

This interpretation is supported by the present work, as O(1) has an average distance to the three nearest K<sup>+</sup> ions of 3.000 Å (77 K) while O(2) is more strongly bonded, with a corresponding average distance of 2.847 Å (77 K). Furthermore, O<sup>-</sup>(1) does not have to pass closer than 2.94 Å (77 K) to any K<sup>+</sup> on its way from one Cl to the next.

In the orthorhombic high-temperature phase of KClO<sub>3</sub> (Ramachandran & Lonappan, 1957) there are equal amounts of ClO<sub>3</sub><sup>-</sup> ions in the same two orientations as observed in the ESR experiments. The ClO<sub>3</sub><sup>-</sup> ions are arranged in chains parallel to *a*. ClO<sub>3</sub><sup>-</sup> ions in the same chain have the same orientation. This suggests that the mechanism behind the phase transition at 523 K may be a systematic exchange of O atoms similar to the exchange of O<sup>-</sup> ions described above.

*Note added in proof:* The recent observation (Wadhawan, 1980) of the formation of domain walls on applying a uniaxial stress to crystals of the monoclinic form of KClO<sub>3</sub> may be explained as follows.

The stress causes slip to occur at the plane  $z = 0$  in the *a* direction. K, Cl, and O(2) with  $z > 0$  and the O(1) atom with  $z < 0$  will slip relative to K, Cl, and O(2) with  $z < 0$  and O(1) with  $z > 0$ . This slip requires Cl–O(1) bonds to be broken and then re-established, *i.e.* the same mechanism we propose for the monoclinic to orthorhombic phase change. The relative translation, *t*, is approximately 2.1 Å. If slipping occurs at all planes  $z = 0, \pm 1, \pm 2 \dots$  in the crystal our model gives a slip of  $t/c/\cos(\beta - 90) = 2.1/7.1/0.94 = 0.31$ .

Wadhawan describes four types of domain walls which he describes as DW1, DW2, DW3, and DW4. When the entire plane slides, then only domain wall DW1 appears. If, however, the slip starts at a particular Cl–O(1) bond, then neighbouring Cl–O(1) bonds with the same *z* value must be broken and Cl–O(1) bonds

with the same *z* value  $\pm 1$  may be broken causing planes of fracture to appear. These planes could be {100}, {110} or {110} and may explain the domain walls DW2, DW3, and DW4, respectively. Other planes such as {011} and {111} are also possible domain walls according to this hypothesis.

Neither Wadhawan nor we attempt to explain the transition to the rhombohedral high-pressure form of KClO<sub>3</sub> (Pistorius, 1972). All three forms of KClO<sub>3</sub> can be described as having distorted rock-salt structures. A cubic cell with  $Z = 4$  and a volume twice that of the monoclinic form, which has  $Z = 2$ , would have  $a = 7.05$  Å. The 'tetragonal' prototype phase proposed by Wadhawan has cell edges which are  $a/2$ ,  $a/2$ , and  $2a$ .

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## Neutron Profile Refinement of 4Na<sub>2</sub>SO<sub>4</sub>·2D<sub>2</sub>O<sub>2</sub>·NaCl

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**Abstract.** 4Na<sub>2</sub>SO<sub>4</sub>·2D<sub>2</sub>O<sub>2</sub>·NaCl, *P4/mnc*,  $a = 10.5270$  (2),  $c = 8.4079$  (3) Å. Neutron powder data (300 K, 1.9 Å) have been refined to give the D atom

positions in the title compound. Final  $R = 10.5\%$ . The arrangement and molecular parameters of the disordered peroxide molecules have now been well

determined. The dihedral angle for the D<sub>2</sub>O<sub>2</sub> molecules is 100·1(6)°. The arrangement of hydrogen bonds within the tunnels found in this structure has also been defined.

**Introduction.** The adduct 4Na<sub>2</sub>SO<sub>4</sub>·2H<sub>2</sub>O<sub>2</sub>·NaCl is a stable carrier of H<sub>2</sub>O<sub>2</sub> (German patent, 1975). A structural investigation (Adams & Pritchard, 1978) has shown that the sulphate groups are arranged in such a way that tunnels are formed in the structure parallel to *c* into which disordered H<sub>2</sub>O<sub>2</sub> molecules are fitted. It proved possible to locate four electron density maxima in each unit of the tunnels, each maximum corresponding to a site half-occupied by an O atom. It can be shown that two types of connectivity for these O atoms are possible (Adams & Pritchard, 1978) which are consistent with two half-occupied orientationally disordered H<sub>2</sub>O<sub>2</sub> molecules. It is not possible to distinguish between these two models on bond-length grounds since both types of connectivity were found in the X-ray study (Adams & Pritchard, 1978) to give O—O distances of 1·33 Å. To clarify the geometry and environment of the H<sub>2</sub>O<sub>2</sub> molecules a neutron diffraction study was undertaken on a sample of the adduct which had been deuterated.

The space group used for the following work is *P4/mnc* with a cell ~10·5 × 10·5 × 8·4 Å. It is known (Adams & Pritchard, 1978), however, that this is a subcell of the true cell since very weak lines are found between the layer lines on X-ray oscillation photographs taken about *a* or *b*. These supercell reflexions contribute to the background of the neutron diffraction trace.

7 g of NaCl were dissolved (in a dry box under N<sub>2</sub>) in 50 ml of a solution of (10 ml) 87% (w/w) H<sub>2</sub>O<sub>2</sub> in (40 ml) D<sub>2</sub>O at 318K. 12 g of anhydrous Na<sub>2</sub>SO<sub>4</sub> were added, with stirring. The undissolved solid was filtered off and the solution allowed to cool. Colourless,

Table 1. *Fractional atomic coordinates and their e.s.d.'s, and U<sub>eq</sub> values*

$$U_{eq} = 1/(6\pi^2) \sum_i \sum_j \beta_{ij} \cdot a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i> (Å <sup>2</sup> )
Na(1)	0·7569 (7)	0·9796 (6)	0·1910 (8)	0·060
Na(2)	0·0000	0·0000	0·5000	0·047
Cl(1)	0·0000	0·0000	0·0000	0·036
S(1)	0·6987 (8)	0·2768 (7)	0·0000	0·016
O(1)	0·8346 (4)	0·2981 (5)	0·0000	0·032
O(2)	0·6369 (3)	0·3351 (3)	0·1432 (4)	0·028
O(3)	0·6691 (6)	0·1369 (4)	0·0000	0·034
O(4)*	0·4963 (10)	0·0651 (7)	0·1932 (11)	0·044
D(1)*	0·5493 (10)	0·0902 (9)	0·1055 (11)	0·029

*N.B.* Refined cell parameters are *a* = 10·5270 (2), *c* = 8·4079 (3) Å. The e.s.d.'s do not include a contribution from the uncertainty in the neutron wavelength (1·9090 Å).

\* These atoms have a site occupancy of 0·5. The isotropic ratio of D to H in the D(1) site is 0·80:0·20.

bipyramidal crystals formed which gave powder diffraction lines consistent with those given by samples prepared as in the literature (German patent, 1975). There is rapid H/D exchange in the H<sub>2</sub>O<sub>2</sub>/D<sub>2</sub>O mixture and the maximum isotopic purity of D in the D<sub>2</sub>O<sub>2</sub> in the final product was calculated to be 87%. The sample was contained in a vanadium tube of diameter 16 mm and data were collected on the high-resolution neutron powder diffractometer D1A at the Institut Laue-Langevin, Grenoble (Hewat & Bailey, 1976). Data ranging from 6 to 160° (2θ) were collected in 22 h at a wavelength of 1·9090 Å. The background was estimated by linear interpolation from regions where no Bragg peaks occurred. Small peaks due to impurities of NaCl and Na<sub>2</sub>SO<sub>4</sub> hydrates were removed from the diffraction record. The structural refinement was carried out by the Rietveld (1969) technique with the programs of Hewat (1973*a,b*) and the X-ray structure as starting point. The D atoms were located from a difference synthesis. A final *R*<sub>nuclear</sub> (Hewat, 1973*a*) = 16%, corresponding to *R* = 10·5%, was obtained. The scattering lengths were from *International Tables for X-ray Crystallography* (1974). Anisotropic thermal parameters were used and corresponded well with the values obtained in the X-ray study (Adams & Pritchard, 1978). The site occupancy of the D atoms was allowed to vary to obtain the isotopic H/D ratio. Final coordinates are given in Table 1 and a figure giving a comparison of calculated and observed profiles has been deposited.\*

**Discussion.** The bond lengths within the SO<sub>4</sub><sup>2-</sup> ion (Table 2) and the Na—O coordination distances (Table 3) agree reasonably well with those found in the X-ray investigation (Adams & Pritchard, 1978). The e.s.d.'s are somewhat smaller in the present study (Table 2). Moreover, the geometry and environment of the H<sub>2</sub>O<sub>2</sub> molecules have been considerably clarified.

The two possible connectivities for O—O bonds (Adams & Pritchard, 1978) are no longer of equal length, *i.e.* 1·32 and 1·37 Å, the latter being closer to the usual value for the peroxide O—O length (Busing & Levy, 1965). In addition the D atoms have been located. Although a wide range of dihedral angles has been reported (varying from ~90 to 180°; Pedersen, 1969) for H<sub>2</sub>O<sub>2</sub>, most are in the region 100–110°. If the atoms are connected as in Fig. 1, then the dihedral angle for the two half-occupied orientationally disordered D<sub>2</sub>O<sub>2</sub> molecules is 100·1°, which is within this usual range for H<sub>2</sub>O<sub>2</sub>.

The location of the D atom also confirms the

\* A list of anisotropic thermal parameters and a figure showing the calculated and observed powder profiles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35779 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°)

		X-ray data*
S(1)—O(1)	1.448 (9)	1.44 (1)
S(1)—O(2)	1.500 (6)	1.47 (1)
S(1)—O(3)	1.505 (9)	1.47 (1)
O(4)—O(4 <sup>l</sup> )	1.37 (1)	1.33 (2)
D(1)—O(4)	0.96 (1)	—
O(1)—S(1)—O(2)	111.4 (4)	110.4 (3)
O(1)—S(1)—O(3)	110.9 (6)	110.0 (6)
O(1)—S(1)—O(2 <sup>ll</sup> )	111.4 (4)	110.4 (3)
O(2)—S(1)—O(3)	108.1 (4)	109.0 (3)
O(2)—S(1)—O(2 <sup>ll</sup> )	106.8 (5)	107.9 (5)
O(3)—S(1)—O(2 <sup>ll</sup> )	108.1 (4)	109.0 (3)

The dihedral angle for D<sub>2</sub>O<sub>2</sub> is 100.1 (6)°

## Symmetry code

(i) 1 - x, -y, z	(x) ½ - x, ½ + y, ½ - z
(ii) x, y, -z	(xi) ½ - x, -½ + y, ½ - z
(iii) x, 1 + y, z	(xii) ½ - x, ½ + y, -½ + z
(iv) 1 - x, 1 - y, z	(xiii) ½ - x, -½ + y, ½ + z
(v) 1 - y, x, z	(xiv) ½ + x, ½ - y, ½ - z
(vi) 1½ - x, ½ + y, ½ - z	(xv) -½ + x, ½ - y, ½ - z
(vii) ½ + y, ½ + x, ½ - z	(xvi) y, 1 - x, z
(viii) ½ + x, ½ - y, -½ + z	(xvii) 1 + x, 1 + y, z
(ix) -½ + x, ½ - y, ½ + z	

\* Adams & Pritchard (1978).

Table 3. Coordination around the cations

Na(1)—O(3 <sup>ll</sup> )	2.485 (8) Å	Na(2)—O(2 <sup>vlll</sup> )	} 2.557 (3) Å
Na(1)—O(4 <sup>lv</sup> )	2.707 (13)	O(2 <sup>lx</sup> )	
Na(1)—O(1 <sup>v</sup> )	2.290 (7)	O(2 <sup>lx</sup> )	
Na(1)—O(2 <sup>vi</sup> )	2.347 (7)	O(2 <sup>xl</sup> )	
Na(1)—O(2 <sup>vll</sup> )	2.316 (7)	O(2 <sup>xll</sup> )	
Na(1)—O(4 <sup>vll</sup> )	2.249 (11)	O(2 <sup>xlll</sup> )	
Na(1)—Cl(1 <sup>xvll</sup> )	3.029 (7)	O(2 <sup>xlv</sup> )	
		O(2 <sup>xv</sup> )	

hydrogen-bonding scheme. In the previous X-ray study (Adams & Pritchard, 1978) it was shown that the peroxide O(4) was close to the sulphate O(3) and O(1<sup>xvi</sup>) and it was therefore possible that the hydrogen bond could be to either of these O atoms since the O...O distances were similar, 2.71 (2) and 2.68 (2) Å respectively. We have found in the neutron study that the O...O distances are less similar than those for the non-deuterated compound: O(4)...O(3) 2.51 (1) and

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## The Structure of Magnetite

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**Abstract.** Fe<sub>3</sub>O<sub>4</sub>, cubic, *Fd3m*, *a* = 8.3941 (7) Å. The structure has been refined to a weighted *R* of 0.033, using 147 unique averaged reflexions collected at room

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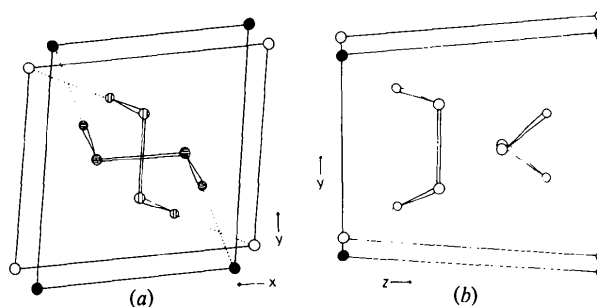


Fig. 1. View of the D<sub>2</sub>O<sub>2</sub> molecules. Each molecule has a site occupancy of 0.5. The hydrogen-bonding scheme O(4)—D(1)...O(3) is shown. (a) Projection on to (001). The centre of the diagram is at *x* = 0.5, *y* = 0.0. (b) Projection on to (100). The centre of the diagram is at *y* = 0.0, *z* = 0.25.

O(4)...O(1<sup>xvi</sup>) 2.85(1) Å. It is likely from these figures that O(4)...O(3) is the hydrogen bond since the O(4)...O(1<sup>xvi</sup>) distance is close to the van der Waals diameter for an O atom. In addition the D atom lies close to the line between O(4) and O(3). We have O(4)—D(1) 0.95 (1), D(1)...O(3) 1.62 (1) Å, O(4)—D(1)...O(3) 163 (1)°.

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temperature on a single-crystal diffractometer with Mo *K*<sub>α</sub> (*λ* = 0.7107 Å) radiation. The oxygen positional parameter (*u*) is 0.2549 (1). The observed *M*—O bond

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