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The Crystal Structure of Sodium Superoxide

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THE CRYSTAL STRUCTURE OF SODIUM SUPEROXIDE

Page 3

By David H. Templeton and Carol H. Dauben

Abstract

1. The crystal structure of sodium superoxide has a face-centered cubic lattice with  $a = 5.490 \pm 0.005 \text{ \AA}$ . The structure is like that of sodium chloride with  $\text{O}_2^-$  ions occupying halide positions with disorderly orientation.

2. The bond distance in the superoxide ion in this crystal is  $1.33 \pm 0.06 \text{ \AA}$ .

THE CRYSTAL STRUCTURE OF SODIUM SUPEROXIDE

By David H. Templeton and Carol H. Dauben

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The superoxides of potassium, rubidium, and cesium ( $\text{O}_2$ , etc.) are readily prepared by reaction of the elements and have long been known.<sup>1</sup> The

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

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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°C and 300 atmospheres pressure.<sup>2</sup>

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- (2) S. E. Stephanou, W. H. Schechter, H. J. Argersinger, and J. Kleinberg, J. Am. Chem. Soc., 71, 1819 (1949).

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We have determined the crystal structure of this compound from x-ray powder diffraction patterns.<sup>3</sup>

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- (3) 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.

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The crystal structures of  $\text{KO}_2$ ,  $\text{RbO}_2$ , and  $\text{CsO}_2$  are known to be

isomorphous with calcium carbide.<sup>4</sup> In this structure<sup>5</sup> a face-centered

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- (4) (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).  
(5) C11-type, Strukturbericht, I, 740 (1931).
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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.<sup>6</sup>

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- (6) (a) E. W. Neuman, J. Chem. Phys., 2, 31 (1934); (b) W. Klemm and H. Sodomann, Z. anorg. allgem. Chem., 225, 273 (1935).
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The samples were received in Fyrex 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 =  $5.490 \pm 0.005 \text{ \AA}$ ) whose relative intensity corresponded with the degree of yellow color. The relative intensity also corresponded to the  $NaO_2$  content reported for each sample<sup>3</sup>, except in some cases where light color indicated exposure to moisture.

Table I

## Unit-Cell Dimensions of Alkali Superoxides

Compound	$\underline{a}$ (Å)	$\underline{c}$ (Å)	$\rho_x$ (g.cm. <sup>-3</sup> )
NaO <sub>2</sub>	5.49	--	2.21
KO <sub>2</sub> <sup>a</sup>	5.71	6.76	14
RbO <sub>2</sub> <sup>a</sup>	6.01	7.04	3.07
CsO <sub>2</sub> <sup>a</sup>	6.29	7.28	3.81

<sup>a</sup>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.

Exposure of yellow samples to moist air caused them rapidly to become white and destroyed the cubic phase. In a sample containing 70% NaO<sub>2</sub> 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<sub>2</sub>. However, the excellent agreement of observed and calculated intensities noted below makes it unlikely that a large defect in oxygen content exists.

Disordered Structures - The intensities of the lines of the NaO<sub>2</sub> phase were estimated by visual comparison with a set of standard marks made on similar film with CuK $\alpha$  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 Figure 1).

Table II

Observed and Calculated Intensities for Disordered Structures

hkl	obs.	1. (x00) <sup>a</sup> x = 0.119	2. (Rotation) x = 0.119	3. (xxx) <sup>a</sup> x = 0.072	4. (xx0) <sup>a</sup> 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	<0.8	2.7	0.9	0.2	0.6
533	<0.8	5.7	2.6	1.8	1.6

<sup>a</sup>Coordinates of a typical oxygen atom, if center of O<sub>2</sub><sup>-</sup> ion is taken as origin.

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.

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

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

where  $\theta$  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  $(f_0 + 3f_0)/4$  and values of  $f_0, f_0'$  and  $f_{Na}^+$  were taken from Internationale Tabellen.<sup>7</sup>

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

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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.	$0.118 \pm 0.003$	$1.30 \pm 0.03$
2. Free rotation	$0.121 \pm 0.003$	$1.33 \pm 0.03$
3. xxx, etc.	$0.071 \pm 0.003$	$1.35 \pm 0.06$
4. xx0, etc.	$0.085 \pm 0.003$	$1.32 \pm 0.05$
		$1.33 \pm 0.06$
O-O Bond in $KO_2^a$		$1.28 \pm 0.07$

<sup>a</sup>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<sup>8</sup> (Figure 2) which has symmetry

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

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$T_h^6$ -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<sup>9</sup>, with symmetry  $O_h^4$ -Pa3m.

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(9) Strukturbericht, I, 174 (1931).

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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 structures 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

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

\*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  $1.33 \pm 0.06 \text{ \AA}$ , (Table III) which includes the probable error ranges of the four structures considered. The agreement of 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 Figure 3. 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.

If the superoxide ion is considered to have a single bond and a three electron bond in the Pauling sense,<sup>10</sup> then it may be expected to be

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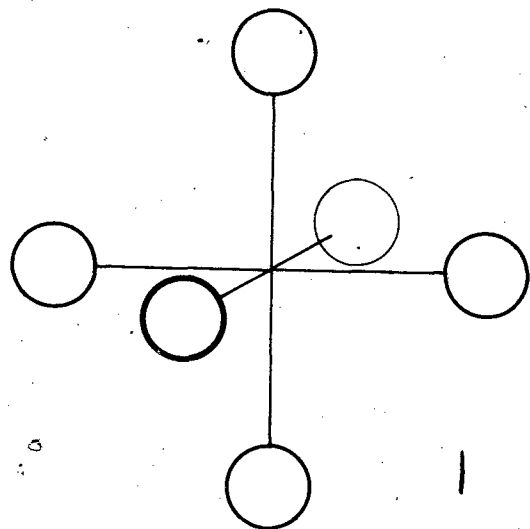
- (10) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, 1945, p. 264.
- 

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  $1.2076 \text{ \AA}^{11}$  and  $1.47 \pm 0.02 \text{ \AA}^{12}$  respectively, of which the average is  $1.34 \text{ \AA}$ , in excellent agreement with our value.

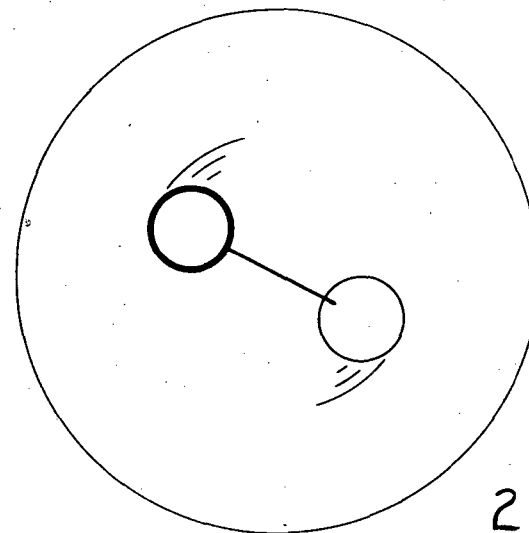
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- (11) G. Herzberg, "Molecular Spectra and Molecular Structure, I. Diatomic Molecules", Prentice-Hall, Inc., New York, 1939, p. 491. Calculated from spectroscopic moment of inertia.
- (12) P. A. Giguère and V. Schomaker, J. Am. Chem. Soc., 65, 2025 (1943). Measured by electron diffraction.
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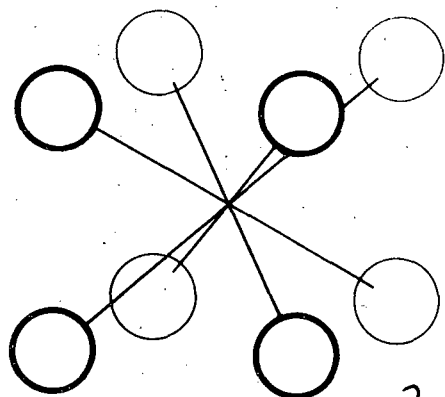
Acknowledgement - The x-ray diffraction patterns were taken by Mrs. L. Jackson. We wish to thank Professor Kleinberg for the samples of sodium oxides and for his interest in the problem. This research was supported in part by the Atomic Energy Commission.



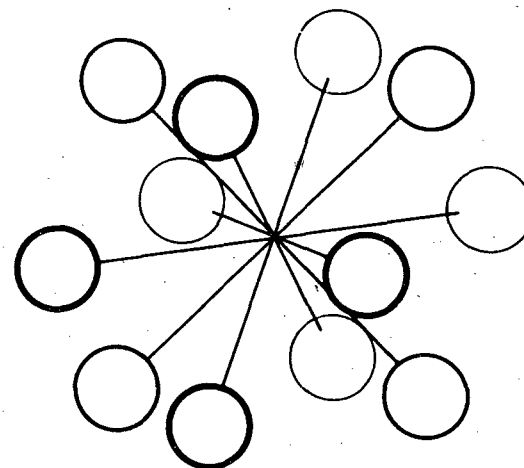
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FIG. 1

POSITIONS WHICH MAY BE OCCUPIED BY A PAIR OF OXYGEN ATOMS IN THE FOUR DISORDERED STRUCTURES PROPOSED FOR  $\text{NaO}_2$ . THE CENTER OF EACH GROUP IS AT A HALIDE POSITION IN THE SODIUM CHLORIDE STRUCTURE.

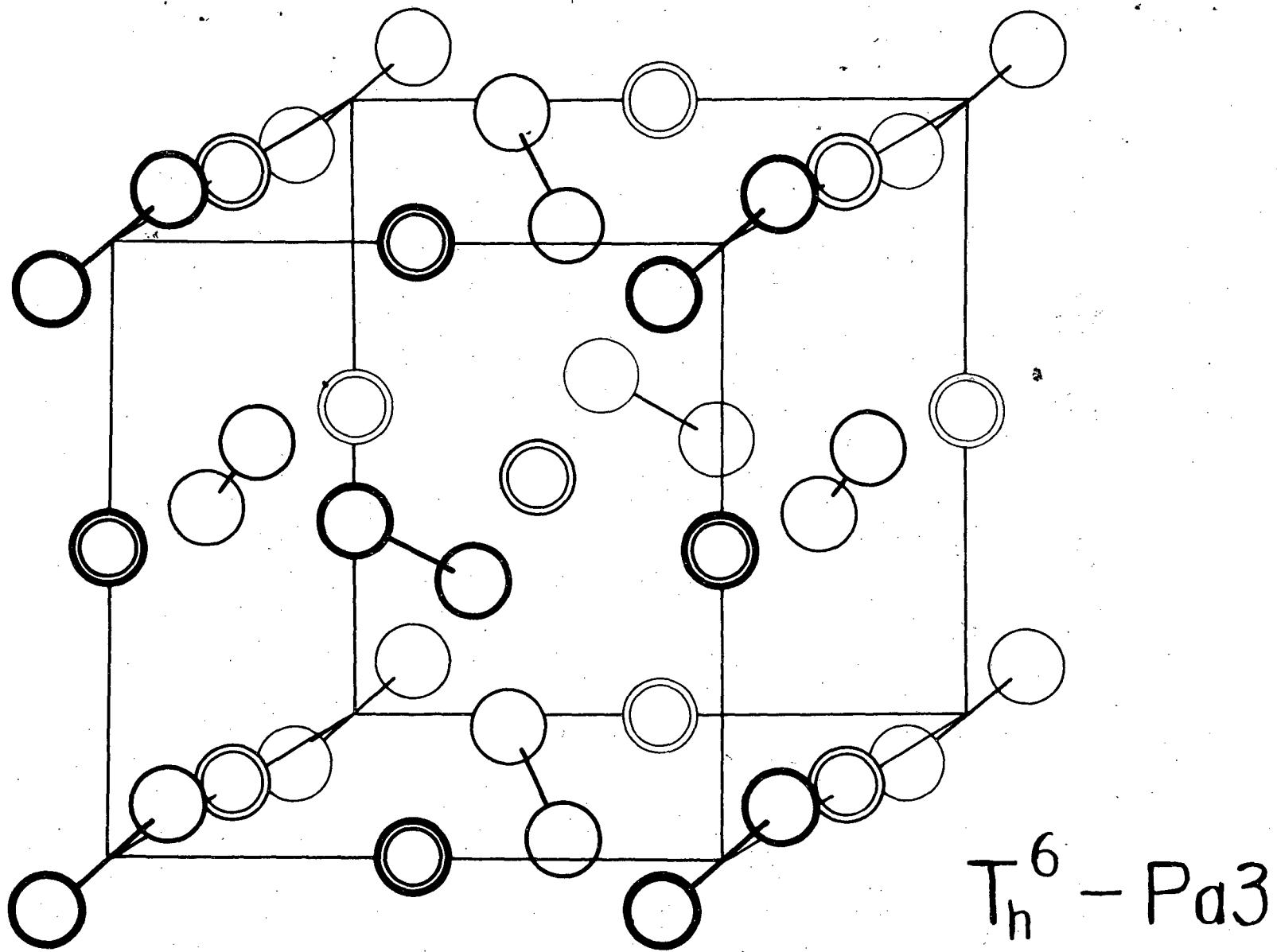


FIG. 2

THE PYRITE STRUCTURE, DRAWN WITH ANION PARAMETER TO FIT  $NaO_2$ . THE PAIRS OF SINGLE CIRCLES ARE OXYGEN, THE DOUBLE CIRCLES, SODIUM

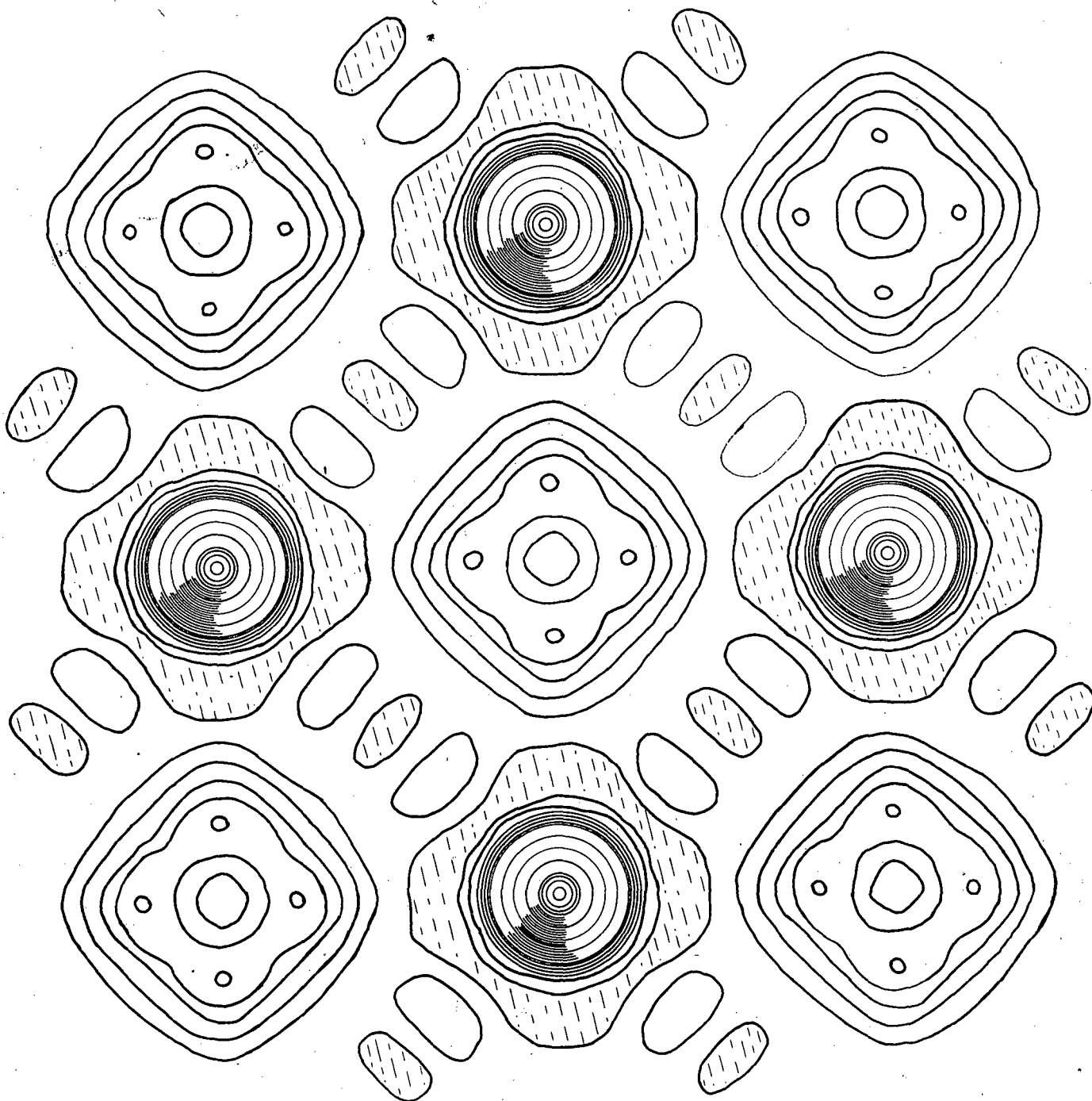


FIG. 3

ELECTRON DENSITY MAP  $xy0$  PLANE OF  $NdO_2$ , CALCULATED WITH AMBIGUOUS TERMS ADJUSTED TO FIT STRUCTURE I. THE CONTOUR INTERVAL IS 1 ELECTRON /  $\text{\AA}^3$ . THE SHADED AREAS ARE NEGATIVE. THE FOUR SMALL CIRCLES IN EACH  $O_2^-$  GROUP ARE MAXIMA; THE CENTRAL CIRCLE, A MINIMUM.