[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

The Crystal Structure of Sodium Superoxide[1]

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The superoxides of potassium, rubidium and cesium (KO_2, etc.) are readily prepared by reaction of the elements and have long been known.[2] The corresponding compound of sodium has only recently been prepared in a reasonably pure state by the reaction of sodium peroxide (the highest oxide ordinarily obtained) with oxygen at approximately 500° and 300 atmospheres pressure.[3] We have determined the crystal structure of this compound from X-ray powder diffraction patterns.[4]

The crystal structures of KO_2, RbO_2 and CsO_2 are known to be isomorphous with calcium carbide.[5] In this structure a face-centered tetragonal (pseudocubic) lattice of metal ions is interpenetrated by a similar face-centered lattice of O_2^- ions, to form a distorted NaCl structure. Each pair of oxygen atoms is oriented with the O–O bond parallel to the tetragonal c axis, and consequently c is somewhat greater than a, as listed in Table I. The existence of O_2^- ions is demonstrated by the X-ray studies and is in agreement with magnetic measurements which indicate one unpaired electron for each two oxygen atoms.[6]

TABLE I

UNIT CELL DIMENSIONS OF ALKALI SUPEROXIDES

Compound	a, Å.	c, Å.	ρx, g. cm.$^{-3}$
NaO_2	5.49	. .	2.21
KO_2[a]	5.71	6.76	2.14
RbO_2[a]	6.01	7.04	3.07
CsO_2[a]	6.29	7.28	3.80

[a] Dimensions of Helms and Klemm, *Z. anorg. allgem. Chem.*, **241**, 97 (1939), are multiplied by the factor 1.0020 to correct to the basis $CuK\alpha_1$ = 1.5405 Å. The densities are recalculated from the resulting numbers.

The samples were received in Pyrex capillaries as mixtures of sodium peroxide, sodium superoxide, and hydration products, ranging in color from bright yellow to white. Powder diffraction pictures taken with copper $K\alpha$ X-rays (filtered with nickel) showed a face-centered cubic phase (a = 5.490 ± 0.005 Å.) whose relative intensity corresponded with the degree of yellow color. The relative intensity also corresponded to the NaO_2 content reported for each sample,[4] except in some cases where light color indicated exposure to moisture.

Exposure of yellow samples to moist air caused them rapidly to become white and destroyed the cubic phase. In a sample containing 70% NaO_2 only the lines of the cubic phase were observed. In all other samples, various complicated patterns were also present. From these observations we deduce that the cubic phase corresponds to sodium superoxide. We cannot exclude on this basis the possibility that a solid solution range exists corresponding to less oxygen than the ideal NaO_2. However, the excellent agreement of observed and calculated intensities noted below makes it unlikely that a large defect in oxygen content exists.

NOTE ADDED IN PROOF:—Recent examination of some mixtures of Na_2O_2 and NaO_2 prepared under more anhydrous conditions by Professor P. W. Gilles of the University of Kansas shows that the solid solubility is not extensive at room temperature. Both phases were clearly observed in samples of 9 and 94 weight % NaO_2. We estimate from the relative intensities of the patterns of the two phases that the two-phase region must extend at least from 5 to 97% NaO_2.

Disordered Structures.—The intensities of the lines of the NaO_2 phase were estimated by

TABLE II

OBSERVED AND CALCULATED INTENSITIES FOR DISORDERED STRUCTURES

hkl	obs.	1. (x00)[a] x = 0.119	2. (Rotation) x = 0.119	3. (xxx)[a] x = 0.072	4. (xx0)[a] x = 0.086
111	<0.8	0.03	0.02	0.02	0.06
200	55	59	57	53	56
220	(22)	22	22	22	22
311	6.3	5.5	6.1	7.8	6.8
222	4.7	3.7	4.8	5.1	5.0
400	1.6	2.6	1.6	0.7	1.3
331	3.6	5.3	3.9	3.4	4.0
420	2.5	3.6	2.9	2.4	2.6
422	1.1	1.1	1.7	1.9	1.4
333		1.9	1.0	0.7	0.7
511		1.2	2.9	5.0	3.4
	3.0	3.1	3.9	5.7	4.1
440	<0.8	0.3	0.5	0.9	0.4
531	1.4	5.0	4.8	4.0	5.1
442		0.2	0.9	1.6	1.3
600		1.0	0.2	0.1	0.2
	0.8	1.2	1.1	1.7	1.5
620	< .8	2.7	0.9	0.2	0.6
533	< .8	5.7	2.6	1.8	1.6

[a] Coördinates of a typical oxygen atom, if center of O_2^- ion is taken as origin.

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(1) Presented before the Division of Physical and Inorganic Chemistry at the Atlantic City Meeting of the American Chemical Society, September 23, 1949.

(2) (a) A. V. Harcourt, *J. Chem. Soc.*, **14**, 267 (1862); (b) W. Holt and W. E. Sims, *ibid.*, **65**, 432 (1894); (c) E. Rengade, *Ann. chim. phys.*, (8) **11**, 348 (1907).

(3) S. E. Stephanou, W. H. Schechter, W. J. Argersinger and J. Kleinberg, THIS JOURNAL, **71**, 1819 (1949).

(4) We are indebted to Dr. S. E. Stephanou and Professor Jacob Kleinberg of the University of Kansas for a number of samples containing sodium superoxide in various amounts, and for analytical data concerning these samples.

(5) (a) W. Kassatoschkin and W. Kotow, *J. Chem. Phys.*, **4**, 458 (1936); (b) A. Helms, *Z. angew. Chem.*, **51**, 498 (1938); (c) A. Helms and W. Klemm, *Z. anorg. allgem. Chem.*, **241**, 97 (1939); C11-type, *Strukturbericht*, **I**, 740 (1931).

(6) (a) E. W. Neuman, *J. Chem. Phys.*, **2**, 31 (1934); (b) W. Klemm and H. Sodomann, *Z. anorg. allgem. Chem.*, **225**, 273 (1935).

visual comparison with a set of standard marks made on similar film with CuKα X-rays with exposure times 1, 2, 4, 8, etc., units. The resulting values, adjusted by a factor to make $\{220\} = 22$, are tabulated in Table II.

These intensities can be explained by a structure derived from that of NaCl by substitution of an O_2^- ion for each chloride ion. To have face-centered symmetry the oxygen pairs must have some kind of disordered orientation. Calculations were made on this basis for four sets of oxygen positions (shown in Fig. 1). (1) Each pair of oxygen atoms is oriented parallel to one of the three cubic axes. (2) The pairs are rotating with no preferred orientation. (3) Each pair is parallel to one of the four body diagonals. (4) Each pair is parallel to one of the six face diagonals.

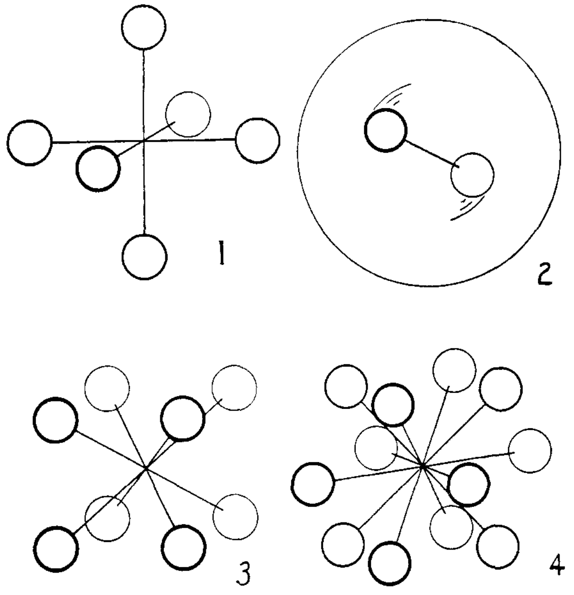

Fig. 1.—Positions which may be occupied by a pair of oxygen atoms in the four disordered structures proposed for NaO_2. The center of each group is at a halide position in the sodium chloride structure.

Intensities were calculated for each arrangement for several values of the oxygen parameter, according to the equation

$$I = \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} p|F|^2 10^{-4} \qquad (1)$$

where θ is the Bragg angle, p is the permutation factor, F is the structure factor, and 10^{-4} is introduced to reduce the numbers to a convenient scale. The atomic scattering power of each oxygen was taken as $[f(O^{-2}) + 3f(O)]/4$ and values of (fO), $f(O^{-2})$ and $f(Na^+)$ were taken from "Internationale Tabellen."[7]

It was found that the ratios of $\{311\}$ to $\{222\}$ and $\{331\}$ to $\{420\}$ are a sensitive function of the oxygen parameter, and that in each of the four cases these two ratios are satisfied for practically the same oxygen parameter. The best set of intensities calculated for each case is listed in Table II. The final oxygen parameters and O–O bond distances, obtained by graphical interpolation, are listed in Table III. The agreement of observed and calculated intensities is reasonably good in every case, and one cannot make a definite choice between the structures. The ratios of the higher order planes are perhaps more favorable to arrangement 3.

It will be of interest to obtain heat capacity and X-ray diffraction data at low temperatures to see if disorder persists to low temperature, and to attempt to determine the degree of freedom of rotation of the O_2^- ions.

TABLE III

OXYGEN PARAMETERS AND O–O BOND DISTANCES IN NaO_2

Oxygen positions		x_0	O–O, Å.
1	$x00$, etc.	0.188 ± 0.003	1.30 ± 0.03
2	Free rotation	.121 ± .003	1.33 ± .03
3	xxx, etc.	.071 ± .003	1.35 ± .06
4	$xx0$, etc.	.085 ± .003	1.32 ± .05
			1.33 ± .06
O–O Bond in KO_2[a]			1.28 ± .07

[a] Kassatochkin and Kotow, *J. Chem. Phys.*, **4**, 458 (1936).

Ordered Structures.—One must consider the case of ordered structures not having the face-centered cubic symmetry (O_h^5–Fm3m) of the above disordered structures. Parallel orientation of the oxygen pairs, like in the tetragonal KO_2 structure or the rhombohedral $NaHF_2$ structure (molecules directed along one body diagonal) would certainly distort the unit cell an observable amount from its cubic shape. Other non-cubic ordered structures we consider unlikely, because of distortion and, also, because other weak lines should be observed since the structure can be face-centered only if the O_2^- ions are equivalent.

The orientation of one O_2^- ion per unit cell along each of the four body diagonals provides in two ways cubic symmetry with an ordered structure. One such arrangement is the pyrite structure[8] which has symmetry T_h^6–Pa3. This is the most economical structure with regard to space, because if the unit cell is subdivided into 8 smaller cubes, each such cube contains one oxygen atom. The other ordered cubic structure is that incorrectly proposed for calcium carbide,[9] with symmetry O_h^4–Pn3m. In this case two of the small cubes each contain four oxygens, while the other six have none. Intensities for planes having *hkl* all even or all odd are the same for these structures as for disordered structure 3 above. An examination of the intensities of other planes, however, shows at least four in each case which should be observed (Table IV), and so these ordered struc-

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(7) "Internationale Tabellen zur Bestimmung Kristallstrukturen," Vol. II, Borntraeger, Berlin, 1935, p. 571.

(8) C2-type, *Strukturbericht*, **I**, 150 (1931).

(9) *Ibid.*, **I**, 174 (1931).

tures are both ruled out. There may be short-range order corresponding to the economical packing of the pyrite structure, without long-range order. This is reasonable because sodium lacks the directional valence properties of the iron in FeS_2, and stacking disorder can be had with this structure without putting two oxygens in the same small cube.

TABLE IV

OBSERVED AND CALCULATED INTENSITIES FOR ORDERED STRUCTURES

hkl	*obs.*	calcd. T_h^6-Pa3	calcd. O_h^4-Pn3m
100	<0.8	0	0
110	< .8	0	5.8[a]
111	< .8	0.02	0.02
200	55	53	53
210, 120	<0.8	4.5[a]	0
211	< .8	5.0[a]	0.7
220	(22)	22	22
300, 221	<0.8	1.1	7.4[a]
310, 130	< .8	0	3.4[a]
311	6.3	7.8	7.8
222	4.7	5.1	5.1
320, 230	<0.8	3.3[a]	0
321, 231	< .8	4.4[a]	1.3
400	1.6	0.7	0.7
410, 140, 322	<0.8	1.8	0.1
411, 330	< .8	0.8	0.01
331	3.6	3.4	3.4
420	2.5	2.4	2.4
421, 241	<0.8	0.3	3.4[a]
332	< .8	0.1	1.2
422	1.1	1.9	1.9
500, 430, 340	<0.8	1.2	0
510, 150, 431, 341	< .8	1.8	0.3
511, 333	3.0	5.7	5.7

[a] These reflections should be observed.

The difference between the structures of sodium and potassium superoxide is reasonable on the following basis: For larger cations, the dumbbell-shaped anion has relatively more room. If it has enough room, its coulombic cation–attraction will be dominant, and it can be expected to orient in the direction of the nearest cations (*i. e.*, along an axis)as it does in KO_2. However, if the cation is very small, the repulsive forces will determine the oxygen orientation, and it is plausible that this will lead to some other type of structure. For example, body diagonal orientation of the pyrite type (with or without order) gives greater atomic distances on the average.

Oxygen Bond Distance.—Although we cannot definitely describe the oxygen positions in the disorderly NaO_2 structure, we can say that the oxygen–oxygen distance is probably in the range 1.33 ± 0.06 Å., (Table III) which includes the probable error ranges of the four structures considered. The agreement of observed and calculated intensities for the four structures is due largely to the fact that the finite size of the oxygen atom makes the electron density appreciable throughout the spherical shell in which the oxygens are located. Also for this reason it is not necessary to consider any more complicated set of oxygen positions. If one divides the observed intensities of $\{333\} + \{511\}$ and $\{442\} + \{600\}$ in an arbitrary manner, electron densities can be calculated, because the sodium atoms control the signs of all F values which are observed. An electron density section was calculated for the $xy0$ plane splitting these intensities to fit structure 1, with the result shown in Fig. 2. This shows the O_2^- ion as a hollow and more or less spherical shell of electron density, with relatively small peaks at the alternate sites of oxygen nuclei. It also gives confirmation to the value of the oxygen parameter.

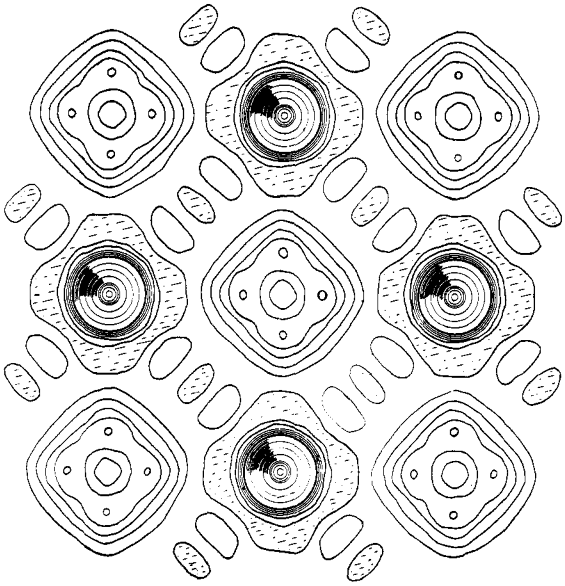

Fig. 2.—Electron density map $xy0$ plane of NaO_2, calculated with ambiguous terms adjusted to fit structure 1. The contour interval is 1 electron/Å. The shaded areas are negative. The four small circles in each O_2^- group are maxima; the central circle, a minimum.

If the superoxide ion is considered to have a single bond and a three electron bond in the Pauling sense,[10] then it may be expected to be intermediate in bond distance between the oxygen molecule with a single bond and two three-electron bonds and the hydrogen peroxide molecule which has a normal single bond. These molecules have the distances 1.2076 Å.[11] and 1.47 ± 0.02 Å.[12] respectively, of which the average is 1.34 Å., in excellent agreement with our value.

Acknowledgment.—The X-ray diffraction patterns were taken by Mrs. L. Jackson. We wish

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[10] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1945, p. 264.

[11] G. Herzberg, "Molecular Spectra and Molecular Structure, I. Diatomic Molecules," Prentice-Hall, Inc., New York, N. Y., 1939, p. 491. Calculated from spectroscopic moment of inertia.

[12] P. A. Giguère and V. Schomaker, THIS JOURNAL, **65**, 2025 (1943), measured by electron diffraction.

to thank Professor Kleinberg for the samples of sodium oxides and for his interest in the problem. This research was supported in part by the Atomic Energy Commission.

Summary

1. The crystal structure of sodium superoxide has a face-centered cubic lattice with $a = 5.490 \pm 0.005$ Å. The structure is like that of sodium chloride with O_2^- ions occupying halide positions with disorderly orientation.

2. The bond distance in the superoxide ion in this crystal is 1.33 ± 0.06 Å.

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Investigations in the Chemistry of Rhenium. I. Oxidation States IV, V and VII[1,2]

BY EUGENE K. MAUN AND NORMAN DAVIDSON

Part of the interest of the chemistry of rhenium is due to the large number of oxidation states in which this metal occurs—in fact, compounds of rhenium for all oxidation numbers between +7 and −1 have been reported. It was the object of this research to characterize more precisely some of the oxidation states of rhenium in aqueous solution. Since many of the rhenium compounds encountered were colored, they were studied by measuring their light absorption with a Beckman spectrophotometer. The various rhenium compounds studied were also characterized by their reactions with some common oxidizing and reducing agents. The present communication describes our studies of the IV, V and VII oxidation states; in a subsequent paper we will report on our observations of the lower oxidation states Re^{-1} and Re^{+1}.

Experimental

Materials.—Samples of rhenium metal powder and of potassium perrhenate were obtained from the University of Tennessee. The rhenium metal was reported to assay 99.5% or better, the chief impurity being silver; the potassium perrhenate was stated to assay 99.8% or better, the chief impurity being rubidium. Solutions of perrhenic acid were prepared by heating the powdered metal with excess 30% hydrogen peroxide.[3,4] In agreement with experiments of Hölemann[5] and Geilmann and Weibke,[6] the perrhenic acid found in 0.025 to 0.05 formal solutions was 3–5% less than expected from the weight of metal taken, as shown by titrations to a methyl red end-point with potassium hydroxide and by precipitation as nitron perrhenate.[7] No molybdate was present and the hydrogen peroxide contained no non-volatile acidic or basic impurities. To detect oxide impurity, a 100-mg. sample of rhenium was treated with hydrogen at 1000°. After cooling under pure nitrogen, it had lost only 1.5 mg. in weight. In view of these experiments, the stated purity of the rhenium, and the similar experience of other investigators[5,6] it appears that the low results for perrhenic acid are due to either (a) volatility or (b) loss in a spray during the solution process.

Potassium hexachlororhenate(IV) was prepared from potassium perrhenate.[8] The Re^{IV} in a 24.71 mg. sample was determined with hot ceric sulfate.[9] A blank of chloride consumed 0.003 meq. of cerium(IV) and the Re(IV) found after correction for this was 0.122 meq. (theory 0.120 meq.). The $ReCl_6^{=}$ in the preparation was determined as Cs_2ReCl_6[10,11] by addition of 0.10 ml. of 0.5 *F* cesium chloride solution to 0.300 ml. of solution containing 7.25 mg. of the preparation of K_2ReCl_6. The resulting precipitate of Cs_2ReCl_6 was washed with concentrated hydrochloric acid and dried at 120°. Its weight was 10.0 mg. (theory 10.1 mg.).

Where not otherwise specified, reagent grade chemicals were used. Ceric ammonium sulfate was used as a standardized *ca.* 0.05 *F* solution in 0.5 *F* sulfuric acid. Solutions of 0.05–0.1 *F* sodium thiosulfate, 0.3 *N* iodine in 7.5% potassium iodide, 0.07 *F* copper sulfate, and 0.1 *N* chlorine in 4 *F* hydrochloric acid were standardized by iodometric titrations, using 0.0150 *F* potassium iodate solutions. Solutions of 0.05–0.15 *F* ferric ammonium sulfate in 0.1 *F* sulfuric acid were also standardized iodometrically using the optimum conditions given by Swift.[12] Stannous chloride solutions 0.05 *F* (0.1 *N*) were standardized just before use against excess iodine, working under carbon dioxide and rinsing out all equipment with this gas. Cuprous chloride was reprecipitated by dilution of a solution in concentrated hydrochloric acid, and the purified solid thus obtained was used to prepare 0.1 *F* solutions in 4 *F* hydrochloric acid which were standardized with ceric sulfate (*o*-phenanthroline end-point). An approximately 0.1 *F* chromic chloride solution in 4 *F* hydrochloric acid was prepared from the solid. For detection of chlorine, a 0.1% solution of *o*-tolidine was prepared in 1.2 *F* hydrochloric acid[13] and stored in the dark.

Spectrophotometry.—Light absorption measurements were made at room temperature on solutions in 3-ml. quartz or corex cells of calibrated path length, 1.00 cm., using a Beckman spectrophotometer. For protection of solutions from oxygen of the air, a number of long-stemmed corex cells capped with ground joints were used. The extinction coefficient ϵ was calculated for a given wave length from the readings of the optical density D relative

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(1) Presented before the Physical and Inorganic Division at the 115th meeting of the American Chemical Society, San Francisco, California, March 28, 1949.

(2) A more detailed account of this research is contained in the Thesis by Eugene K. Maun, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, California Institute of Technology, June, 1949.

(3) W. Feit, *Angew. Chem.*, **46**, 216 (1933).

(4) J. T. Dobbins and J. K. Colehour, THIS JOURNAL, **56**, 2054 (1934).

(5) H. Hölemann, *Z. anorg. Chem.*, **202**, 277 (1931).

(6) W. Geilmann and F. Weibke, *ibid.*, **195**, 289 (1931).

(7) W. Geilmann and A. Voigt, *ibid.*, **193**, 311 (1930).

(8) L. C. Hurd and V. A. Reinders, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 178.

(9) W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, **222**, 56 (1935).

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(11) E. Enk, *Ber.*, **64**, 791 (1931).

(12) E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

(13) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand Co., New York, N. Y., 1947, Vol. II, p. 464.