Refinement of the Crystal Structure of Magnesium Sulphate Heptahydrate (Epsomite) by Neutron Diffraction

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The crystal structure of orthorhombic $MgSO_4,7H_2O$ has been refined anisotropically to a final *R* of 0·048 over 900 independent neutron reflexions from a synthetic crystal. For the positional parameters of the 14 crystallographically independent hydrogen atoms, estimated standard deviations are *ca.* 0·007 Å, double those for the other atoms. All hydrogen atoms (mean O–H 0·964 Å) are engaged in hydrogen bonds, ranging from 2·692(7) to 2·982(7) Å. The W(7) water molecule, unique in that it is not co-ordinated to the magnesium, is engaged in relatively weak [(2·820(7) and 2·903(7) Å] appreciably non-linear hydrogen bonds; it may be partially absent in water-deficient natural specimens. The assumption of coplanarity of water atoms and oxygen-acceptor atoms proves to be an unreliable guide to hydrogen positions.

FOR crystals of inorganic hydrates which contain atoms of moderately high atomic number, direct location of hydrogen atoms by *X*-ray diffraction is feasible only when the data are rather accurate. Plausible water-hydrogen positions (within a radius of *ca.* 0·2 Å) may be estimated by several less direct procedures. Of these, (i) electrostatic-energy minimization,[1,2] (ii) peak searching between short oxygen–oxygen contacts in a final Fourier-difference map,[3] and (iii) spectroscopic, *e.g.* n.m.r.,[4] measurements all allow some check on postulated hydrogen sites, but this is hardly true for those predicted [5,6] largely on the basis of (iv) expected environment of hydrogen-bonded water molecules.[7,8] Neutron diffraction not only yields the hydrogen positions directly (ref. 9 and refs. therein) but it also enables an estimate to be made of the reliability of these less direct approaches.

Magnesium sulphate crystallizes as mono-, di-, tetra-, hexa-, and hepta-hydrates.[10] The orthorhombic heptahydrate, the mineral epsomite, $MgSO_4,7H_2O$, is sufficiently closely isostructural with the nickel salt morenosite [11] for heavy-atom positions from the latter to provide satisfactory starting co-ordinates for a successful *X*-ray refinement of the $MgSO_4,7H_2O$ structure. Hydrogen-atom positions inferred by method (iv) and consistent with a three-dimensional Fourier synthesis thus derived [12] led to σ values of *ca.* 0·23 Å. In epsomite, SO_4^{2-} tetrahedra and $Mg(H_2O)_6^{2+}$ octahedra (which effectively increase the cation size [13]) are linked by hydrogen bonds which also involve the other water molecule, W(7), which is not co-ordinated to magnesium. The hydrogen-bonding system is likely to be significant in understanding the mechanism of the ready dehydration [10] $M^{2+}SO_4,7H_2O \rightleftharpoons M^{2+}SO_4,6H_2O$ [M = Mg, Ni, *etc.*] and the deficiency in water content of some natural specimens.[14,15] A three-dimensional neutron-diffraction investigation was undertaken in order to locate the hydrogen atoms of the several water molecules more precisely.

EXPERIMENTAL

Crystal Data.[12]—$MgSO_4,7H_2O$, $M = 246·5$, Orthorhombic, $a = 11·868(10)$, $b = 11·996(10)$, $c = 6·857(7)$ Å, $U = 976(2)$ Å^3, $D_m = 1·676$, $Z = 4$, $D_c = 1·677(4)$. Space group $P2_12_12_1$ (No. 19, D_2^4).

Neutron Measurements.—From a batch grown just above room temperature from aqueous solution of commercial $MgSO_4,7H_2O$, a crystal of dimensions 0·3 × 0·3 × 0·5 cm^3, well developed on {110} and elongated along *c*, was selected and set up about the ϕ rotation axis of a Ferranti automatic single-crystal diffractometer at the DIDO reactor, Atomic Energy Research Establishment, Harwell. Neutron intensity data for a wavelength monochromatized to 1·17 Å were collected for the *hkl* reflexions up to 2θ 90° (ω—2θ scanning in 26 steps of 0·08° in ω for the peak, plus 4 steps on each side for the background; monitor count 4×10^4 per step). Since the crystal remained transparent at the end of the experiments and the intensity of the standard reflection remained constant, no change in water content was suspected.

Setting angles were computed with a program written by Powell. Of 1073 reflections with $2\theta \leqslant 90°$, 173 were rejected because the integrated intensity was $<3\sigma$. A program by Curry gave structure amplitudes and their σ values. No correction was made for absorption; extinction is discussed later.

Structure Refinement.—The following neutron scattering lengths [16] were used: S 2·8, Mg 5·2, O 5·77, and H $-3·72 \times 10^{-13}$ cm. The parameters derived from the *X*-ray analysis [12] gave *R* 0·18. Anisotropic least-squares refinement for all atoms, and based on 900 observed structure amplitudes was carried out with the ORFLS program of the '*X*-Ray '63' system [17] (and subsequent modifications) on the Chilton ATLAS computer; it was considered complete when all parameter shifts were $<\sigma$. Unitary weighting, *w*, gave acceptable $\Sigma w\Delta^2$ for groups of reflexions.

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TABLE 1

Fractional positional co-ordinates and vibrational parameters (Å^2), for each atom, with the significant figures of the estimated standard deviations in parentheses. The second line associated with each atom contains the significant figures of Δ, defined as the *X*-ray parameter value minus the neutron value, and |Δ|/σ (see text)

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Mg	0·4226(3) 3 1·0	0·1060(3) 3 1·0	0·0392(6) −52 8·2	0·88(10) 8 0·7	1·32(12) −11 0·8	1·36(13) −49 3·6	0·21(10) −10 0·9	−0·06(9) 1 0·1	0·10(11) −7 0·6
S	0·7259(5) 7 1·4	0·1835(6) 4 0·7	0·4909(9) −4 0·4	0·83(19) 13 0·7	1·84(24) −57 2·3	0·88(20) 1 0·1	0·25(20) −42 2·0	−0·10(18) 0 0	−0·19(22) −16 0·6
O(1)	0·6857(4) −4 0·7	0·0747(3) 3 0·6	0·4268(7) 9 0·9	4·05(19) −22 0·7	1·56(13) −6 0·3	3·06(17) −52 2·2	−0·83(14) 31 1·4	−0·42(16) 33 1·4	−0·04(14) −4 0·2
O(2)	0·8498(2) 8 2·2	0·1869(4) −1 0·2	0·4835(6) −14 0·2	1·10(10) −9 0·6	3·15(16) 13 0·6	2·32(14) −35 1·8	0·18(11) 5 0·3	0·01(11) 9 0·6	0·18(14) 18 0·9
O(3)	0·6884(3) 0 0	0·2063(4) 0 0	0·6908(6) −4 0·5	2·18(15) −55 3·0	4·10(21) −47 1·7	2·02(15) −70 3·8	−0·66(14) 38 2·1	0·16(13) 26 1·6	−0·62(15) −9 0·5
O(4)	0·6807(3) 1 0·2	0·2722(3) −6 1·2	0·3617(6) −12 1·4	1·67(12) 13 0·8	2·29(16) −51 2·6	2·59(15) −41 1·9	0·03(12) 14 0·9	−0·48(12) −25 1·4	0·49(3) 10 0·5
W(1)	0·2651(3) 4 0·9	0·1743(4) 3 0·53	0·0026(7) 12 1·3	1·72(12) −31 1·9	2·87(16) 7 0·3	2·23(17) −57 2·8	0·85(13) 6 0·4	−0·06(14) 1 0·1	−0·25(17) −2 0·1
W(2)	0·4724(3) −8 1·9	0·2478(3) 0 0	0·1990(5) 2 0·3	1·27(13) −14 0·8	2·00(13) −4 0·2	1·91(13) −44 2·6	−0·28(11) −11 0·7	0·09(13) 1 0·1	−0·53(13) 0 0
W(3)	0·4696(3) −5 1·2	0·1755(4) 3 0·5	−0·2214(6) 0 0	1·48(15) 10 0·5	2·81(16) −10 0·4	1·89(14) −29 1·6	−0·16(13) −10 0·6	0·35(13) −12 0·7	0·50(14) 32 1·7
W(4)	0·5828(3) 0 0	0·0462(4) 1 0·2	0·0787(7) −14 1·4	1·92(14) −12 0·7	3·10(18) −22 0·9	2·79(18) −70 3·0	1·34(14) 20 1·1	−0·94(15) −19 1·0	−0·91(16) −9 0·4
W(5)	0·3760(3) 1 0·2	−0·0387(3) −7 1·7	−0·1118(6) −7 1·2	2·21(15) −1 0·1	1·53(16) 14 0·7	1·94(15) −49 2·5	−0·42(12) −14 0·9	−0·15(13) −2 0·1	−0·24(13) 9 0·6
W(6)	0·3621(4) 1 0·2	0·0342(3) 0 0	0·2929(6) −22 3·9	1·94(17) −2 0·1	2·48(16) 23 1·0	2·35(17) −81 3·8	0·01(13) −18 1·1	0·42(15) −9 0·5	0·50(14) 32 1·7
W(7)	0·4908(4) 8 1·4	0·4375(4) 2 0·4	0·9383(6) 1 0·1	2·99(17) 11 0·5	2·04(17) −3 0·1	2·55(16) −26 1·2	−0·02(15) 25 1·3	0·11(14) 41 2·2	0·42(14) −19 1·0
H(1)	0·2346(6) 94 1·0	0·2215(6) 75 0·8	0·1058(11) −8 0·1	2·17(24)	3·99(32)	2·43(25)	0·77(23)	0·29(21)	−0·56(28)
H(2)	0·2377(5) −37 0·4	0·1990(7) 70 0·7	−0·1222(11) −112 0·5	2·29(24)	4·18(34)	2·05(26)	0·87(23)	−0·37(21)	0·18(26)
H(3)	0·4216(5) 134 1·2	0·2719(6) −19 0·2	0·3044(12) 256 1·3	2·08(22)	3·26(29)	3·28(32)	0·11(22)	0·75(24)	−1·08(26)
H(4)	0·5478(5) −148 1·5	0·2518(5) −58 0·6	0·2596(10) 84 0·4	1·67(24)	2·79(25)	3·12(28)	−0·13(19)	−0·40(20)	−0·75(24)
H(5)	0·4236(5) −46 0·5	0·2222(6) 118 1·2	−0·3062(11) 298 1·5	2·09(23)	3·23(29)	3·26(29)	−0·28(23)	−0·18(24)	0·91(28)
H(6)	0·5479(5) 11 0·1	0·1842(6) 38 0·4	−0·2569(9) −129 0·7	1·57(24)	3·04(24)	2·21(25)	−0·08(19)	0·35(18)	−0·15(22)
H(7)	0·6271(6) 49 0·5	0·0574(6) −24 0·2	0·1934(12) 86 0·4	2·75(26)	3·57(30)	2·96(29)	0·27(24)	−0·67(28)	−0·26(26)
H(8)	0·6139(8) −139 1·4	−0·0176(9) −16 0·2	0·0170(15) 80 0·4	5·35(44)	6·40(49)	4·62(42)	4·03(43)	−1·22(37)	−2·59(41)
H(9)	0·3668(5) −108 1·1	−0·1065(6) −95 1·0	−0·0357(12) 23 0·1	3·29(26)	2·01(25)	4·25(32)	0·21(24)	−0·45(27)	0·36(26)
H(10)	0·4217(7) 63 0·3	−0·0541(6) −11 0·1	−0·2239(13) 71 0·4	3·49(27)	3·38(31)	3·53(34)	0·09(26)	0·40(30)	−0·41(29)
H(11)	0·2840(6) −30 0·3	0·0262(7) 68 0·7	0·3207(11) −7 0·1	2·60(30)	4·21(33)	3·78(33)	−1·12(24)	0·84(24)	0·99(28)
H(12)	0·4067(7) −117 1·2	0·0001(6) 79 0·8	0·3926(11) 114 0·6	4·58(33)	3·50(33)	2·18(25)	0·26(28)	−0·21(28)	0·86(25)
H(13)	0·4252(7) 58 0·6	0·4834(7) 86 0·9	0·9562(12) 188 1·0	3·57(30)	3·64(31)	3·54(33)	0·42(30)	−0·04(28)	0·23(29)
H(14)	0·4746(7) −104 1·1	0·3681(7) 19 0·2	1·0014(15) −6 0·1	4·13(31)	2·80(32)	5·84(42)	−0·68(27)	2·08(37)	0·07(34)

Allowance was made for secondary extinction by refining a *g* factor;[18] its final value was 0·0092(10) × 10^{24} cm^2. The final *R* value was 0·048 for the 900 reflexions listed in Supplementary Publication No. SUP 20635 (7 pp, 1 microfiche).* A final Fourier-difference synthesis revealed only statistically distributed peaks with maximum height ±0·06 × 10^{-12} cm Å^{-3}.

In Table 1, the upper entries for each atom give the final fractional atomic co-ordinates together with the coefficients, B_{ij} in the expression $\exp\left\{-\frac{1}{4}\sum_{i=1}^{3}\sum_{j=1}^{3}B_{ij}h_ih_ja_i^*a_j^*\right\}$.

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1972, Issue No. 24.

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DISCUSSION

Since the neutron analysis confirms (see Tables 1—3) the main features of the crystal structure (see Figure) as given by Baur,[12] only the configuration of the water molecules and the associated hydrogen bonding are discussed in detail. The trend of bond lengths is consistent with Baur's [19] correlation with bond strength, p, received by oxygen atoms. Thus the 'overbonded' atoms O(2), O(4), W(2), and W(5) have the longest bonds to S or Mg; generally, those hydrogen bonds with p(donor)–p(acceptor) positive are shorter than others.

TABLE 2

Interatomic distances (Å) and angles (°) (O–S–O) in the SO_4 group, uncorrected (A) and corrected for thermal motion (B, C, D): lower (B) and upper (C) limits and riding model (D). The estimated standard deviations are 0·006 Å and 0·4° for distances and angles, respectively

	A	B	C	D
S–O(1)	1·458	1·466	1·530	1·482
S–O(2)	1·472	1·474	1·540	1·484
S–O(3)	1·467	1·470	1·542	1·483
S–O(4)	1·485	1·487	1·543	1·496
Mean	1·471	1·474	1·539	1·486

	Distance	Angle
O(1) · · · O(2)	2·399	109·9
O(1) · · · O(3)	2·402	110·5
O(1) · · · O(4)	2·412	110·1
O(2) · · · O(3)	2·397	109·3
O(2) · · · O(4)	2·402	108·7
O(3) · · · O(4)	2·393	108·3
Mean	2·401	

TABLE 3

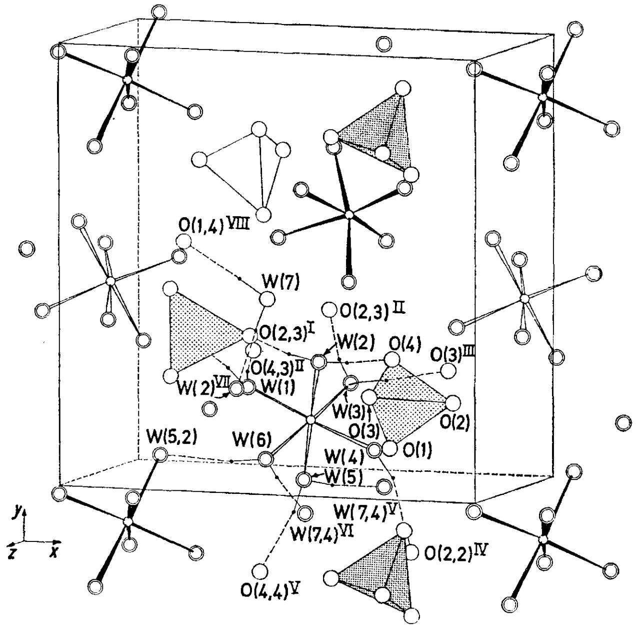
Interatomic distances (Å) and angles (°) (W–Mg–W) involving the magnesium co-ordination polyhedron: corrections for thermal motion and estimated standard deviations as in Table 2

	A	B	C	D
Mg–W(1)	2·057	2·058	2·107	2·065
Mg–W(2)	2·109	2·110	2·144	2·114
Mg–W(3)	2·050	2·051	2·092	2·058
Mg–W(4)	2·051	2·054	2·107	2·063
Mg–W(5)	2·096	2·097	2·134	2·103
Mg–W(6)	2·070	2·072	2·113	2·079
Mean	2·072	2·074	2·116	2·080

W(1) · · · W(2)	2·941	89·8°
W(1) · · · W(3)	2·873	88·8
W(1) · · · W(5)	2·980	91·7
W(1) · · · W(6)	2·848	87·3
W(6) · · · W(2)	2·948	89·7
W(6) · · · W(4)	3·007	93·7
W(6) · · · W(5)	2·915	88·8
W(5) · · · W(4)	2·961	91·2
W(5) · · · W(3)	2·899	88·8
W(3) · · · W(4)	2·907	90·3
W(3) · · · W(2)	3·011	92·8
W(2) · · · W(4)	2·871	87·3
Mean	2·930	

W(5)–Mg–W(2)	177·8°
W(1)–Mg–W(4)	177·0
W(6)–Mg–W(3)	175·3

The Water Molecules.—The geometries of the water molecules and of their hydrogen-bonded environments are summarized in Table 4 (where several different best planes α, β, γ, δ are introduced) and Table 5, where a



Clinographic projection of the crystal structure of epsomite down the z axis. Atoms involved in hydrogen bonds are labelled only for the asymmetric set of Table 1. Bonds of the magnesium (small open circles) polyhedra in black are nearer (in the z direction) than those in white; proximity of the sulphate tetrahedra is in the decreasing sequence: dark grey, light grey, white. Sulphate oxygens are shown as single circles and water oxygens as double circles. The hydrogen H(7) of water W(4) is not shown since it is obscured by O(1); O(3,3^{I}), to which W(1) is linked, is obscured by a sulphate tetrahedron

TABLE 4

For each water molecule, the following weighted least-squares planes ($Ax + By + Cz - D = 0$) for fractional co-ordinates are listed: (i) α for the three atoms of the water molecule, (ii) β for the water molecule and the two oxygen atoms accepting the hydrogen bonds, and (iii) either δ for these five atoms plus the co-ordinated cation or γ for the atoms in columns C, F, G of Table 5. For each plane, $\chi^2 = (d/\sigma)^2$ where d is the distance of an atom from the plane in question

		A	B	C	D	χ^2
W(1)	α	9·333	7·336	−0·597	3·751	0
	β	8·715	7·998	−0·874	3·721	21
	δ	6·660	9·768	−1·018	3·711	1569
W(2)	α	0·860	11·341	−2·179	2·783	0
	β	0·407	11·351	−2·206	2·562	13
	γ	11·374	−2·454	−1·367	4·493	0
W(3)	α	1·009	9·072	4·449	1·081	0
	β	0·550	9·010	4·516	0·834	12
	δ	1·196	9·922	3·791	1·617	975
W(4)	α	−7·399	−7·036	3·545	−4·358	0
	β	9·924	3·861	−3·045	5·801	197
	δ	−7·050	−6·190	4·232	−3·693	5542
W(5)	α	9·740	2·716	3·597	3·155	0
	β	9·699	2·073	3·770	3·154	18
	γ	−2·913	−5·251	5·931	−1·555	0
W(6)	α	0·173	10·352	3·464	1·431	0
	β	1·441	10·725	2·957	1·728	55
	δ	1·298	10·545	3·182	1·774	88
W(7)	α	4·566	4·248	5·845	9·584	0
	β	7·785	5·368	4·168	9·989	260
	γ	−4·393	10·885	−1·366	1·324	0

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[19] W. H. Baur, *Trans. Amer. Cryst. Assocn.*, 1970, **6**, 129.

convenient generalized notation is used for referring to interatomic distances and angles. According to a modification[8] of the water-molecule classification,[20] in terms of lone-pair co-ordination, W(2) and W(5) are of type *H*, and W(7) is of type *E*; W(1), W(3), W(4), and W(6) [note the $\overline{CF}\alpha$ angles and $\overline{F}\alpha$ distances in Table 5] * are of type *D* (*i.e.* hybrids between configurations with Mg along the bisector of the lone-pair orbitals and a configuration with Mg in contact with only one lone-pair orbital). Evidently, this hybrid water-molecule configuration (the possibility of which was hinted at in a footnote to ref. 20) is not uncommon.[8,9] For W(4), W(6), and W(7), the acceptor-oxygen atoms lie out of the water-molecule plane α (Table 4 and 5); indeed, for W(4) and W(7), departure from planarity is appreciable, as evidenced (Table 4) by χ^2 for plane β. In view of the frequency of these deviations,[8] it would seem that it is not always justifiable to calculate hydrogen positions on the basis of the coplanarity of the water molecule with the two acceptor oxygens.

TABLE 5

Interatomic distances (Å) and angles (°) for water molecules and atoms in contact with them. *F* and *G* are Mg ions to which the water molecule is co-ordinated, or H atoms from which the water molecule accepts hydrogen bonds. σ Values are 0·009 Å and 0·8° for interatomic distances and angles involving hydrogen atoms; others are as shown. Columns *A*—*G* list the distances between the atom given and the corresponding α (and, where appropriate, γ) planes of Table 4; σ values for these are 0·013 Å if they involve hydrogen atoms and 0·007 Å otherwise

A	*B*	*C*	*D*	*E*	*F*	*G*	$\overline{AB}$ $\angle ABC$	$\overline{AC}$ $\angle ACE$	$\overline{BC}$ $\angle BCD$	$\overline{CD}$ $\angle CDE$	$\overline{CE}$ $\angle \overline{CF}\alpha$	$\overline{DE}$ $\angle \overline{CG}\alpha$	$\overline{CF}$ $\angle \overline{BA}\alpha$	$\overline{CG}$ $\angle \overline{DE}\alpha$	$\overline{BD}$ $\angle FCG$	$\angle\alpha\gamma$ $\angle\beta\gamma$
O(3,3I) ···	·H(1)—	W(1)-	H(2)	··· O(4,3II)	Mg		1·732	2·703	0·976	0·963	2·768	1·810	2·056		1·587	
−0·023				−0·178	0·947		172·8	117·2	109·9	172·9	27·4		0·8	5·6		
O(2,3I) ···	H(3)—	W(2)-	H(4)	··· O(4)	Mg	H(14III)	1·758	2·734	0·985	0·961	2·728	1·772	2·109	1·980	1·563	86·5
−0·057				0·101	−1·303	1·797	170·9	97·2	106·9	173·1	38·2	−63·5	1·8	−3·4	103·6	84·5
−1·989	−0·781		−0·779	2·087												
O(2,3II) ···	H(5)—	W(3)-	H(6)	··· O(3III)	Mg		1·854	2·825	0·975	0·967	2·692	1·726	2·050		1·582	
−0·039				0·109	0·481		173·9	105·3	109·1	176·4	−13·6		1·2	−3·5		
O(1) ···	H(7)—	W(4)-	H(8)	··· O(2,2IV)	Mg		1·758	2·704	0·956	0·950	2·982	2·089	2·051		1·516	
0·272				0·804	0·625		169·7	101·0	105·4	156·0	−17·7		−8·9	−22·6		
O(4,4V) ···	H(9)—	W(5)-	H(10)	··· W(7,4V)	Mg	H(11,2III)	1·965	2·923	0·972	0·959	2·756	1·804	2·096	1·961	1·577	78·6
−0·1666				0·058	1·390	−1·767	168·0	121·9	109·5	172·1	−41·6	64·4	4·9	−1·8	108·0	81·2
2·641	0·834		−0·717	−2·199												
W(5,2) ···	H(11)-	W(6)-	H(12)	··· W(7,4VI)	Mg		1·961	2·909	0·952	0·957	2·792	1·842	2·070		1·569	
0·336				−0·045	−0·125		169·6	117·9	110·6	172·0	3·5		−9·8	1·4		
O(1,4VIII) ···	H(13)-	W(7)-	H(14)	··· W(2VII)	H(10,4IX)	H(12,4VIII)	1·980	2·820	0·962	0·959	2·903	1·892	1·803	1·842	1·534	87·6
0·565				0·634	−0·818	1·723	161·8	101·5	106·2	161·0	26 9	−69·4	−17·4	−18·7	96·3	89·5
2·084	0·763		−0·770	−2·340												

In crystal hydrates,[8] the co-ordinated cations often do not lie symmetrically about the plane α (compare angles $\overline{CF}\alpha$ and $\overline{CG}\alpha$ in Table 5) of the water molecule, *i.e.* they do not lie exactly along the idealized directions of the lone-pair orbitals and in the plane orthogonal to the water plane α (see the αγ, βγ, $\overline{CF}\alpha$, and $\overline{CG}\alpha$ angles in Table 5); this is true for W(2), W(5), and W(7) in epsomite. Thus the assumption of tetrahedral co-ordination of the water molecule is not always a reliable basis for hydrogen-atom location.

Despite the appreciable spread (97·2—121·9°) of acceptor–W–acceptor angle (*ACE*), the H–W–H angles (*BCD* in Table 5) range only from 105·4 to 110·6° (mean 108·2°). As usual, deformation of the W–H–acceptor angle[21] appears to be easier than that of the H–W–H angle; in fact, all the W–H–acceptor angles show significant deviations from 180° (for a linear hydrogen bond), although these deviations are large only for W(4)–H(8) ··· O(2,2$^{\text{IV}}$) and for the two bonds to W(7). The W(4)–H(8) ··· O(2,2$^{\text{IV}}$) hydrogen bond (Table 5) is the longest (2·982 Å) and least linear in the structure, and its hydrogen H(8) [2·089 Å from O(2,2$^{\text{IV}}$)] has the largest temperature factor.

W(7) is unique among the water molecules in that it is not co-ordinated by Mg and that it possesses two rather weak (2·820 and 2·903 Å) and appreciably non-linear (161·8 and 161·0°) hydrogen bonds. In view of the similarities between the structures of epsomite and hexahydrite,[22] these results help to explain the ready reversibility of the $MgSO_4,7H_2O$ (epsomite) ⇌ $MgSO_4,6H_2O$ (hexahydrite) process and the deficiency of water content in some natural specimens of epsomite.[14,15] Accordingly, atoms in this water molecule exhibit slightly larger thermal parameters (Table 6). None of the intrawater interproton distances (*BD* in Table 5) in epsomite or in leonhardtite,[23] $MgSO_4,4H_2O$, is unusually long, despite the report of 1·66 ± 0·02 Å in kieserite, $MgSO_4,H_2O$, from proton resonance.[24]

The O–H bond lengths (mean 0·964 Å) have a narrow

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* Atoms are designated as follows: a single value in parentheses (or no value) denotes an atom of the asymmetric unit listed in Table 1; a second figure, ranging from 2 to 4, is included for related atoms in the positions $\frac{1}{2} - x, \bar{y}, \frac{1}{2} + z$; $\frac{1}{2} + x, \frac{1}{2} - y, \bar{z}$; and $\bar{x}, \frac{1}{2} + y, \frac{1}{2} - z$. Roman numerals represent the following translations: I, $-a, c$; II, $-a$; III, $-c$; IV, $a, -c$; V, $a, -b$; VI, $a, -b, c$; VII, c; VIII, a, c; IX, a.

[20] R. Chidambaram, A. Sequeira, and S. K. Sikka, *J. Chem. Phys.*, 1964, **41**, 3616.

[21] W. C. Hamilton and J. A. Ibers, 'Hydrogen Bonding in Solids,' Benjamin, Amsterdam, 1968.

[22] A. Zalkin, H. Ruben, and D. H. Templeton, *Acta Cryst.*, 1964, **17**, 235.

[23] W. H. Baur, *Acta Cryst.*, 1964, **17**, 863.

[24] G. Handel, B. Schnabel, B. Jungnickel, T. Taplick, and K. Heide, *Krist. Tech.*, 1971, **6**, 193.

spread from 0·950 to 0·985 Å (Table 7); W–acceptor bond lengths range from 2·692 to 2·982 Å. While H · · · O increases linearly *vs.* O · · · O, there is little evidence in epsomite for decrease in the length of W–H with increase of either H · · · O or O · · · O.[8]

TABLE 6

Parameters characterizing the principal directions (1, 2, 3) of thermal vibration for the atoms in the structure: root-mean-square amplitude (column *A*) and angles which the principal directions make with the *a* (*B*), *b* (*C*), and *c* (*D*) axes

		A/Å	*B*/°	*C*/°	*D*/°
Mg	1	0·13	111	121	39
	2	0·14	78	41	52
	3	0·10	24	112	81
S	1	0·10	116	74	31
	2	0·16	77	17	101
	3	0·10	30	97	61
O(1)	1	0·19	76	100	17
	2	0·24	22	105	106
	3	0·13	73	18	85
O(2)	1	0·17	91	101	11
	2	0·20	85	12	79
	3	0·12	5	95	90
O(3)	1	0·16	19	77	103
	2	0·24	107	22	105
	3	0·15	81	72	20
O(4)	1	0·16	63	35	111
	2	0·20	106	59	35
	3	0·13	32	106	63
W(1)	1	0·17	81	81	12
	2	0·21	63	30	102
	3	0·13	29	118	94
W(2)	1	0·14	113	57	42
	2	0·18	102	43	103
	3	0·12	26	66	80
W(3)	1	0·16	52	108	44
	2	0·20	90	24	66
	3	0·12	38	75	124
W(4)	1	0·16	85	55	36
	2	0·25	60	47	123
	3	0·11	30	117	77
W(5)	1	0·16	94	112	22
	2	0·17	25	114	95
	3	0·12	66	33	69
W(6)	1	0·17	130	48	113
	2	0·20	74	48	46
	3	0·14	44	71	128
W(7)	1	0·19	110	61	36
	2	0·20	20	83	71
	3	0·15	87	30	120
H(1)	1	0·18	56	89	34
	2	0·24	73	22	103
	3	0·14	40	112	121
H(2)	1	0·17	129	77	42
	2	0·24	69	21	89
	3	0·14	46	106	48
H(3)	1	0·18	51	49	66
	2	0·24	78	130	43
	3	0·14	41	112	123
H(4)	1	0·17	116	42	60
	2	0·22	97	127	38
	3	0·14	27	74	70
H(5)	1	0·17	77	132	45
	2	0·23	99	46	46
	3	0·16	16	74	93
H(6)	1	0·17	67	77	27
	2	0·20	96	13	102
	3	0·13	24	90	114
H(7)	1	0·20	117	46	55
	2	0·22	63	44	121
	3	0·17	40	92	50
H(8)	1	0·22	59	87	31
	2	0·38	54	45	113
	3	0·14	129	46	79
H(9)	1	0·20	23	75	72
	2	0·24	110	84	21
	3	0·15	102	16	101
H(10)	1	0·21	44	46	95
	2	0·23	60	115	41
	3	0·19	119	54	50
H(11)	1	0·23	52	107	43
	2	0·25	102	33	60
	3	0·13	41	62	117
H(12)	1	0·22	101	30	63
	2	0·24	13	77	90
	3	0·15	84	116	27
H(13)	1	0·21	119	86	29
	2	0·23	53	42	74
	3	0·20	129	49	114
H(14)	1	0·21	123	44	64
	2	0·30	56	94	35
	3	0·17	52	46	111

TABLE 7

Interatomic angles (σ 0·8°) and distances (σ 0·009 Å) for water molecules; the latter are corrected for thermal motion:[a] uncorrected (*A*), lower (*B*) and upper (*C*) limits, and riding model (*D*)

		Distances/Å			
	Angles/°	*A*	*B*	*C*	*D*
W(1)–H(1)	109·9	0·976	0·977	1·126	0·987
W(1)–H(2)		0·963	0·964	1·112	0·977
W(2)–H(3)	106·9	0·985	0·988	1·119	1·006
W(2)–H(4)		0·961	0·963	1·089	0·970
W(3)–H(5)	109·1	0·975	0·976	1·108	0·989
W(3)–H(6)		0·967	0·967	1·101	0·970
W(4)–H(7)	105·4	0·956	0·956	1·130	0·962
W(4)–H(8)		0·950	0·962	1·212	1·006
W(5)–H(9)	109·5	0·972	0·975	1·112	0·993
W(5)–H(10)		0·959	0·964	1·098	0·985
W(6)–H(11)	110·6	0·952	0·955	1·129	0·975
W(6)–H(12)		0·957	0·960	1·118	0·980
W(7)–H(13)	106·2	0·962	0·964	1·123	0·980
W(7)–H(14)		0·959	0·963	1·163	0·987
Mean	108·2	0·964	0·967	1·124	0·984

[a] W. R. Busing and H. A. Levy, *Acta Cryst.*, 1964, **17**, 142.

Comparison of Neutron and X-Ray Parameters.—In addition to the neutron parameters, Table 1 lists the significant figures of Δ [*X*-ray parameter[12] minus neutron parameter] and the ratio of |Δ| to its standard error: $\sigma = [\sigma^2(\text{neutron}) + \sigma^2(X\text{-ray})]^{\frac{1}{2}}$. As a check on freedom from systematic errors in the two sets of parameters and on the appropriateness of their apparent standard deviations, a half-normal probability plot[25] of |Δ| showed a slope of 1·1 and zero intercept. This means that the |Δ| values are normally distributed and that the *X*-ray and neutron standard deviations have been estimated reasonably, at least for the heavy atoms for which σ(neutron) and σ(*X*-ray) are com-

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[25] S. C. Abrahams and E. T. Keve, *Acta Cryst.*, 1971, **A27**, 157.

parable; for the hydrogen atoms, σ is almost independent of σ(neutron). Since $|\Delta|$ (Table 1) is only occasionally larger than σ, one can regard the X-ray and neutron structures as statistically equal (including the thermal parameters), so that [9] there is no chemical significance in the differences $|\Delta|$ between X-ray and neutron parameters. Randomness of the $|\Delta|$ values must be associated with absorption, a common systematic error; but it will be small in each case, for μ is very low for neutrons and the X-ray data, obtained by use of Mo-K_α radiation, were collected along four different directions and averaged. Even so, since the z and B_{33} values generally have the largest values of $|\Delta|/\sigma$, some systematic error appears to be present along the z direction.

Baur derived [12] hydrogen-atom co-ordinates from heavy-atom positions by approach (iv), refined them by least-squares, and checked them by a difference Fourier. The present results emphasize that assumption (iv) (hydrogens coplanar with the water-oxygen and the acceptor-oxygen atoms) can be an unsatisfactory predictor of hydrogen co-ordinates. However, in this structure, as was also found [26] for $Na_2HAsO_4,7H_2O$, least-squares refinement of the X-ray data gave hydrogen parameters in agreement, within the large X-ray σ values, with those obtained by neutron diffraction.

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[26] G. Ferraris, D. W. Jones, and J. Yerkess, *Acta Cryst.*, 1971, **B27**, 354.