

There is a tendency to form definite WO_4 ions, removing the double oxide character of the pure spinel. In the other tungstates, fully discrete WO_4 tetrahedra are present; in the potassium and rubidium salt each alkali ion is surrounded by 8 oxygen atoms, while in the caesium salt with the β - K_2SO_4 structure, one caesium ion is surrounded by 10, and the other by 9 oxygen atoms.

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A Nuclear Magnetic Resonance Study of Magnesium Thiosulphate Hexahydrate*

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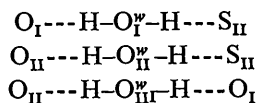
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The angular dependence of the nuclear magnetic resonance spectrum of single crystals of $MgS_2O_3 \cdot 6H_2O$ has been studied in four planes of rotation with a view to establishing the proton-proton vectors. The experimentally determined vectors were employed to (a) confirm the hydrogen-bonding scheme predicted by the X-ray authors, (b) resolve the conflict with a previous n.m.r. study of $MgS_2O_3 \cdot 6H_2O$ and, (c) determine the coordinates of the hydrogen atoms.

1. Introduction

The X-ray studies of Nardelli, Fava & Giral di (1962) give the space group of $MgS_2O_3 \cdot 6H_2O$ as *Pnma* with unit-cell dimensions $a = 9.32$, $b = 14.36$, $c = 6.87$ Å, and with $Z = 4$. The structure consists of alternating layers of $Mg(OH_2)_6^{2+}$ octahedra and $S_2O_3^{2-}$ tetrahedra perpendicular to the b axis. Each octahedron is linked by OH---O hydrogen bonding to four neighboring octahedra in the same layer and to four tetrahedra in the two adjacent layers. The hydrogen-bonding scheme suggested by Nardelli *et al.* (1962) is as follows:



where the designations of Nardelli *et al.* are used, except for H_2O , which is replaced here by O^w .

A study of the angular dependence of the nuclear magnetic resonance spectrum of $MgS_2O_3 \cdot 6H_2O$ in one plane of rotation has been made previously by Visweswaramurthy (1963). The p-p (proton-proton) vectors given by Visweswaramurthy were inconsistent with the hydrogen-bonding scheme above. The finding of this inconsistency (El Saffar, 1968) led to the present investigation.

2. Experimental

Large single crystals of commercial-grade $MgS_2O_3 \cdot 6H_2O$ were grown from saturated aqueous solutions. The samples were cut in approximately cylindrical form and varied in volume from 1 to 4 cm³. They were mounted in Teflon holders which were in turn attached to a simple indexed head which allowed rotation about the axis of the cylinder. The measurements were made at room temperature. The resonance spectrum was re-

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corded with a Varian wide-line n.m.r. spectrometer Model V4210 operated at 16 MHz. The n.m.r. probe was placed in the gap of a 12" electromagnet connected to a Varian Fieldial power supply Model V-Fr 2100 and equipped with field-sweep gear. Many of the significant recordings were made with the use of a Varian

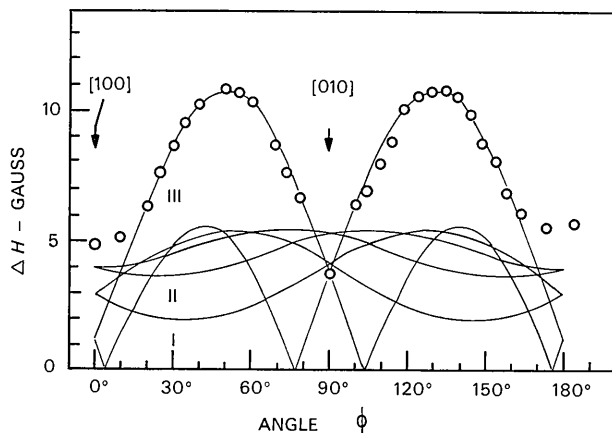


Fig. 1. Resonance diagram showing the angular dependence of ΔH in the ab plane. This is used in partial determination of the p-p vector III. The smooth curves are obtained from equation (1) and the experimental vectors given in Table 1. These curves illustrate that most of the resonance components fall within 6 gauss of the centre of the spectrum.

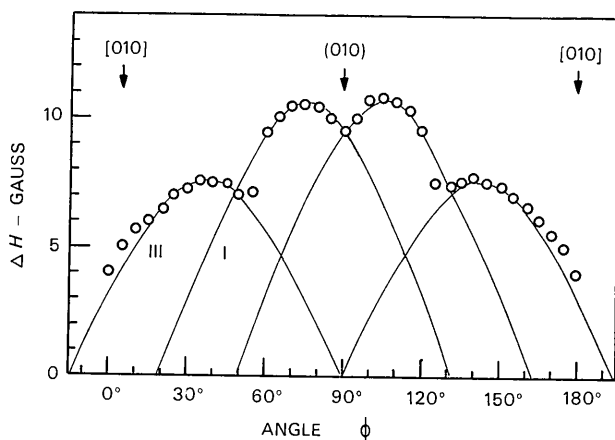


Fig. 2. Resonance diagram obtained by rotating the crystal about an axis containing b and intersecting (010) at a point 32° from c . This diagram is used in partial determination of vectors I and III. The smooth curves are obtained from equation (1) and the experimental vectors I and III given in Table 1.

C-1024 integrating computer to enhance the signal-to-noise ratio.

Since the method employed to determine the p-p vectors in this compound is a modification of Pake's n.m.r. techniques (Pake, 1948), a brief description of the latter technique appears in order. The hydrates normally studied by a straight application of the Pake technique are simple hydrates with only one nonequivalent water molecule per unit cell. A single crystal of about 1 cm^3 in volume is rotated about an axis perpendicular to the applied magnetic field, \mathbf{H}_0 , and the n.m.r. spectra are recorded at regular angular intervals. The n.m.r. spectrum corresponding to any p-p direction will have two resonance components whose separation may be expressed by the relation

$$\Delta H = \frac{3}{2} \mu r^{-3} (3 \cos^2 \delta \cos^2 (\Phi - \Phi_0) - 1), \quad (1)$$

where ΔH is the shift of each component from the center of the spectrum (the free proton resonance), μ is the proton magnetic moment, r is the p-p distance, δ is the angle between the p-p vector and its projection on the plane of rotation, Φ_0 is the angle between this projection and an arbitrary direction in the plane of rotation, and Φ is the angle between this arbitrary direction and \mathbf{H}_0 . A resonance diagram obtained from plotting ΔH vs. Φ should then yield the magnitude and direction of the p-p vector. This technique has been modified by Holcomb & Pedersen (1963) so that the p-p vector could be determined with a high degree of precision for simple hydrates.

The unit cell of $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ has three nonequivalent water molecules and a space-group symmetry which produces a total of twelve nonparallel p-p directions. A spectrum obtained with \mathbf{H}_0 pointing in a general direction should, therefore, have twenty-four resonance components which may be reduced to twelve when \mathbf{H}_0 is in one of the symmetry planes (100), (010), (001). It is obvious that even in these planes, considerable overlap of the resonance components occurs and produces a poorly-resolved spectrum. However, most of these components fall within 6 gauss of the centre of the spectrum as indicated by the smooth curves in Fig. 1. As a result of this the few resonance components that fall outside this range are generally well resolved. These 'outer' components normally belong to p-p vectors with $\delta \leq 25^\circ$. It is the positions of these outer components relative to the free proton resonance which constitutes our experimental observations (open circles in Figs. 1 and 2).

Table 1. The orientations of the experimental and calculated proton-proton vectors, given in terms of α_0 , β_0 and γ_0 , the angles that the vector makes with the crystallographic axes a , b and c respectively

The HOH angle is calculated from the experimental proton-proton distance, r , on the assumption that OH is 0.987 \AA .

Vector	Experimental				Calculated				
	α_0	β_0	γ_0	r (Å)	$\angle \text{HOH}$	α_0	β_0	γ_0	$\angle \text{XOX}$
I	68°	75°	27.5°	1.58	106°	62.3°	78.7°	30.5°	110°
II	73	85	18	1.59	107	75.0	87.0	15.0	95.5
III	51	42	81	1.56	104.5	53.5	40.3	74.5	104

Useful information may be obtained from the magnitudes and orientations of the maximum values of ΔH , ΔH_{\max} , observed in the planes of rotation. Determination of values of ΔH_{\max} corresponding to the same p-p vector in two planes of rotation enables one to substitute the numerical values of ΔH , Φ , Φ_0 in two equations of the type (1) above. This is sufficient for a unique determination of the p-p vector. It was found necessary here to determine the angular dependence of the outer components in four planes of rotation in order to establish the p-p vectors of the three non-equivalent water molecules. These planes are (100), (010), (001), and a fourth plane which contains b , and intersects (010) at a point 32° from c .

3. Results

The magnitude and direction of the vector (p-p)_{III} were determined by the use of equation (1), and the values of $(\Delta H)_{\max}$ were obtained from the resonance diagrams of Figs. 1 and 2. Similarly, (p-p)_I was obtained from the resonance diagrams of Fig. 2 and the plane (010), and (p-p)_{II} from the resonance diagrams in the planes (100) and (010). The magnitudes and directions of all three p-p vectors determined are given in Table 1 and Fig. 3. The error involved in determining each p-p vector is estimated to be less than 4° . Two values of r are calculated for each vector, one from each plane of rotation. These values of r are found to agree within 1%.

The experimental p-p vectors I, II and III are assigned to the water molecules H_2O_I , H_2O_{II} and H_2O_{III} respectively. This assignment is based on the agreement between the observed p-p directions and the corresponding H-H directions calculated from the H-bonding scheme suggested by Nardelli *et al.* (Fig. 3 and Table 1). The calculation was made on the assumption that the two H atoms lie at equal distances from their O^w on the lines joining the latter atom to the H-bond acceptor ions.

The HOH angles (Table 1) were calculated from the experimental p-p distance on the assumption that the O-H distance is 0.987 \AA (El Saffar, 1966). The fractional coordinates of the H atoms (Table 2) were calculated

by use of the p-p vectors determined, the X-ray structure, and a method previously described by the author (El Saffar, 1966).

Table 2. Hydrogen coordinates calculated from the X-ray structure and the n.m.r. experimental vectors

	x/a	y/b	z/c
H(Ia)	0.878	0.108	0.272
H(Ib)	0.814	0.136	0.068
H(IIa)	0.108	0.163	0.075
H(IIb)	0.158	0.153	0.854
H(IIIa)	0.921	0.079	0.644
H(IIIb)	0.816	0.998	0.680

4. Discussion

The n.m.r. method outlined in section 2 and employed to determine the p-p vectors in $MgS_2O_3 \cdot 6H_2O$ has

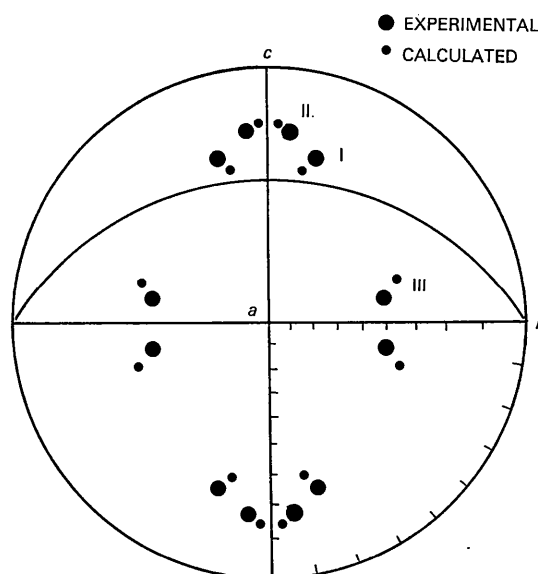


Fig. 3. Stereographic projection showing the directions of the observed and calculated proton-proton vectors. The solid lines represent the planes of rotation used to study the angular dependence of the n.m.r. spectrum.

Table 3. Distances and angles relating to the H bonds in $MgS_2O_3 \cdot 6H_2O$, and to the OH---S type bonds in $Na_2S_2O_3 \cdot 5H_2O$

The atoms are represented in the designation of the X-ray authors except for O^w which replaces H_2O in the designation for $MgS_2O_3 \cdot 6H_2O$.

Compound	Bond	OH---X	H---X	$\angle O-H---X$	$\angle H-O---X$
$MgS_2O_3 \cdot 6H_2O$	$O_I^w \text{---} S_{II}$	3.245 Å	2.27 Å	172°	6°
	$O_I^w \text{---} O_I$	2.799	1.82	172	5
	$O_{II}^w \text{---} S_{II}$	3.195	2.21	172	6
	$O_{II}^w \text{---} O_{II}$	2.658	1.68	172	5
	$O_{III}^w \text{---} O_I$	2.684	1.70	177	2
	$O_{III}^w \text{---} O_{II}^w$	2.859	1.91	162	12
	$O(6) \text{---} S(1)$	3.37	2.40	169	8
$Na_2S_2O_3 \cdot 5H_2O$	$O(7) \text{---} S(1)$	3.35	2.37	176	3
	$O(8) \text{---} S(1)$	3.27	2.43	158	16
	$O(8) \text{---} S(1)$	3.46	2.61	161	14

been applied to many hydrates (El Saffar, 1966, 1968). Some of these hydrates have since been studied by neutron diffraction. Detailed comparison shows that the experimental vectors obtained by n.m.r. are in rather good agreement with the corresponding neutron-diffraction results. The consistency of the p-p vectors given in Table 1 with the H-bonding scheme suggested by the X-ray authors, verifies the correctness of the H-bonding scheme and testifies to the validity of the n.m.r. method.

The conflict between the n.m.r. results reported here and those of Visweswaramurthy (1963) may be resolved by modifying Visweswaramurthy's Fig. 2 from which he obtained all his results. As the Figure stands, the Pake curves shown (*c* axis rotation) do not satisfy the point-group symmetry since those curves are not symmetrical about the *a* axis. The point-group requirement is satisfied provided the Pake curve labelled 2 is discarded and the Φ scale is shifted so that *a* is at $\Phi = 20$ or -30° . If the shift -30° is accepted, the Pake curves labelled 1 and 3 in Visweswaramurthy's Fig. 2 conform with the results reported here.

Distances and angles relating to the hydrogen bonds are given in Table 3. It is interesting to note a correspondence between the OH---*X* distances and the related $\angle\text{O-H---}X$ for $\text{MgS}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$. The shortest OH---S bond (3.195 Å) and the shortest OH---O bond (2.658 Å) belong to $\text{H}_2\text{O}_{\text{II}}$. Equal 'bending' of these bonds ($\angle\text{O-H---}X = 8^\circ$) may be due to the fact that the OH---S and OH---O interactions in this case are of equal strength. The same may be said about the

interactions relating to $\text{H}_2\text{O}_{\text{I}}$. The angles and distances relating to $\text{H}_2\text{O}_{\text{III}}$ given in Table 3 agree with the general observation that shorter hydrogen bonds tend to deviate less from linearity than longer ones (Hamilton, 1962). This tendency has been recently explained (Chidambaram & Sikka, 1968) on the basis of a modified Lippincott-Schroeder potential function for the hydrogen bond.

Hydrogen bonds of the type OH---S, have not been studied, to the author's knowledge, by neutron diffraction. It is, therefore, considered useful to give the angles and distances relating to OH---S bonds found in $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. This compound was investigated by Taylor & Beevers (1952) with the use of X-rays, and by Murty & El Saffar (1962) by the use of n.m.r.

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The Geometrical Basis of Crystal Chemistry. X. Further Study of Three-Dimensional Polyhedra.

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A further study is made of the three-dimensional polyhedra of part VII which conform to the equation

$$\sum f_n[4 - (2 - n)(2 - p)] = 2p(2 - t)$$

for tessellations (*n*, *p*), where *t* is the number of tunnels connecting each repeat unit to its neighbours. An investigation is made of the relation between a 3-D polyhedron and its complement, (*i.e.* the space not occupied by the polyhedron) and of those polyhedra which can be constructed with plane equilateral triangular faces, the 3-D homologues of the triangulated Platonic solids.

In part VII (Wells & Sharpe, 1963) a study was made of tessellations (*n*, *p*) for which *p* exceeds the highest value attainable in a plane net. For example, in the series (*3*, *p*) the cases *p* = 3, 4, and 5 correspond to convex polyhedra, and *p* = 6 to the plane triangulated net.

It was shown that certain tessellations (*3*, *p*) with *p* ≥ 7 may be inscribed on infinite surfaces which arise by uniformly inflating the links of 3-dimensional nets to form systems of tunnels which meet at the points of the original net. The links of the tessellations are geode-