Expansion Coefficients and Transformation Characteristics of Solid Oxygen

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As determined by x rays on polycrystalline samples, the rhombohedral β-oxygen phase (stable from 23.8 to 43.7°K) has a linear expansion coefficient $\Delta l/l = 1150 \times 10^{-6}$ per °K in the a direction and a very small, but definitely negative expansion coefficient in the c direction. The expansion coefficient of γ-oxygen (stable from 43.7 to 54.3°K) is also quite high, $\Delta l/l = 780 \times 10^{-6}$ per °K. Diffraction patterns of the α, β, and γ phases, photographed during temperature cycling, showed that a grain of α forms from a grain of β with the (001) plane of α forming the (00.1) plane (hexagonal indices) of β without changing its orientation, and vice versa, martensitically. However, β forms from γ with a breakup into near-randomly oriented smaller and/or highly distorted β grains.

INTRODUCTION

RECENTLY Jahnke[1] pointed out that there are discrepancies of the order of 10% in the published values of molar volumes of the various phases of solid oxygen; this conclusion is based on considerations of the known volume changes at the transitions (23.8 and 43.7°K) and of molar volumes derived from x-ray densities. In our own studies of α-oxygen[2,3] we found the molar volume to be 20.92 cc/mole, which, when subtracted from Hörl's[4] value for β-oxygen, 21.40 cc/mole, gives a volume change at the transformation of 0.48 cc/mole. This is much greater than the 0.12 cc/mole derived by Stevenson,[5] who used the Clausius-Clapeyron equation, the pressure dependence of the α-β transition temperature, and the known[6–9] heat of transformation. In addition, we had noticed, in some earlier powder patterns of β-oxygen, that some peaks shifted position much more than others, as a function of temperature. This evidence convinced us that a careful investigation of the temperature dependence of the lattice parameters of γ- and β-oxygen should be made; the results of this and of an investigation of β-α and γ-β transformation characteristics are reported below.

METHOD

The method employed has been described in our study of solid argon.[10] The axes of rhombohedral β-oxygen were derived by a least-squares method from 9 to 12 lines of the powder patterns. The sample was prepared by cycling the solid oxygen several times through the γ-β transformation at 43.8°K, yielding a fine-grained polycrystalline sample with very little preferred orientation. The sample was then strain-relieved by annealing, usually overnight, around 31°K, where no grain growth was observed. Attempts were made to increase the accuracy of the determinations of changes in the c-axis lattice constant. A few samples were annealed overnight at 42°K, which caused considerable grain growth. The 00.3 reflection was used from a crystallite oriented to reflect when the sample was approximately in the parafocusing position and the shift of this reflection as a function of temperature was determined. The shift in this reflection was small (of order 0.04–0.06° in 2θ) and did not provide a precision value of the expansion coefficient.

It is practically impossible to produce a fine-grained sample of cubic γ-oxygen, since it recrystallizes in minutes. Therefore, in measuring γ-oxygen we used the technique described above for large-grained β-oxygen and which had also been employed for measuring the lattice constants of argon near the melting point.[10] We looked for crystals that reflected when the sample was oriented in or near the parafocusing position, and we determined the position of their reflections as a function of temperature.

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* Formerly named The Institute for the Study of Metals.
[1] J. Jahnke, J. Chem. Phys. 47, 336 (1967).
[2] C. S. Barrett, L. Meyer, and J. Wasserman, J. Chem. Phys. 47, 592 (1967).
[3] C. S. Barrett and L. Meyer, Phys. Rev. 160, 694 (1967).
[4] E. M. Hörl, Acta Cryst. 15, 845 (1962).
[5] R. Stevenson, J. Chem. Phys. 27, 673 (1957).
[6] W. F. Giauque and H. L. Johnston, J. Am. Chem. Soc. 51, 2300 (1929).
[7] K. Clusius, Z. Phys. Chem. B3, 41 (1929).
[8] H. J. Hoge, J. Res. Natl. Bur. Std. 44, 321 (1950).
[9] A. C. Boravik-Romanov, M. P. Orlova, and P. G. Strelkov, Dokl. Acad. Nauk SSSR 99, 699 (1954).

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[10] C. S. Barrett and L. Meyer, J. Chem. Phys. 41, 1078 (1964).

EXPANSION CHARACTERISTICS

The results are given in the tables and figures. Tables I and II list smoothed values of the lattice parameters (from a curve through the powder pattern data) and the molar volumes derived from them. Figure 1 shows the temperature dependence of the a and c axes of β-oxygen and Fig. 2, the calculated molar volumes of the three phases of solid oxygen, as well as the volume changes at the transitions, the latter being taken from Refs. 1 and 5.

The linear expansion coefficient of γ-oxygen is very high: $\Delta l/l = 780 \times 10^{-6}$ per °K. This value is practically independent of temperature. The total change in molar volume over the entire temperature range (11°K) is about 2.5%.

In β-oxygen, despite a 5% volume contraction at the transformation from γ, $\Delta l/l$ of the a axis increased to 1150×10^{-6} per °K (also almost independent of temperature). What is even more extraordinary, powder patterns indicated a very small but negative expansion coefficient for the c axis. The curve for c in Fig. 1 and the tables represent one attempt to judge the expansion coefficient; in this attempt the 31.5°K point is given less than average weight. The error bars in Fig. 1 represent the internal consistency of the data that was indicated by the least-squares computation for each powder pattern. In another attempt, a straight line fitted by least squares to points that were given equal weights again yielded a negative, though smaller, expansion coefficient. With the large-grained samples, each of three runs (two on cooling, one on heating) confirmed that the 00.3 reflection shifted in the direction indicating a small expansion coefficient which was again negative in sign, though somewhat larger than in Fig. 1. None of the experiments provide an accurate value of the coefficient; we conclude only that it is much smaller in absolute value than that for the a axis, negative in sign, and perhaps—because of the high anisotropy—dependent upon grain size, apparently being larger the larger the grains and the more nearly the conditions approach those of a single crystal.

The total volume change in the 20° spread of the β range is 4.6%. From our data, Hörl's[4] lattice parameters fit a temperature of 35°K, not 28°K as he stated.

In contrast to the great contractions in the high-temperature phases, we observed no change in the lattice parameters of the α-phase between 23 and 4°K.

It should be noted that all the samples used were polycrystalline, and that single crystals might give different expansion coefficients, as in graphite.[11]

The expansion coefficient of solid argon was studied thoroughly[10,12] and makes a good basis of comparison with regard to the anharmonicity of lattice vibrations. Just below the melting point, the linear-expansion

Table I. Lattice parameters and molar volumes of β-oxygen.

T (°K)	a_0 (Å)	c_0 (Å)	v_m (cm³)
26	3.272	11.2770	20.990
28	3.280	11.2765	21.092
30	3.286	11.2760	21.168
32	3.293	11.2755	21.258
34	3.300	11.2750	21.347
36	3.307	11.2745	21.437
38	3.315	11.2740	21.540
40	3.324	11.2735	21.656
42	3.332	11.2730	21.760

coefficient of argon is $510 \times 10^{-6}/°K$, a good deal smaller than the 780×10^{-6} value of γ-oxygen. The expansion coefficient of argon decreases sharply with temperature, whereas the γ-oxygen value remains constant.

The temperature dependence of the lattice parameters of β-oxygen is indeed quite unusual. The γ-β transformation is accompanied by a contraction of about 5%. γ-oxygen is soft and transparent, β-oxygen is opaque and hard. In spite of this fact, the expansion coefficient in the a direction of the rhombohedral lattice is almost double that of the linear-expansion coefficient of γ-oxygen. The negative expansion coefficient of the c axis can be a consequence of the shape of the oxygen molecules. Because they are barrel-shaped with the long axis normal to the ab plane (001), when they are squeezed together in the a direction during cooling they have less room for tilting out of alignment perpendicular to the (001) plane. We assume that, because of this, the effective spacing of the (001) layers is increased, resulting in an increase in the c axis.

The extrapolation of the curve of the molar volume of β-oxygen to the temperature of the α-β transformation at 23.8°K is somewhat uncertain, but it is clear that there must be only a very small difference between the molar volumes of β and α at that temperature. Our values can now be considered to be consistent with the value given by Stevenson: 0.12 cc/mole, within experimental error.

The magnitude of the density changes with temperature makes it impossible to analyze the specific heat of γ- and β-oxygen in terms of the Debye theory. The usefulness of Debye temperatures derived by fitting Debye curves to the specific heats of γ- and β-oxygen, must be considered to be extremely doubtful.[13,14]

Table II. Lattice parameters cc and molar volumes of γ-oxygen.

T (°K)	a_0 (Å)	v_m (cm³)
44	6.7420	23.070
46	6.7533	23.186
48	6.7626	23.282
50	6.7768	23.429
52	6.7891	23.557

[11] Y. Baskin and L. Meyer, Phys. Rev. 100, 544 (1955).
[12] O. G. Peterson, D. N. Batchelder, and R. O. Simmons, Phys. Rev. 150, 703 (1966).

[13] C. H. Fagerstrom and A. C. Hollis Hallett, Am. Acad. Sci. Fennicae A210, 210 (1966).
[14] A. Landau, E. J. Allen, and H. L. Welsh, Spectro. Acta 18, 1 (1962).

TRANSFORMATION CHARACTERISTICS

It has been claimed several times[8,9,13] that the α-β transformation in solid oxygen is second order. We pointed out in an earlier paper[3] that consideration of the structures leads to the conclusion that the transformation is first order and of the martensitic type. Martensitic transformations are sensitive to strain and can easily imitate second-order transformations. Residual strains can aid or inhibit such a transformation so that the transformation of a strained sample does not take place at the transition temperature itself, but is spread out over a range of temperatures.

The temperature at which a martensitic transformation begins spontaneously on cooling, M_s, usually differs appreciably from the highest temperature at which the transformation can be forced to begin by plastically deforming the sample, M_d; the temperature M_d is nearer the temperature of equilibrium between the two phases than M_s, which often exhibits appreciable undercooling.[15] In our work, deformation did not affect the temperature of the β-α transformation, which always took place at the same temperature (within the accuracy of our measurements, $\pm 0.25°K$), consistent with the value in the literature, 23.8°K. Giauque and Johnston[6] report fluctuations in the transition temperature of the order of 0.1°K; Hoge[8] also reports hysteresis effects. The question arises whether or not the transformation temperature observed in calorimetric studies and structure determinations is an M_s point at a temperature well below that of equal free energies in the β and α phases. If the samples were single crystals, this would be possible; however, all the present experiments were performed on polycrystalline samples. Since there is a highly anisotropic expansion coefficient in β-oxygen, this creates appreciable strain in the crystallites so that, even during very slow cooling, the sample should be strained enough to induce the β-α transformation whenever it is thermodynamically possible. In other words, in polycrystalline samples the asymmetry in the thermal contraction should always determine M_d rather than M_s, even without external deformation.

The α-β transformation cannot be second order for quite general, theoretical reasons. Landau and Lifshitz[16] derived a theorem that a second-order transformation is only possible if the number of symmetry elements changes in specific ways, which always include a factor of 2 but never a factor of 3. They explicitly state that a transformation in which the number of symmetry elements changes by a factor of 3 *cannot* be second order. α-oxygen (space group $C2/m$) has four symmetry elements; β-oxygen (space group $R\bar{3}m$) has twelve
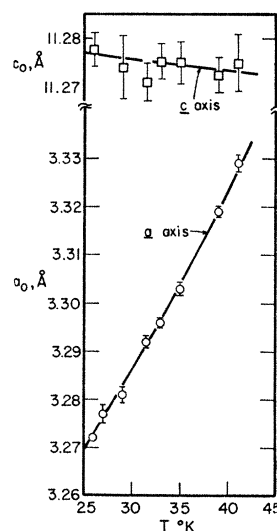

FIG. 1. Temperature dependence of directly measured values of the lattice parameters of β-oxygen. Open circles indicate a-axis values; open squares, c-axis values.

symmetry elements. This clearly shows that the α-β transition cannot be of second order.[17]

Certain characteristics of the transformation became evident when spotty Debye patterns were prepared from a stationary sample which had been annealed at 42°K overnight and which had undergone considerable grain growth. Figure 3 (top) shows the reflections from a sample in the α phase, each reflecting crystallite producing a slightly distorted spot. When warmed through the α-β transformation, with the x-ray beam and sample orientation unchanged, the spots of the (001) ring re-

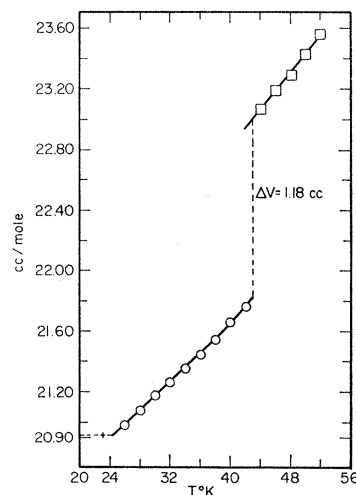

FIG. 2. Temperature dependence of the molar volumes of the three phases of solid oxygen, including the transitions. Open squares indicate γ-oxygen values; open circles, β-oxygen values: + indicates α-oxygen value.

[15] C. S. Barrett and T. B. Massalski, *Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1966), 3rd ed., p. 531.

[16] L. D. Landau and E. M. Lifshits, *Statistical Physics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1958), p. 445.

[17] We are indebted to Professor L. M. Falicov for discussions clarifying this point.
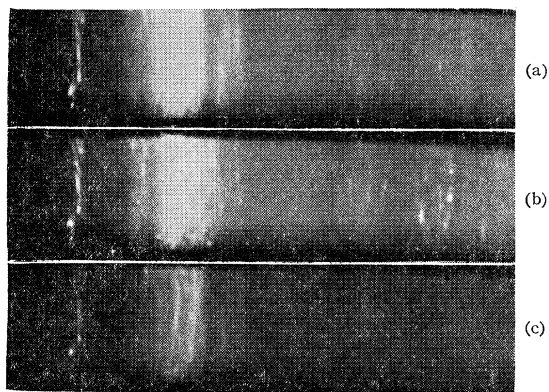
FIG. 3. Debye patterns of solid oxygen above and below the α-β transformation temperature (a) (top) α-oxygen; (b) (center) β-oxygen; (c) (bottom) return to α-oxygen. CuK radiation, stationary sample.

main in the same position, but other Debye rings are altered (center). Cooling back down into the α range, the original spots on all rings are recovered (bottom), showing that the crystals transformed from one phase into the other and back again regain their original orientations and that no major reconstruction of the crystallites takes place. The retention of the spots from (001) of α-oxygen (the left-most Debye ring in Fig. 3) when the sample transformed to β-oxygen shows that the crystallites of β are related in orientation to those of α in such a way that (00.1) of β (hexagonal axes) in each crystallite is parallel to (001) of the crystallite of α from which it formed. Similarly, on cooling again, this orientation relationship holds. Additional cycling caused similar behavior, the only prominent change noticed being a tendency toward increasing imperfection in the crystallites. These orientation relationships are indicative of a martensitic type of transformation and would be expected if $(001)_\alpha$ layers transform into $(00.1)_\beta$ layers as suggested in our earlier discussion of the transformation.[3]
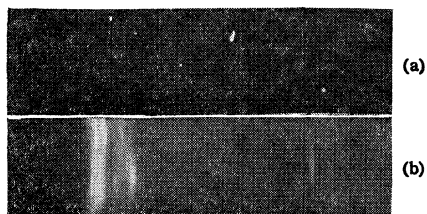

FIG. 4. Debye patterns of solid oxygen before and after the γ to β transformation. (a) (top) γ-oxygen; (b) (bottom) β-oxygen.

Figure 4 shows, in contrast, the γ-β transformation. The big crystals of γ-oxygen (top) produced sharp spots which disappeared in the transformation. Broad Debye-Scherrer rings with no sharp spots appeared (bottom), indicating that the γ crystal broke up into many small and/or highly distorted crystallites of β during the transition; some preferred orientation is evident, for the intensity along the rings is not uniform. Cycling through the γ-β transformation several times produces Debye-Scherrer patterns with rings of uniform intensity, indicating that a fine-grained specimen with random orientation has been produced. In contrast to this, the grains going through the α-β transition were invariably found again in their original orientation, even after repeated cycling.
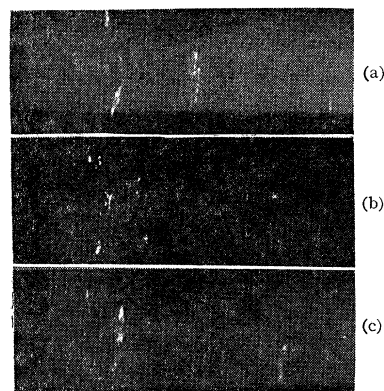

FIG. 5. Debye patterns of solid nitrogen above and below the transformation temperature. (a) (top) β-nitrogen; (b) (center) α-nitrogen; (c) (bottom) return to β-nitrogen.

Figure 5 shows similar diffraction patterns for the α-β transition in solid nitrogen, for comparison. One single pass through the transformation in this case eliminates all trace of the original crystals; there appears to be no orientation relationship between the phases, though experiments with single crystals to confirm this are not available.
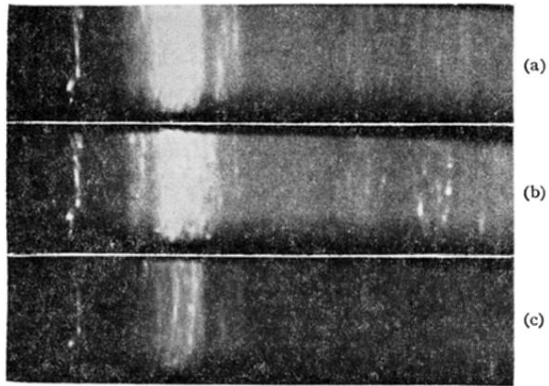
ACKNOWLEDGMENTS

FIG. 3. Debye patterns of solid oxygen above and below the α-β transformation temperature (a) (top) α-oxygen; (b) (center) β-oxygen; (c) (bottom) return to α-oxygen. CuK radiation, stationary sample.
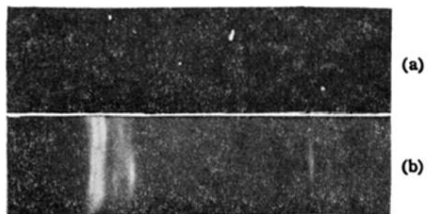
Fig. 4. Debye patterns of solid oxygen before and after the γ to β transformation. (a) (top) γ-oxygen; (b) (bottom) β-oxygen.
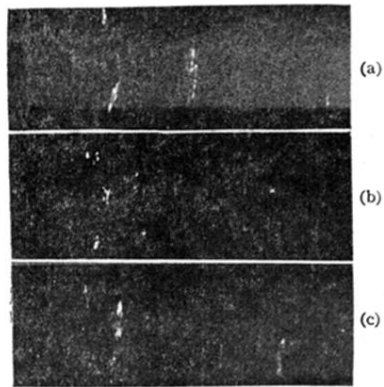
FIG. 5. Debye patterns of solid nitrogen above and below the transformation temperature. (a) (top) β-nitrogen; (b) (center) α-nitrogen; (c) (bottom) return to β-nitrogen.