from the Clapeyron equation is 0.033 ± 0.001°/atm. However, the difference between freezing and triple point as reported above is only 0.012°. The difference of 0.021° results from the solubility of air, which, if Raoult's law is obeyed, amounts to 0.04 mole per cent.

Effect of Impurities on the Freezing Point of Phthalic Anhydride.—The effects of various probable impurities on the freezing point of phthalic anhydride determined in the Rossini apparatus are listed in Table III, singly, in pairs, and finally, all seven together. The amount of fumaric acid which could be added was limited because of its low solubility in molten phthalic anhydride. Maleic acid dehydrated, resulting in twice the freezing point depression calculated from the quantity added.

The freezing points of all the mixtures, except that in which both benzoic acid and phthalic acid were present as impurities, agreed with calculated values within experimental error. In this case the depression was only 0.70 of the calculated value. Because of this discrepancy, the melting behavior of this mixture was investigated in the calorimeter. Table IV lists the melting data obtained on this mixture. The points (first three in Table IV) at low fraction melted, deviate from the linearity of the points (last four in Table IV) at high fraction melted. Hence, they were left out of the least squares treatment. This type of behavior is characteristic of systems in which there is solid solution formation. The experimental triple point depression, ignoring solid solution formation by neglecting the mentioned points, was 0.75 of the value calculated assuming Raoult's law and a liquid-soluble, solid-insoluble impurity.

TABLE IV

PHTHALIC ANHYDRIDE WITH PHTHALIC ACID AND BENZOIC ACID ADDED AS IMPURITIES

t, °C. (calcd.)[a]	t, °C. (obsd.)	$1/X$	t, °C. (calcd. − obsd.)
128.464	128.737	5.126	−0.273
129.416	129.495	3.338	− .079
129.691	129.733	2.822	− .042
130.136	130.136	1.985	.000
130.284	130.279	1.708	+ .005
130.423	130.432	1.446	− .009
130.545	130.540	1.217	+ .005

[a] Calculated from the least squares equation t°C. = 131.93 − 0.5324/X, obtained by treating only the last four points.

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

Polymorphism of Sodium Superoxide

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The structures of sodium superoxide have been studied by powder and single crystal X-ray diffraction methods at low temperatures. NaO_2 (I) stable above −50°, has a disordered pyrite structure, with a = 5.49 Å. at 25°. The disorder probably is dynamic. NaO_2 (II) exists from −50 to −77° with the pyrite structure, with a = 5.46 A. at −70°. The oxygen parameter is u = 0.43. NaO_2 (III) exists below −77° with the marcasite structure, space group Pnnm, with a = 4.26 Å., b = 5.54 Å. and c = 3.44 Å. at −100°. The oxygen parameters are x = 0.12 and y = 0.43.

Previous work in this Laboratory[1] has shown that the crystal structure of sodium superoxide, NaO_2, at room temperature is similar to that of sodium chloride. The superoxide ion, O_2^-, is located at the anion position with rotational disorder. A search by the X-ray diffraction technique for low-temperature ordered forms, suggested by this disorder, has revealed two whose structures are described in the present paper. Single crystal X-ray diffraction data have also yielded more detailed information concerning the angular distribution of the rotation of the superoxide ion at room temperature.

We designate the three forms of sodium superoxide as I, II and III in decreasing order of temperature ranges of stability. Todd[2] has observed peaks in the heat capacity curve at 196.5 and 223.3°K. which correspond to the transition temperatures which we determine less accurately by the X-ray experiments. Zhdanov and Zvonkova[3] reported unit cell dimensions for NaO_2(I) and NaO_2(II) (which they designated as β and α, respectively) which are not in good agreement with our results. They also observed that sodium superoxide tends to become antiferromagnetic at the transition I → II.

Experimental

Sodium superoxide and potassium superoxide samples were provided by Dr. John L. Margrave. Single crystals of sodium superoxide of cubic habit (about 0.1 to 0.3 mm. on an edge) were obtained by slow evaporation of a liquid ammonia solution. Previous attempts to grow crystals by fusion and slow cooling failed because of decomposition. The crystals or powdered samples were sealed in Pyrex capillaries under an atmosphere of argon dried with molten sodium. For the low temperature photographs, the samples were cooled by a stream of nitrogen produced by electrical evaporation of the liquid. The temperature was measured by a thermocouple near the sample with an accuracy estimated as ±5°. Powder and Weissenberg photographs were taken in cameras of radius 2.86 cm. with Cu $K\alpha$, X-rays, λ = 1.5418 Å. Intensities were estimated visually by comparison with spots made with a set of exposure times.

Crystal Structure of NaO_2 (I).—In the previous work[1] four different models of the rotational disorder were considered: (1) orientation parallel to the three axial directions, (2) spherical symmetry, (3) orientation parallel to the four

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[1] D. H. Templeton and C. H. Dauben, THIS JOURNAL, **72**, 2251 (1950).

[2] S. S. Todd, *ibid.*, **75**, 1229 (1953).

[3] G. S. Zhdanov and Z. V. Zvonkova, *Doklady Akad. Nauk S. S. S. R.*, **82**, 743 (1952); read only in abstract form, *C. A.*, **46**, 6893 (1952).

cube diagonals, and (4) orientation parallel to the six face diagonals. Because of coincidences of lines and failure to observe the very weak reflections, the powder diffraction data could not be used to distinguish between these models. However, the Weissenberg photographs allowed removal of this ambiguity. The intensity ratios listed in Table I show that model 3 is the only one consistent with the observed data. The intensities of the other reflections, which are omitted for brevity, are less decisive in choosing between the structures, but in no case is there any significant disagreement with model 3. The maximum ratio of 600 (not observed) to 442 is less sensitive than that of 600 to 440 because the former ratio required the comparison of two different photographs.

TABLE I

WEISSENBERG INTENSITY RATIOS FOR NaO_2 (I)

hkl	$\frac{511}{531}$	$\frac{600}{442}$	$\frac{600}{440}$	$\frac{620}{440}$
Obsd.	3	<0.5	<0.25	<0.25
Calcd.				
1	0.5	8	6	5
2	1.2	0.9	0.8	0.9
3	2.4	0.2	0.2	0.1
4	1.3	0.6	1.0	0.7

The structure of NaO_2 (I) can be considered to be a disordered pyrite structure. These calculations do not imply that the axis of the superoxide ion must lie exactly parallel to a cube diagonal, but rather that the rotation is hindered to such an extent that such an orientation is more probable than others. Since NaO_2 (II), which is discussed below, has the pyrite structure, the II → I transition is an order–disorder one. Because this transition is reversible and rapid compared with the time for an X-ray exposure (one hour) the disorder at room temperature probably is dynamic rather than static.

Crystal Structure of NaO_2 (II).—In the powder diffraction pattern of NaO_2 cooled below −50° other lines than those found in patterns of NaO_2 (I) appeared, indicating a primitive rather than face-centered symmetry. Intensities had already been calculated[1] for the two possible cubic ordered structures, space groups T_h^6–Pa3 and O_h^4–Pn3m. Comparison of the observed and calculated intensities (Table II) shows that NaO_2 (II) has the pyrite structure,[4] space group T_h^6. In this structure the atomic positions are

4 Na in 4 (b): $0, 0, 0;\ 0, {}^1/_2, {}^1/_2;\ {}^1/_2, 0, {}^1/_2;\ {}^1/_2, {}^1/_2, 0$
8 O in 8 (h): $\pm(u, u, u;\ u, {}^1/_2 - u, {}^1/_2 + u;\ {}^1/_2 + u, u, {}^1/_2 - u;\ {}^1/_2 - u, {}^1/_2 + u, u)$ with $u = 0.43$

In Table II the calculated intensities are based on $u = 0.428$. The agreement is not sensitive to a variation of a few units in the third decimal place of the parameter.

TABLE II

POWDER INTENSITIES FOR NaO_2 (II)

hk	Intensity Obsd.	Intensity Calcd.[a]	*hkl*	Intensity Obsd.	Intensity Calcd.[a]
100	0	0	321	4	4.4
100	0	0	400	1	0.7
111	0	0.02	410	2	1.8
200	43	53	411, 330	1	0.8
210	3	4.5	331	4	3.4
211	4	5.0	420	3	2.4
220	25	22	421	0	0.3
300, 221	1	1.1	332	0	0.1
310	0	0	422	3	1.9
311	7	7.8	500, 430	1	1.2
222	5	5.1	510, 431	2	1.8
320	3	3.3	511, 333	4	5.7

[a] Reference 1.

At −70° $a = 5.46 \pm 0.01$ Å. for NaO_2 (II), compared with $a = 5.490 \pm 0.005$ Å. for NaO_2 (I) at 25°. Zhdanov and Zvonkova[3] give 5.30 and 5.44 Å. for −70 and 20°, respectively; we offer no explanation for the discrepancy.

Crystal Structure of NaO_2 (III).—The powder pattern of sodium superoxide cooled below −77° is complex, but shows a resemblance to those of NaO_2 (I) and (II). Single crystals cooled through the transition become highly twinned, but do not become randomly oriented powders. These facts suggested that the structures are closely related.

A single crystal, which by chance was oriented with the (110) direction of the cubic unit cell parallel to the axis of the capillary, when cooled below −77° gave rotation patterns in which most of the spots fell into well-defined layer lines. Weissenberg photographs were taken of the zero and first layers. It was found possible to sort out the reflections into four sets, which coincided by pairs in the zero layer, and which corresponded to a small triclinic unit cell. The four sets were related by symmetry in such a way that the composite pattern appeared to have symmetry mmm with respect to the rotation axis. The orientations of the sets were reproducible when the sample was warmed and cooled again, but the relative intensities of the sets changed enough to show that they were due to different crystals. Except for this fact, the pattern could have been explained as that of a single crystal with a very large unit cell and a correspondingly large (and unreasonable) number of extinctions.

It was possible to transform the triclinic unit cell to one which was orthorhombic within the accuracy of the measurements and oriented with [111] as the rotation axis. For this unit cell at −100°, $a = 4.26$ Å., $b = 5.54$ Å. and $c = 3.44$ Å. With two molecules, the calculated density is 2.25 g. cm.$^{-3}$, compared with 2.24 for NaO_2 (II) and 2.21 for NaO_2 (I). The orthorhombic b axis corresponds to one of the cubic axes, while a and c correspond to half diagonals of a face of the cubic unit.

The shape of the unit cell and its orientation with respect to the cubic unit cell immediately suggest a structure like that of marcasite, the orthorhombic form of FeS_2.[5] This structure is confirmed by the powder intensity data listed in Table III.

TABLE III

POWDER INTENSITIES FOR NaO_2 (III)

d,Å.	*hkl*	Intensity Obsd.	Intensity Calcd.	*d*,Å.	*hkl*	Intensity Obsd.	Intensity Calcd.
3.38	110	<2	0.5	1.54	112	<2	1
2.93	011	<2	2	1.52	221, 131	8	12
2.77	020	80	68	1.46	022	8	12
2.68	101	160	160	1.40	230	<2	0
2.41	111	6	10	1.38	040, 122, 310	8	14
2.32	120	16	15	1.34	202	3	4
2.13	200	12	12	1.32	140	<2	1
1.99	210	3	5	1.30	212	<2	2
1.93	121	48	61	1.29	231	4	6
1.72	211, 002	20	38	1.27	320	2	1
1.69	130, 220	20	17	1.23	141	2	2
1.63	031	4	6	1.21	132, 222	6	9

The space group is Pnnm (D_{2h}^{12}) with atomic positions

2 Na in 2 (a): $0, 0, 0;\ {}^1/_2, {}^1/_2, {}^1/_2$
4 O in 4 (g): $\pm(x, y, 0;\ {}^1/_2 - x, {}^1/_2 + y, {}^1/_2)$ with $x = 0.12$ and $y = 0.43$

The oxygen parameters are taken from the electron density section shown in Fig. 1, which was computed from the powder intensity data. The corresponding O–O distance is 1.28 Å. This value cannot be considered to be more accurate than ±0.10 Å. because of diffraction errors in the Fourier series. The intensity data from the Weissenberg photographs were too poor to be useful for improving the oxygen parameters.

The data listed in Table III include no corrections for absorption or temperature. All reflections permitted by the space group with $d > 1.21$ are included. The smallest spacing included in the calculation of Fig. 1 is 1.00 Å.

The orientations of the twins observed for NaO_2 (III) can be described as follows: There are two pairs each related by reflection in the 101 plane. The pairs are related to each other by a rotation of 180° about the [111] axis. The b axis common to one pair is nearly but not exactly perpendicular to the b axis of the other pair. The predominance

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

(5) C18-type, *ibid.*, **I**, 495 (1931).

of these four orientations among the many that are possible must be due to the confinement within the capillary. A few reflections in the zero layer and several between the layer lines indicated additional twins, but it was impossible to ascertain their orientations.

The structure of NaO_2 (III) was determined independently of that of marcasite. The similarity was first suggested to us by Professor J. D. McCullough of the University of California at Los Angeles.

It may be pointed out that the oxygen positions in NaO_2 (III) are almost identical with half of those in NaO_2 (II). Thus the transition II → III involves the rotation of half of the superoxide ions so that each ion is parallel to one of two cube diagonals, according to a regular pattern, rather than to one of four diagonals. Thus it is not surprising that there is a correlation between the orientations of a crystal of III and the crystal of II from which it is formed.

Sodium cyanide, which at room temperature has a cubic structure similar to that of NaO_2 (I), at −10° is transformed into an orthorhombic structure.[6] The relation between the cubic and orthorhombic cells is just the same as in sodium superoxide. The difference in the structures is that in the low sodium cyanide the cyanide groups all are oriented in the same way, while in NaO_2 (III) the superoxide ions have two orientations. As a result the relative dimensions of the orthorhombic cells in the two cases are rather different.

Comparison with Potassium Superoxide.—The color of sodium superoxide changes gradually with temperature from white at −100° to bright yellow at 25°. At more elevated temperatures the color darkens to orange. According to our observations the color changes do not seem to be associated with the transformations. A similar color behavior of potassium superoxide was discussed by Neuman[7] who concluded that the yellow color disappeared within 15° of a transition detected by thermal measurements at −75.5°. Todd[2] observed the transition at −79.7°. By the powder technique we have shown that this transformation involves a change from the tetragonal form[8] which is stable at room temperature to a less symmetrical structure whose complicated patterns have not been indexed. We have not studied single crystals of potassium superoxide.

At elevated temperatures, potassium superoxide is cubic like NaO_2 (I).[3,9] It is interesting that while the transitions of sodium superoxide and the low temperature transition of potassium superoxide are reasonably rapid and reversible, the high temperature transition of potassium superoxide is sluggish.[9]

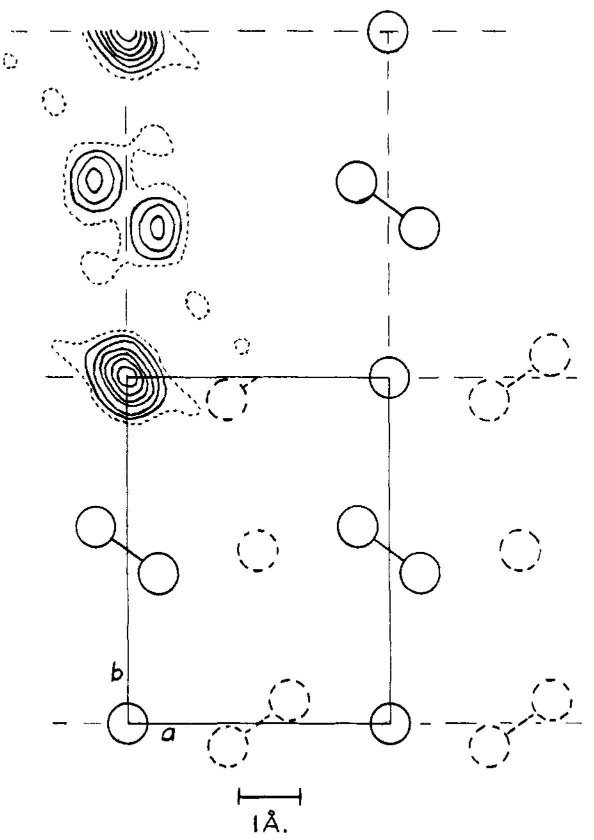

Fig. 1.—Composite electron density section at $z = 0$ and map of structure of NaO_2 (III). The contour intervals are arbitrary. In the lower portion of the map the solid circles represent atoms at $z = 0$ and the broken circles atoms at $z = {}^1/_2$. The two oxygen atoms in each superoxide ion are joined by a line.

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