

The Crystal Structure of α -Potassium Superoxide*

By S. C. ABRAHAMST† AND J. KALNAJS

Laboratory for Insulation Research, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

(Received 10 March 1955).

The lattice constants of α -potassium superoxide have been remeasured, and the tetragonal unit cell is found to be $a = 5.704 \pm 0.005$, $c = 6.699 \pm 0.005$ Å at 25° C. The coordinates have been refined by the method of least squares and by triple Fourier series. Geiger-counter methods were used to measure the intensities diffracted by a powder specimen. The O–O bond length is 1.28 ± 0.02 Å, and there are two kinds of closest K–O contact, of length 2.71 and 2.92 Å.

Introduction

An understanding of the various kinds of bond which link two oxygen atoms together is likely to provide considerable insight into the mechanism of bond formation by higher members of the VI_b group of elements. These elements are characterized by possession of two *s* and four *p* valence electrons. The case of oxygen is simplified by the non-availability of *d* orbitals, which appear to be important for sulfur (Abrahams, 1954), selenium (McCullough & Marsh, 1950) and probably also for tellurium. This restriction leaves the wave functions involving only two oxygen atoms more susceptible to exact solution, and hence emphasizes the importance of precise measurements of the molecular constants for such systems.

Accurate determinations of the length of the O–O bond have now been made in the case of the oxygen molecule (Babcock & Herzberg, 1948), where the distance is 1.2074 ± 0.0001 Å; Trambarulo, Ghosh, Burrus & Gordy (1953) report 1.278 ± 0.003 Å in ozone. Abrahams & Kalnajs (1954) find 1.49 ± 0.04 Å in the peroxide ion, and Abrahams, Collin & Lipscomb (1951) measure 1.49 ± 0.02 Å in hydrogen peroxide.

A fifth kind of O–O bond exists in the superoxide ion [O–O]⁻, and several attempts have been made to measure this bond length. Kasatochkin & Kotov (1937) were the first to elucidate the crystal structure of the α -potassium compound. Using a cylindrical powder camera with unfiltered Cu *K* radiation, and with the sample sealed within glass capillaries, they were able to observe nine single powder lines with a total intensity range of 1 to 10. The structure contains a single parameter of position, and this was varied by discrete steps until the observed structure factors compared most closely with those calculated. The temperature factors were neglected in this process. The parameter value giving the best agreement was 0.095, corresponding to an O–O bond distance of

1.28 Å, with an estimated uncertainty of ± 0.07 Å.

Carter, Margrave & Templeton (1952) have shown that α -potassium superoxide transforms above 60–100° C. into a new modification, which has cubic symmetry, with $a_0 = 6.09 \pm 0.01$ Å. β -Potassium superoxide is said to be disordered, and no bond-length measurements have been made on it.

Two determinations of the length of the O–O bond in sodium superoxide have been reported. Templeton & Dauben (1950) give the distance as 1.33 ± 0.06 Å and Zhdanov & Zvonkova (1952) as 1.31 ± 0.03 Å. In this crystal also, the superoxide ion appears to be disordered, and does not lend itself to a determination of high accuracy.

The crystal structure of potassium superoxide has been reinvestigated by us using modern methods in order to measure the O–O bond distance therein with greater accuracy.

Experimental

α -Potassium superoxide was prepared by two methods. The first was similar to Helms & Klemm's (1939) method, in which the two elements are allowed to react in liquid ammonia at -30 to -50 ° C. This preparation yielded a product of 95% purity, calculated as KO₂. The second method was an adaptation of Kazarnovskii & Raikhshtein's (1947) method, wherein metallic potassium is oxidized at 180° C. in a stream of 20% oxygen in nitrogen, gradually increasing the oxygen content to 100%. After the potassium had been thus calcined in oxygen at 370° C. for 8 hr., the cooled reaction tube was transferred to a dry box because of the extreme deliquescence of the superoxide, and the powder was then ground and passed through a 325-mesh sieve into smaller tubes. These tubes were flushed with oxygen and sealed, and the powder was then annealed at 120° C. for 15 hr. This material, on analysis, gave 99.1% of the theoretical potassium content (K was determined by standard methods), and 99.2% of the theoretical oxygen value (determined volumetrically by decomposition of the superoxide with platinum black). This preparation was

* Sponsored by the Office of Naval Research, the Army Signal Corps and the Air Force under ONR Contract N5ori-07801.

† Present address: Chemistry Department, The University, Glasgow W. 2, Scotland.

used for the determination of the lattice constants and intensities.

The X-ray methods used have previously been described (Abrahams & Kalnajs, 1954). However, to protect the surface of the sample on transferring it from the dry box to the diffractometer, the filled sample-holder was covered with a glass slide, which was removed only after it was in position inside the protective chamber. The reduced ratio of peak heights to background level in the present crystal, as compared with barium peroxide (Abrahams & Kalnajs, 1954), resulted in an average accuracy in intensity of only about 3%. An independent check on the accuracy of the observations was made by comparing two sets of structure factors, derived from the intensities in the usual way, and resulting from two different preparations of the superoxide. The comparison ratio $\Sigma|F_o(1)| - |F_o(2)| \div \Sigma|F_o(1)|$ had a value 0.048. Cu $K\alpha$ radiation was used throughout. The James & Brindley (1931) atomic form factors for potassium and oxygen were employed. All calculations were carried out on International Business Machines, except for the Fourier series, which were summed using Beever-Lipson strips.

Crystal data

α -Potassium superoxide, KO_2 ; m.p. 380° C.; $D_o = 2.158$ g.cm.⁻³ (Kasatochkin & Kotov, 1937), $D_c = 2.166$ g.cm.⁻³; tetragonal with $a = 5.704 \pm 0.005$ and $c = 6.699 \pm 0.005$ Å. (Kasatochkin & Kotov (1937) found 5.70 and 6.72 Å; Helms & Klemm (1939) gave 5.70 and 6.75 Å.) Absent reflections, (hkl) only for $h+k, k+l, l+h = 2n+1$. Space group $F4/mmm$ (chosen by Kasatochkin & Kotov). Four formula-molecules per unit cell. Volume of the unit cell is 217.9 Å³. Absorption coefficient for Cu $K\alpha$ ($\lambda = 1.5418$ Å) is 181.9 cm.⁻¹. Total number of electrons per unit cell, $F(000)$, is 140.

Analysis of the structure

Kasatochkin & Kotov (1937) demonstrated that the cation in α -potassium superoxide is at $(0, 0, \frac{1}{2})$ and the oxygen atoms at $(0, 0, z; 0, 0, \bar{z})$, and reported the value of z as 0.095. In the present study it was decided to evaluate two additional parameters, namely, the thermal-vibration parameters for each atom. Each of these parameters was assumed to be isotropic, for it had been shown in the isostructural case of barium peroxide that the effect of this assumption, upon z , was negligible. The refinement process was carried out at first by the method of least squares. The structure factor has the form

$$F(hkl) = 8f_o \exp\{-B_1(\sin \theta/\lambda)^2\} \\ \times \cos 2\pi lz \pm \sum_{l=2n}^{l=2n+1} 4f_K \exp\{-B_2(\sin \theta/\lambda)^2\},$$

and in the first model adopted, z was given the value 0.095 and B_1 and B_2 were taken as equal to 2.3 Å². This value was obtained by a consideration of the decrease in magnitude of the observed structure factors (Table 1) with increasing angle. In applying the method of least squares, each equation of condition was given unity as its weight. Although intensities were recorded for 39 lines, only 25 were single and used in the least-squares analysis. Three normal equations were thus obtained and solved, and the solutions were applied to the original parameters. New structure factors could then be calculated, and hence a new iteration could be undertaken. The third such iteration produced corrections to the parameters that were smaller than the errors to be feared in them. This was taken as a sign of convergence in the method, and the final parameters were then $z = 0.0955$; $B_1 = 3.42$ Å² and $B_2 = 3.29$ Å². The structure factors calculated on the basis of these parameters are given in Table 1, and have a value $R_1 = 0.076$.

Table 1. Observed and calculated structure factors for α -potassium superoxide

hkl	d_o (Å)	d_c (Å)	F_o	F_c	hkl	d_o (Å)	d_c (Å)	F_o	F_c
111	3.457	3.456	17.7	-17.4	404	1.087	1.086	13.2	+ 9.3
002	3.350	3.350	74.0	+72.0	135	1.076	1.076	26.3	-25.1
200	2.856	2.853	90.5	+91.6	206	1.040	1.040	6.4	+ 7.4
202	2.172	2.172	53.7	+53.7	244	1.015	1.015	26.5	+ 8.6
220	2.018	2.017	69.0	+68.8	440	1.009	1.009		+21.5
113	1.953	1.954	47.9	-44.8	153	1.001	1.000	14.3	-15.4
311	1.742	1.742	54.4	-13.5	226	0.976	0.977	7.5	+ 6.9
222	1.729	1.728		+42.2	351	0.968	0.968	18.0	- 7.2
004	1.676	1.675	10.5	+15.7	442	0.966	0.966		+15.0
204	1.444	1.444	11.5	+13.1	600	0.950	0.951	33.5	+18.5
400	1.427	1.427	35.0	+43.1	335	0.949	0.949		-18.3
133	1.404	1.404	27.6	-29.2	117	0.931	0.931	20.0	-14.5
331	1.320	1.319	47.3	-10.8	602	0.915	0.916	10.2	+13.2
402	1.313	1.312		+28.1	260	0.902	0.902	26.0	+16.2
224	1.290	1.289	<11.0	+11.6	353	0.897	0.896		-11.9
240	1.276	1.276	70.7	+35.4	406	0.880	0.879	5.5	+ 5.5
115	1.272	1.272		-35.2	262	0.872	0.871	7.6	+11.5
242	1.192	1.192	23.4	+23.6	444	0.864	0.864	< 6.0	+ 6.2
333	1.153	1.152	20.9	-21.0	155	0.859	0.859	14.2	-14.0
006	1.116	1.117	6.7	+ 8.0	137	0.845	0.845	13.7	-11.1
151	1.105	1.104	9.7	- 8.5					

All the F_o terms in Table 1 were then used as coefficients in a triple Fourier series to compute the electron density along the line $0, 0, z$, which contains both the potassium and the oxygen ions (Fig. 1, lower, curve). The position of the center of gravity of the electron-density profile for oxygen, taken as z , was 0.0955. In case the observed Fourier series gave a value of z in error owing to artificial termination, a second series was evaluated, using the corresponding F_o terms in Table 1 (i.e. those resulting from the final set of coordinates derived by the least-squares process). This series is shown in Fig. 1 (upper curve), and the consequent value of z is 0.0957. The true value of z ,

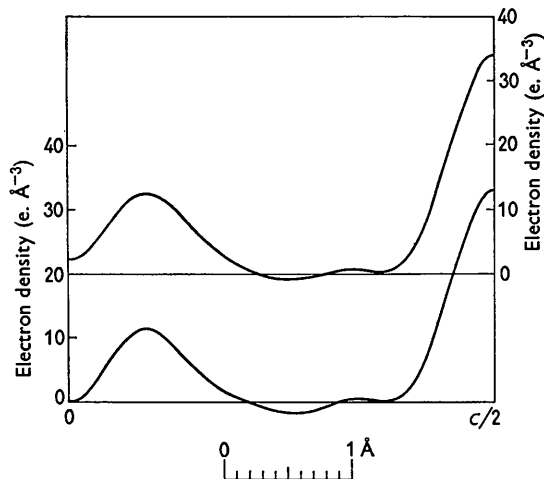


Fig. 1. Electron-density profile along the line $0, 0, z$, computed with triple Fourier series. Upper curve has calculated $F(hkl)$ as coefficients in the series, lower curve has observed $F(hkl)$. Left-hand scale refers to lower curve.

on applying the usual backshift correction, is then 0.0953.

Oxygen-oxygen bond length

The average of the values of z , obtained by the method of least squares and the triple Fourier series, was assumed to be the closest approximation. This resulting value of $z = 0.0954$ corresponds to the length 1.28 Å for the O-O bond in the superoxide ion.

Uncertainties in the parameters

The probable errors in z , B_1 and B_2 , computed by the method of least squares, are ± 0.0017 ; ± 0.30 and ± 0.13 Å², respectively. Each oxygen atom then has a probable error of 0.01 Å and hence the probable error in the O-O bond length is 0.02 Å. The estimated standard deviation in z , derived by the Fourier series method, was estimated by Cruickshank's (1949) method to be 0.01 Å for the oxygen atom. Again, the estimated standard deviation in the length of the O-O bond is double this, namely, 0.02 Å.

The final value for the uncertainty in this bond length is thus ± 0.02 Å.

Interionic distances

In this structure, like that of barium peroxide, each cation is surrounded by 10 oxygen atoms. The arrangement of K-O contacts is shown in Fig. 2. There

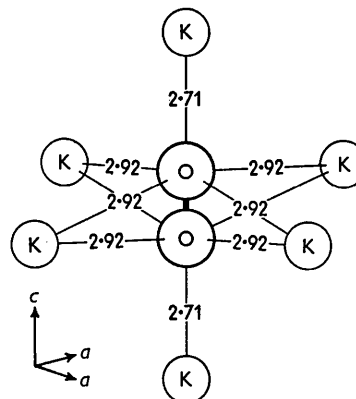


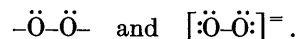
Fig. 2. Octahedral environment of superoxide ion, with closest-contact distances (in Ångström units) indicated.

are two such sets of smallest contact distances, one of 2.71 Å, parallel with c , and one of 2.92 Å, in direction approximately normal to c .

Discussion

The two kinds of anion-cation closest contact in this crystal, of 2.71 and 2.92 Å, are analogous to the corresponding distances of 2.68 and 2.79 Å in barium peroxide (Abrahams & Kalnajs, 1954). Here, the shorter distance appears to be that of a typical, close, ionic contact between oxygen and potassium. However, the usual values of ionic radii cannot rigidly apply here, since the special shape factor associated with the anion has not been taken into account. It is not apparent why the atoms in this crystal are subject to rather large thermal vibrations, whereas in the isostructural barium peroxide the thermal vibration is very small.

The lengths of the various O-O bonds (r_{O-O}) now determined may be used in establishing a bond-order/bond-length relationship for oxygen. In the case of the covalent peroxide group and of the peroxide ion, the measured value of r_{O-O} is identical at 1.49 Å. Each of these bonds also has about the same magnetic susceptibility, $\chi = -18 \times 10^{-6}$ (Neiding & Kazarnovskii, 1950). This bond may hence be formulated as an electron-pair bond of order zero, thus:



A second value of the bond-order/bond-length relationship may be derived from the data for the oxygen molecule, in which $r_{O-O} = 1.2074$ Å in the $^3\Sigma_g^-$ (ground) state, which corresponds closely to a bond order of unity. Intermediate bond-order/length relationships may be had from the measurements on

ozone and on the superoxide ion. In the case of ozone, with $r_{O-O} = 1.278 \text{ \AA}$. Trambarulo *et al.* (1953) show the most likely bond order to be 0.5. Magnetic susceptibility measurements suggest (Pauling, 1940) the superoxide ion contains a three-electron bond, $[\ddot{O} \cdots \ddot{O}]^-$, and thus this bond, with $r_{O-O} = 1.28 \text{ \AA}$, should also have an order of about 0.5. The resulting curve is then very similar to the corresponding order/length curve for carbon.

We would like to thank Prof. A. von Hippel for his interest in this work.

References

- ABRAHAM, S. C. (1954). Technical Report 83, ONR Contract N5ori-07801, Laboratory for Insulation Research, Massachusetts Institute of Technology.
 ABRAHAM, S. C., COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 15.
 ABRAHAM, S. C. & KALNAJS, J. (1954). *Acta Cryst.* **7**, 838.

- BABCOCK, H. D. & HERZBERG, L. (1948). *Astrophys. J.* **108**, 167.
 CARTER, G. F., MARGRAVE, J. L. & TEMPLETON, D. H. (1952). *Acta Cryst.* **5**, 851.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 HELMS, A. & KLEMM, W. (1939). *Z. anorg. Chem.* **241**, 97.
 JAMES, R. W. & BRINDLEY, G. W. (1931). *Z. Kristallogr.* **78**, 470.
 KASATOCHKIN, V. & KOTOV, V. (1937). *Zh. tekhn. Fiz.* **7**, 1468.
 KAZARNOVSKII, I. A. & RAIKHSHTEIN, S. I. (1947). *Zh. fiz. Khim.* **21**, 245.
 MCCULLOUGH, J. D. & MARSH, R. E. (1950). *Acta Cryst.* **3**, 41.
 NEIDING, A. B. & KAZARNOVSKII, I. A. (1950). *Dokl. Akad. Nauk, SSSR.* **74**, 735.
 PAULING, L. (1940). *The Nature of the Chemical Bond*. Ithaca: Cornell University Press.
 TEMPLETON, D. H. & DAUBEN, C. H. (1950). *J. Amer. Chem. Soc.* **72**, 2251.
 TRAMBARULO, R., GHOSH, S. N., BURRUS, C. A., JR. & GORDY, W. (1953). *J. Chem. Phys.* **21**, 851.
 ZHDANOV, G. S. & ZVONKOVA, Z. V. (1952). *Dokl. Akad. Nauk, SSSR.* **82**, 743.

Acta Cryst. (1955). **8**, 506

The Determination of the Elastic Constants of Germanium by Diffuse X-ray Reflexion

BY S. C. PRASAD AND W. A. WOOSTER

Crystallographic Laboratory, Cavendish Laboratory, Cambridge

(Received 24 March 1955)

The elastic ratios c_{12}/c_{11} and c_{44}/c_{11} have been measured by the diffuse reflexion of X-rays from a single crystal of germanium. The values obtained were respectively 0.38 and 0.52. When these results are combined with the already known cubic compressibility the elastic constants can be evaluated as $c_{11} = 13.3$, $c_{12} = 5.1$, $c_{44} = 7.0 \times 10^{11}$ dyne cm.⁻².

Introduction

A crystal of germanium with a circular face of 12 mm. diameter cut parallel to the (100) plane was loaned to the authors by Prof. Lark Horowitz, Purdue University, Indiana, U.S.A. The crystal was etched to remove the imperfection on the surface. This was used in conjunction with a Geiger-counter spectrometer in the manner already described (Ramachandran & Wooster, 1951) to determine the intensity of scattering from small volume elements of reciprocal space along lines (rekhas) passing through the reciprocal point (relp) 400. The rekhas chosen were parallel to [100], [010] and [110]. The intensity of first-order diffuse scattering is proportional to the reciprocals of c_{11} and c_{44} for the rekhas [100] and [010] respectively. The corresponding intensity for the rekha parallel to [110] is proportional to

$$1/(c_{11} - c_{12}) + 1/(c_{11} + c_{12} + 2c_{44}).$$

Thus, from the measurement on the rekha parallel to [110] the third constant c_{12} can be determined.

Experimental results

The results of observations along the three rekhas parallel to [100], [010] and [110] passing through the relp 400, using Cu $K\alpha$ radiation are given in Table I (R is expressed in cm. on a representation of the reciprocal lattice such that the radius of the reflecting sphere for Cu $K\alpha$ radiation is 50 cm.).

Corrections were made for divergence, though only the ψ correction exceeds 1%. A correction of 2% was applied on account of the second-order diffuse scattering.

The ratios of the elastic constants found from these results were as follows:

$$c_{12}/c_{11} = 0.38(1), \quad c_{44}/c_{11} = 0.52(4).$$