

O(9) are part of the Ca(2) oxygen coordination polyhedron and that O(7) and O(9) form the common edge between two Ca(2) polyhedra. Since the two Ca atoms across this edge are the ones in question, it may be concluded from the positions and partial bond strengths of these O atoms that an explanation exists within the limitations of the model adopted here.

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## The Crystal Structure of $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot \text{NaCl}$

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The structure of  $4\text{Na}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}_2 \cdot \text{NaCl}$  has been refined to  $R = 0.071$ . The unit cell is tetragonal [ $a = 10.53$  (1),  $c = 8.42$  (1) Å] and there exists a supercell with an  $a$  and  $b$  repeat four times larger than the basic cell used for the structure determination. The  $\text{H}_2\text{O}_2$  molecules appear to have orientational disorder but this is only a consequence of using the smaller cell: they are held within infinite tunnels (parallel to  $c$ ) by hydrogen bonds to O atoms of the sulphate groups. The coordination around eight of the  $\text{Na}^+$  ions is distorted octahedral, whereas around the other there is a regular eightfold coordination with tetragonal-prismatic symmetry.

## Introduction

This crystallographic study was prompted by our continued interest in perhydrates, *i.e.* compounds containing  $\text{H}_2\text{O}_2$  of crystallization, *e.g.*  $\text{Na}_2\text{CO}_3 \cdot 1\frac{1}{2}\text{H}_2\text{O}_2$  (Adams & Pritchard, 1977). Such compounds can function as solid-state carriers of the technologically important  $\text{H}_2\text{O}_2$ . The great stability of the title compound (Kao Soap Co. Ltd & Nippon Peroxide Co. Ltd, 1975) has led to its use in the bleaching and detergent industries. However, this stability is not reflected in short strong hydrogen bonds formed by the  $\text{H}_2\text{O}_2$ . Two peaks appear in the OH stretching region of the IR spectrum at 3200 and 3450  $\text{cm}^{-1}$  corresponding to  $\text{O} \cdots \text{O}$  hydrogen bonds of 2.75 and 2.81 Å (Pimentel & Sederholm, 1956). These values are slightly above the upper limit of values previously reported for perhydrates (Pedersen, 1967). IR spectroscopy also shows that the  $\text{H}_2\text{O}_2$  molecules in the structure cannot be *trans* planar since the sharp 880  $\text{cm}^{-1}$  peak characteristic of  $\text{H}_2\text{O}_2$  is present. A preliminary differential scanning calorimetric study of the adduct confirmed that decomposition does not occur until the very high temperature (for perhydrates) of 180°C and, since different  $\Delta H$  values were recorded on different runs, there is some evidence for  $\text{H}_2\text{O}_2$  being ejected from the crystals followed by gas-phase decomposition (only some of which would occur on, and be catalysed by, the sample pan and consequently be measured).

The initial X-ray investigation revealed a tetragonal cell with  $a = 10.53$  (1),  $c = 8.42$  (1) Å but the presence of much weaker layer lines shows that this is merely a subcell; the true, full cell remains tetragonal but  $a$  and  $b$  are increased to 42.12 Å. The structure of the subcell has been determined in this work.

## Experimental

3 g of NaCl were dissolved in 20  $\text{cm}^3$  50% w/w  $\text{H}_2\text{O}_2$  solution at 45°C followed by the addition of 5 g of anhydrous  $\text{Na}_2\text{SO}_4$ . The undissolved solid was filtered off and the solution allowed to cool. Colourless, square bipyramidal crystals which gave Guinier photographs identical to those of samples prepared according to the patent literature (Kao Soap Co. Ltd & Nippon Peroxide Co. Ltd, 1975) appeared on standing.

One crystal (0.1 × 0.2 × 0.3 mm) was used for collecting the data ( $h0l-h5l$ ,  $hk0-hk1$ ) with a Stoe Weissenberg camera. 1950 individual reflections were measured by the SRC Microdensitometer Service: these reduced to 350 unique intensities after merging between film packs taking symmetry into consideration.

Scattering factors used were those from *International Tables for X-ray Crystallography* (1974) with sulphate O atoms taken as  $\text{O}^{1/2-}$  (the average of the  $\text{O}^-$  and  $\text{O}^0$ ).

## Determination of the structure

The systematic absences observed initially ( $hk0$  no conditions;  $0kl$ ,  $k + l = 2n$ ;  $hhl$  no conditions;  $h00$ ,  $h = 2n$ ;  $hh0$  no conditions) gave the space group as either  $P4n2$  or  $P4_2/mnm$ . An  $N(z)$  test indicated that the cell was noncentrosymmetric. However, the validity of this test was in some doubt as the weak reflections, unobserved by the microdensitometer, had not been included. Solution was, therefore, attempted in  $P4n2$  with *MULTAN* (Germain, Main & Woolfson, 1971) and the 80 highest  $E$  values ( $> 1.42$ ). The set of phases with the highest absolute figure of merit gave an  $E$  map in which the  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions were recognizable. It did not prove possible at this stage to locate the  $\text{H}_2\text{O}_2$  molecules.

Least-squares refinement with an overall isotropic temperature factor followed by a difference synthesis [both procedures calculated with the XRAY system (Stewart, Kruger, Ammon, Dickinson & Hall, 1972)] revealed the  $\text{H}_2\text{O}_2$  which exhibited orientational disorder. Inclusion of the  $\text{H}_2\text{O}_2$  molecules with a population parameter of 0.5 and the use of individual isotropic thermal parameters reduced  $R$  to 0.11. Anisotropic refinement with the removal of the 301, 101 and 111 reflections (suffering from extinction) gave an  $R$  of 0.061, although the thermal parameters of some of the O atoms became non-positive-definite. The low value of  $R$  was not reflected in satisfactory bond lengths. An attempted refinement in the centrosymmetric space group  $P4_2/mnm$  was unsuccessful.

At this point a re-examination of the observed structure factors showed that of the  $hhl$  class of reflections, 26 had even values of  $l$  while only two had odd values. These two reflections (115 and 441) were extremely weak (on the limit of detection of the microdensitometer) and were consequently omitted. Examination of the diffraction conditions ( $hk0$  no conditions;  $0kl$ ,  $k + l = 2n$ ;  $hhl$ ,  $l = 2n$ ) gave the true space group as the centrosymmetric  $P4/mnc$  or the non-centrosymmetric  $P4nc$ . Refinement in  $P4/mnc$  gave a final  $R$  of 7.1%, whereas a refinement attempted in  $P4nc$  diverged. The bond lengths and angles were more

Table 1. Final atomic coordinates

The population parameter for the peroxide O(4) is 0.5.  
The  $z$  parameters for S(1), O(1) and O(3) are fixed.  
The  $x, y, z$  parameters for Na(2) and Cl(1) are fixed.

	$x$	$y$	$z$
S(1)	0.6968 (3)	0.2767 (3)	0.0000
O(1)	0.8316 (8)	0.3002 (9)	0.0000
O(2)	0.6374 (6)	0.3336 (6)	0.1414 (6)
O(3)	0.6720 (9)	0.1388 (8)	0.0000
O(4)	0.4888 (15)	0.0620 (13)	0.2043 (15)
Na(1)	0.7582 (5)	0.9831 (4)	0.1908 (5)
Na(2)	0.0000	0.0000	0.5000
Cl(1)	0.0000	0.0000	0.0000

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

S(1)—O(1)	1.44 (1)
S(1)—O(2)	1.47 (1)
S(1)—O(3)	1.47 (1)
O(4)—O(4)	1.33 (2)
	1.33 (2) } see Discussion
	1.08 (2) }
O(1)—S(1)—O(2)	110.4 (3)
O(1)—S(1)—O(3)	110.0 (6)
O(1)—S(1)—O(2 <sup>l</sup> )	110.4 (3)
O(2)—S(1)—O(3)	109.0 (3)
O(2)—S(1)—O(2 <sup>l</sup> )	107.9 (5)
O(3)—S(1)—O(2 <sup>l</sup> )	109.0 (3)

## Symmetry code

(i)	$x, y, \bar{z}$	(xiv)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$
(ii)	$1 - x, -y, z$	(xv)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$
(iii)	$\frac{1}{2} + y, -\frac{1}{2} + x, \frac{1}{2} - z$	(xvi)	$\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} + z$
(iv)	$\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$	(xvii)	$\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$
(v)	$y, 1 - x, z$	(xviii)	$-\frac{1}{2} + y, -\frac{1}{2} + x, \frac{1}{2} + z$
(vi)	$1 + x, 1 + y, z$	(xix)	$\frac{1}{2} - y, \frac{1}{2} - x, \frac{1}{2} - z$
(vii)	$x, 1 + y, z$	(xx)	$-1 + x, -1 + y, z$
(viii)	$1 - x, 1 - y, z$	(xxi)	$1 - x, 1 - y, -z$
(ix)	$1 - y, x, z$	(xxii)	$-1 + x, -1 + y, -z$
(x)	$1\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$	(xxiii)	$1 - y, -1 + x, z$
(xi)	$\frac{1}{2} + y, \frac{1}{2} + x, \frac{1}{2} - z$	(xxiv)	$-1 + y, 1 - x, -z$
(xii)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} + z$	(xxv)	$-1 + y, 1 - x, z$
(xiii)	$-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} - z$	(xxvi)	$1 - y, -1 + x, -z$

Table 3. Coordination around the ions (see also Fig. 1)

Na(1)—Cl(1 <sup>vi</sup> )	3.016 (9) Å
Na(1)—O(3 <sup>vii</sup> )	2.47 (1)
Na(1)—O(4 <sup>viii</sup> )	2.65 (2)
Na(1)—O(1 <sup>ix</sup> )	2.35 (1)
Na(1)—O(2 <sup>x</sup> )	2.384 (9)
Na(1)—O(2 <sup>xi</sup> )	2.295 (9)
Na(1)—O(4 <sup>xii</sup> )	2.25 (2)
Na(2)—O(2 <sup>xiii</sup> ), O(2 <sup>xiiii</sup> ), O(2 <sup>xv</sup> ), O(2 <sup>xvi</sup> ), O(2 <sup>xvii</sup> ), O(2 <sup>xviii</sup> ), O(2 <sup>xix</sup> )	2.565 (8)
Cl(1)—Na(1 <sup>xx</sup> ), Na(1 <sup>xxi</sup> ), Na(1 <sup>xxii</sup> ), Na(1 <sup>xxiii</sup> ), Na(1 <sup>xxiv</sup> ), Na(1 <sup>xxv</sup> ), Na(1 <sup>xxvi</sup> )	3.016 (9)
Cl(1 <sup>vi</sup> )—Na(1)—O(3 <sup>vii</sup> )	85.6 (3)°
Cl(1 <sup>vi</sup> )—Na(1)—O(4 <sup>viii</sup> )	149.7 (4)
Cl(1 <sup>vi</sup> )—Na(1)—O(1 <sup>ix</sup> )	84.1 (3)
Cl(1 <sup>vi</sup> )—Na(1)—O(2 <sup>x</sup> )	88.0 (3)
Cl(1 <sup>vi</sup> )—Na(1)—O(2 <sup>xi</sup> )	89.7 (3)
Cl(1 <sup>vi</sup> )—Na(1)—O(4 <sup>xii</sup> )	169.6 (4)
O(3 <sup>vii</sup> )—Na(1)—O(4 <sup>viii</sup> )	77.6 (4)
O(3 <sup>vii</sup> )—Na(1)—O(1 <sup>ix</sup> )	84.8 (4)
O(3 <sup>vii</sup> )—Na(1)—O(2 <sup>x</sup> )	173.7 (3)
O(3 <sup>vii</sup> )—Na(1)—O(2 <sup>xi</sup> )	93.3 (4)
O(3 <sup>vii</sup> )—Na(1)—O(4 <sup>xii</sup> )	84.3 (5)
O(4 <sup>viii</sup> )—Na(1)—O(1 <sup>ix</sup> )	69.5 (4)
O(4 <sup>viii</sup> )—Na(1)—O(2 <sup>x</sup> )	108.0 (4)
O(4 <sup>viii</sup> )—Na(1)—O(2 <sup>xi</sup> )	116.1 (4)
O(4 <sup>viii</sup> )—Na(1)—O(4 <sup>xii</sup> )	23.7 (5)
O(1 <sup>ix</sup> )—Na(1)—O(2 <sup>x</sup> )	94.4 (4)
O(1 <sup>ix</sup> )—Na(1)—O(2 <sup>xi</sup> )	173.6 (3)
O(1 <sup>ix</sup> )—Na(1)—O(4 <sup>xii</sup> )	92.6 (5)
O(2 <sup>x</sup> )—Na(1)—O(2 <sup>xi</sup> )	86.7 (4)
O(2 <sup>x</sup> )—Na(1)—O(4 <sup>xii</sup> )	102.0 (5)
O(2 <sup>xi</sup> )—Na(1)—O(4 <sup>xii</sup> )	95.3 (5)

reasonable in the centrosymmetric refinement and the estimated standard deviations of these parameters were considerably lower although the overall model remained the same. The final results reported here are those from the refinement in  $P4/mnc$ . It did not prove possible to locate the H atoms.\* Final atomic coordinates, bond lengths and angles, and the coordination around the ions are given in Tables 1, 2 and 3.

## Discussion

The sulphate ion has S—O lengths which are in the range usually found (Brown, 1974) and is reasonably regular. The environment about the  $\text{Cl}^-$  ion is slightly unusual; it is eightfold tetragonal prismatic with  $\text{Cl}^- \cdots \text{Na}^+$  distances of 3.016 (9) Å which is slightly longer than that in NaCl (2.82 Å; Tucker & Senio, 1956). Na(2) also has this type of coordination in that it is surrounded by eight O atoms donated by the sulphate groups in a regular array possessing fourfold symmetry. The  $\text{Na} \cdots \text{O}$  distances are all equal (space-group symmetry) at 2.565 (8) Å (Fig. 1). This type of coordination is very unusual for  $\text{Na}^+$  which, almost invariably, has octahedral coordination, but occasionally has higher coordination numbers of up to 12 (Marezio, Dernier, Chenavas & Joubert, 1973). In the crown ethers, probably the best known example of  $\text{Na}^+$  in eightfold coordination (Mercer & Truter, 1973), there are six surrounding O atoms in an equatorial plane and two axial O atoms. Na(1) (Fig. 1) has what is basically octahedral symmetry except that one of the coordination positions is taken up by O atoms of the peroxide group. Since these molecules are disordered, not all the O atoms will appear near one Na(1). Although the thermal ellipsoid found for Na(1) is very elongated there is no evidence from difference maps for two slightly displaced sites for the ion.

Each  $\text{H}_2\text{O}_2$  molecule lies in a distorted cube of O atoms and these cubes extend parallel to  $c$  giving infinite tunnels (Figs. 2 and 4). While the positions of

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33286 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

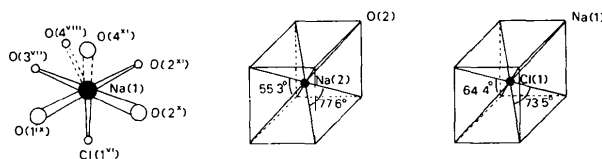


Fig. 1. Coordination around the  $\text{Na}^+$  and  $\text{Cl}^-$  ions. All the atoms in the coordination sphere of Na(2) are O(2) in different equivalent positions. All the atoms in the coordination sphere of Cl(1) are Na(1) in different equivalent positions.

the O atoms of these molecules have been determined unequivocally (each with population parameter 0.5, *i.e.* one molecule or two O atoms per site), there is some difficulty in deciding on the connectivity between the atoms. If we take the disorder at its face value then we have several possible orientations for the  $\text{H}_2\text{O}_2$

molecule:  $\text{O}(4)\text{--O}(4^{\text{II}})$  1.33 Å,  $\text{O}(4)\text{--O}(4^{\text{III}})$  1.33 Å, and  $\text{O}(4)\text{--O}(4^{\text{IV}})$  1.08 Å. The last can reasonably be discounted since the bond length is too short. Two possible arrangements remain, however, which appear equally likely, *i.e.* two disordered molecules of  $\text{O}(4)\text{--O}(4^{\text{II}})$  type or  $\text{O}(4)\text{--O}(4^{\text{III}})$  type (Fig. 3). It might even happen that each of the four possible  $\text{H}_2\text{O}_2$  molecular orientations could be occupied (molecular site occupancy 0.25). Either arrangement leaves the atomic positions the same (Figs. 3 and 4).

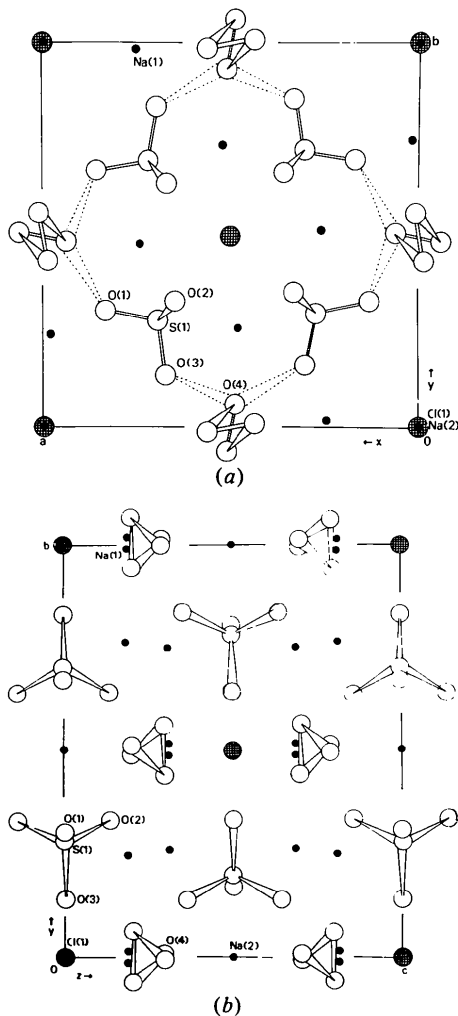


Fig. 2. (a) Projection of the structure on to (001) from  $z = 0.0$  to  $z = 0.5$ . (b) Projection of the structure on to (100). Only half the sulphate groups are shown (for clarity).

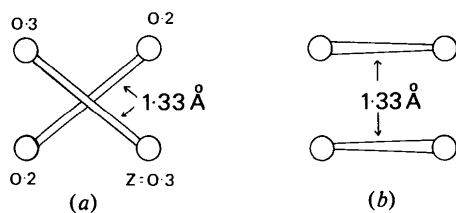


Fig. 3. Two types of connectivity in the disordered  $\text{H}_2\text{O}_2$  molecules consistent with the atomic positions and bond lengths. (a)  $\text{O}(4)\text{--O}(4^{\text{II}})$  type. (b)  $\text{O}(4)\text{--O}(4^{\text{III}})$  type.

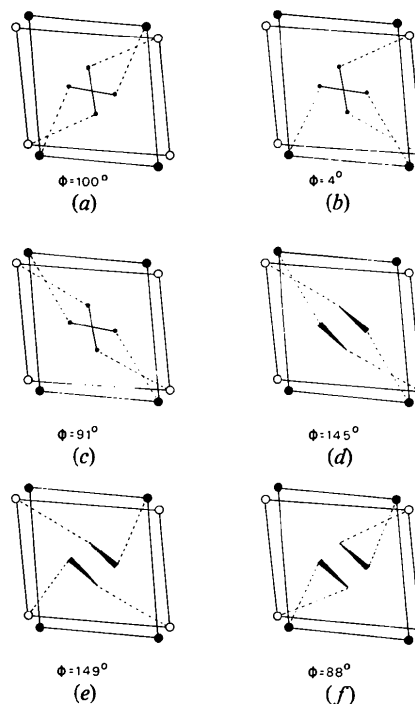


Fig. 4. (a)–(c)  $\text{O}(4)\text{--O}(4^{\text{II}})$  type molecules. (d)–(f)  $\text{O}(4)\text{--O}(4^{\text{III}})$  type molecules. Within each subset the cases are shown where two short (a and f), one short and one long (b and e) and two long (c and d) hydrogen bonds are formed. The dihedral angle  $\phi$  is given in each case.  $\circ$  Oxygen atoms forming tunnels at  $z = 0.0$ ,  $\bullet$  oxygen atoms forming tunnels at  $z = 0.5$ .

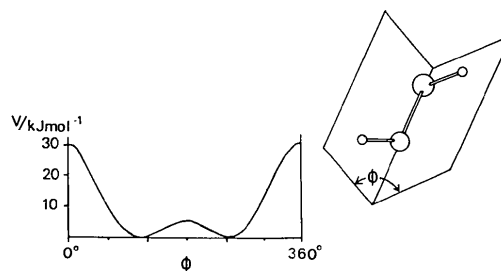


Fig. 5. The hindering potential of the free  $\text{H}_2\text{O}_2$  molecule (Hunt, Leacock, Peters & Hecht, 1965).

The distances from O(4) to O(1<sup>v</sup>) and O(3), 2.86 (2) and 2.71 (2) Å, are consistent with two possible hydrogen bonds from each peroxide OH group although the second of these would obviously be preferred as a stronger bond. There are six possible hydrogen-bonding schemes which are consistent with the two types of peroxide bonding [O(4)—O(4<sup>ii</sup>) or O(4)—O(4<sup>iii</sup>)] shown in Fig. 4. The difference in energy between the shorter and longer hydrogen bond (from the IR data) is  $\sim 3 \text{ kJ mol}^{-1}$ . The rotational energy barrier for  $\text{H}_2\text{O}_2$  (Fig. 5) is of this order of magnitude, at least between dihedral angles of 80 and 280°. Thus the longer hydrogen bonds would be formed if: (i) the

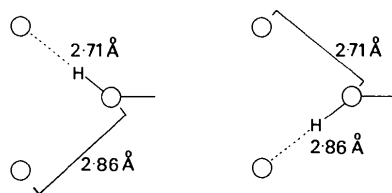


Fig. 6. Hydrogen-bonding geometries differing in the position of the H atom of the  $\text{H}_2\text{O}_2$  molecules. The non-bonded interaction distance in each case is approximately equal to the sum of the van der Waals radii.

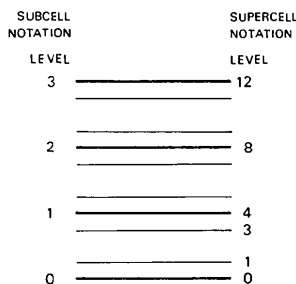


Fig. 7. Variation of intensities on different layer lines. Crystal set to oscillate about  $\mathbf{a}$ . The levels  $4n + 2$  (supercell notation) are missing.

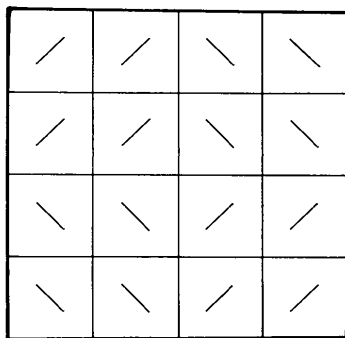


Fig. 8. One ordered arrangement of  $\text{H}_2\text{O}_2$  molecules (schematic) which is consistent with the intensities of the layer lines of the superlattice. The subdivisions are of the superlattice units into sublattice blocks.

geometry is such that a short hydrogen bond would be very non-linear or (ii) if the dihedral angle,  $\phi$ , went outside the 80 to 280° range. Only the model of Fig. 4(b) would be ruled out on dihedral-angle grounds. The O—O...O angles are also reasonable for hydrogen bonding [(a) 99.6, (c) 120.6, (f) 97.3°] except for (d) at 167.3° and (e) 167.3 and 97.3°. It is difficult to decide which of the remaining (a), (c) and (f) models would give lower energy configurations. In all the bonding schemes the non-bonded O...O interaction is just about equal to twice the sum of the van der Waals radii (Fig. 6).

Unfortunately it is not possible to say much about the arrangement of the  $\text{H}_2\text{O}_2$  molecules, even if the information about the intensities of the superlattice lines is taken into consideration (Fig. 7). With the supercell indexing, all lines with index  $4n$  are strong while those with index  $4n + 2$  are missing. The  $4n + 1$  and  $4n + 3$  lines are fairly weak. It can be shown that these facts are consistent with any ordered arrangement of  $\text{H}_2\text{O}_2$  molecules providing that for any particular atom there is a corresponding one at a  $\frac{1}{4}$  supercell repeat away. One of the simpler of such arrangements is shown schematically in Fig. 8.

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