker, and P. E. Cade, J. Chem. Phys. **46**, 3341 (1967). We thank Dr. Cade for informing us of these results prior to publication.

[6] C. S. Barrett and T. B. Massalski, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1966), 3rd ed., Chap. 18.

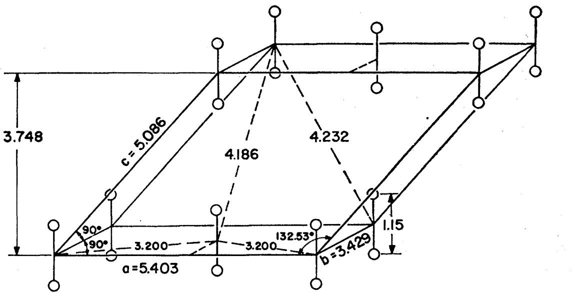


FIG. 1. Unit cell of α-O_2 (monoclinic) with atom positions indicated, as determined by x rays (Ref. 1), and cell dimensions in Å.

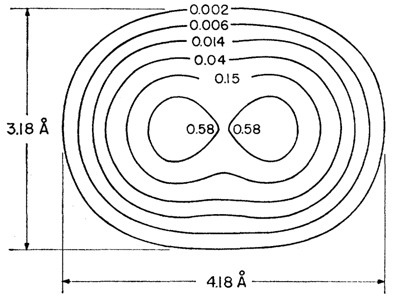


FIG. 3. Contours of electron density in O_2 molecule according to Hartree-Fock calculations by Bader, Henneker, and Cade (Ref. 5).

cule at this 0.002 contour is reproduced in Fig. 3. This molecular shape is characterized by a major axis of 7.9 Bohr units (4.18 Å) along the bond direction and, normal to this, a width of 6.0 Bohr units (3.18 Å). The observed intermolecular distance of 3.23 Å matches the latter remarkably well.

Four near neighbors of each molecule in the structure are also located along the lines joining the $(\frac{1}{2},\frac{1}{2},0)$ position to the corner points (1,0,1) and (1,1,1) (see Fig. 1), with a distance between centers of 4.186 Å. These rows of molecules lie in the $(\bar{2}01)$ plane, and, as indicated by the drawing of this plane (Fig. 4), the size and shape of the molecular electron-density contour at the 0.002 level again brings the molecules into contact There are thus two rows in the (001) plane and two in the $(\bar{2}01)$ that are close-packed.

Two more molecules exist near each given molecule, namely, those with centers located in the $+b$ and $-b$ directions from it. These molecular centers are at a distance of 3.429 Å. These are not in contact with the given one unless some molecular rotation or oscillation is assumed. It may be possible to state various "reasons" for a lack of contact, but it should be pointed out, in connection with our discussion of molecular "shape," that the 3.429 Å spacing would allow an oscillation of each molecule about the *a* direction of the unit cell as an axis, with an amplitude such that the effective "width" of the molecule is increased in the *b* direction from 3.18 to 3.429 Å. Reference to Fig. 3 shows that tilting the molecule from the normal to (001) by only about 30° would increase the distance from the center to the 0.002 contour by the required amount in the direction of these two neighbors. An oscillation of this type and this magnitude (±30°) of all molecules would not necessarily destroy the antiferromagnetic structure. A different statement can also be made: The three-dimensional network of tightly packed rows of molecules makes a rigid framework in which there is room for such oscillation, whether or not the intermolecular forces permit appreciable rotational or oscillatory movement.

Returning to Fig. 1, we see that the length of the *c* axis may be taken to be the result of contact along two close-packed rows lying in the $(\bar{2}01)$ plane, which is shown in Fig. 4, and which is inclined 9.5° to the right of the vertical. A twin of this crystal would contain this plane inclined equally to the left of the vertical. This is indicated in Fig. 5. The angular difference between these two positions means that a small shear is sufficient to displace a crystal into its twin; specifically, a pure shear of 19° in one sense in the [100] direction would convert a crystal into its twin, and a reverse shear would untwin it. (Deviations from the [100] direction are excluded since they would make intermolecular distances between nearest neighbors in adjacent (001) planes unequal.)

Because of the simple nature and small magnitude of the twinning shear, defects in stacking are likely to be common in actual crystals. These may be stacking faults, double-deformation faults, or twin faults, and may be frequent enough to cause recognizable effects in

FIG. 2. Projection of molecules in α-O_2 on (001), with 0.002 contours of electron density of the molecule indicated.

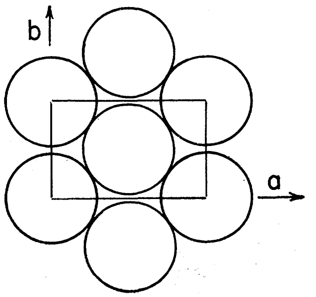
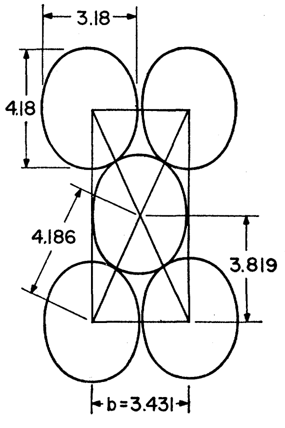


FIG. 4. The $(\bar{2}01)$ plane of α-O_2 showing rows of molecules in contact at the 0.002 contour level of the electron density.



$(\bar{2}01)$ Plane

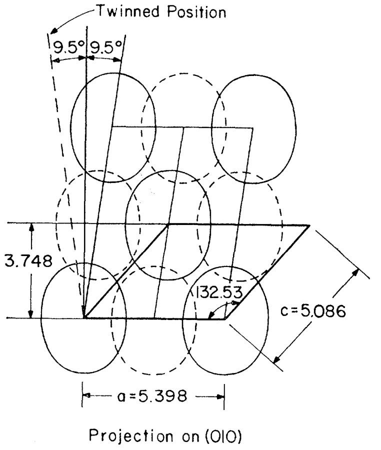


FIG. 5. Projection of α-O_2 on (010) plane showing the 19° shear to produce a twin.

the diffraction patterns and, possibly, also in other physical measurements. The background scattering in the $2\theta = 30°$–$37°$ range of our diffraction patterns[1] may be ascribed to such faults. If the fault plane is predominantly the (001), many reciprocal lattice points will be elongated into rods normal to this, i.e., parallel to the c^* axis of reciprocal space, but the (0,0,1) points will remain sharp. In general, the largest peaks of the diffraction pattern should be noticeably broadened. On the other hand, the (001) peak should remain sharp, as was observed.

III. α-β TRANSFORMATION

What little is known about the α-β transformation does not preclude its being of the martensitic type. If the displacements of (001) planes are such as to produce a three-layer stacking sequence, $ABCABC\cdots$, a more symmetrical atom configuration will result. Since this is frequently the nature of a displacive, martensitic transformation from a lower temperature modification of a crystal to a higher-temperature one, we shall examine the effect of these displacements on the α structure to see how closely the result resembles β-O_2 when we make some very simple assumptions.

Let the threefold axis of the β phase $[111]_\beta$ be assumed midway between the directions $[001]_\alpha$ and the analogous direction in the twin of α, $[001]_{\alpha\mathrm{tw}}$. Then the $(001)_\alpha$ planes become $(111)_\beta$ planes, and the interplanar spacing $d_{001\alpha}$ becomes $d_{111\beta}$. Hörl's value for $d_{111\beta}$ (rhombohedral axes, or $\frac{1}{3}$ of the hexagonal c axis) is 3.752 Å, whereas our value[1] for $d_{001\alpha}$ is 3.751 Å.

If this shift left the molecular positions in the $(001)_\alpha$ plane unchanged, the volume per atom would remain unchanged, but the molecules of the adjacent (001) layers would tend to displace the configuration in (001) into a hexagonal array. If the intermolecular distances in $(001)_\alpha$ in this array are equalized and equal to a_{hex}, the new structure would be rhombohedral.

Let us turn now to the experimental fact that $a_{\mathrm{hex}} = 3.308$ Å (Hörl).[6] The hexagonal arrangement of nonrotating molecules with their bonds nearly normal to the $(001)_\beta$ plane would leave gaps between them; on the other hand, if the molecules were spherically rotating they would have to be compressed from a contact spacing of 4.18 down to 3.308 Å. We therefore assume that the O-O bond in each molecule is tipped at an angle to the threefold axis and precesses around it, as has already been proposed by Alikhanov,[2] who thought a tilt of approximately 30° would be satisfactory. Using the contour map of Bader, Henneker, and Cade, however, a tilt of about 75° would be required to give contact at the 0.002 contour with $a_{\mathrm{hex}} = 3.308$ Å. A tilt even as large as this would nevertheless retain the contacts along the close-packed rows in the $(\bar{2}01)$ plane with center-to-center distances of 4.18 Å, because of the shape of the contour.

If the antiferromagnetism survives this tilting and wider separation of the molecules, the exchange interactions should be lessened and the moments should be less perfectly aligned than in α-O_2; this is in accord with Collins's conclusion that only local magnetic order is present in the β phase.[3]

As in other transformations of this general type, it it would be expected that elastic constants would change with increasing rapidity as the temperature approaches the temperature of equal free energy of the α and β phases.

IV. ORIENTATION RELATIONSHIP BETWEEN α AND β

The close relationship between the structures and the small shear that converts one to the other strongly suggest that the transformation is martensitic in nature and that the two phases are related in orientation. We propose that on both heating and cooling there is a martensitic shear in the $[100]_\alpha$ direction on the $(001)_\alpha$ plane (or the equivalent shear in the β phase for the reverse transformation). On this basis the phenomenological theories[6] for transformations should apply in detail, but even by inspection it is possible to predict the approximate relationship: The basal plane of β should be parallel to the (001) plane of α, and a close-packed row in the basal plane of β should be approximately parallel to the a axis of α.

V. ORDER OF α-β TRANSFORMATION

Stewart[7] classified the α-β transformation of oxygen as second order because, in his studies of the pressure-volume curve, he could not unambiguously detect an abrupt volume change at the transition that would have required classification as first order. Recent measurements of specific heats near 23.8° have been reported by Fagerstroem and Hollis Hallett.[8] They found a sharp

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[7] J. W. Stewart, J. Phys. Chem. Solids **12**, 122 (1959).

[8] C. H. Fagerstroem and A. C. Hollis Hallett, Ann. Acad. Sci. Fennicae **AVI**, 210 (1966).

λ-shaped spike with no evidence of latent heat. This, too, would suggest that the transformation is of second order. A more definitive method of characterizing a transformation, however, is to compare calculated densities at the temperature where the free energies of the two phases are equal, using x-ray data to give the calculated densities.

The density of β-O_2 at a temperature no higher than 28°K is given by Hörl[4] as 1.495 g/cm^3 = 21.40 cm^3/mole, whereas our x-ray results yield a calculated density of 1.530 g/cm^3 = 20.91 cm^3/mole at 23°K. There is, therefore, a distinct volume change in the transformation amounting to about 0.49 cm^3/mole, and on this basis the transformation must be classified as first order. Stevenson[9] derives a value of 0.12 cm^3/mole for the volume change from the Clausius-Clapeyron equation by using his own data for the pressure dependence of the transformation temperature, and the heat of transformation from Giauque and Johnston.[10] This is also evidence of a first-order transition.

The transformation mechanism presented in this paper, and the accumulated evidence from transformations in other materials in which a martensitic-type change of shape is involved,[6] shows how the transformation can easily simulate features of second-order transformations. Because of the lattice deformation involved in the transformation, stresses can aid it or interfere with it, depending upon their nature; the surroundings of a sample (container walls, grain boundaries, other phases, etc.) can inhibit it and may prevent it from going to completion. Thus, the latent heat and the volume change accompanying the transformation may be spread over a temperature range instead of occuring at a uniquely defined temperature.

Note added in proof. With further investigation of the lattice constants of β-O_2 we find that the a-axis of the rhombohedral structure has an unusually high expansion coefficient: $\Delta l/l = 1150\times10^{-6}$/deg; The c-axis has a negative expansion coefficient: -21×10^{-6}/deg. The molar volume of β-O_2 changes by 4.6% over the stability range, reaching a value at the α-β transformation temperature that indicates a difference in molar volume between α- and β-O_2 of about 0.1 cc/mole, in good agreement with Stevenson's value.[9] A detailed detailed report on expansion and transformation characteristics will be published.

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[10] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. **51**, 2300 (1929).