On the Crystal Chemistry of Salt Hydrates. II. A Neutron Diffraction Study of $MgSO_4.4H_2O$*

By Werner H. Baur

Chemistry Department, Brookhaven National Laboratory, Upton, Long Island, New York, U.S.A.

The crystal structure of $MgSO_4.4H_2O$ has been refined, single-crystal neutron diffraction data for the three main zones being used. The hydrogen positions which were found are essentially those which have been deduced from X-ray data in an earlier investigation (Baur, 1962). The mean value of the O_w–H bond lengths is 0·97 Å. The O_w–H–O bonds are bent considerably. One hydrogen atom does not participate in hydrogen bonding, as can be concluded from the geometry of its surroundings and its thermal motion.

Introduction

The results of the X-ray crystal structure determination of $MgSO_4.4H_2O$ were presented in a previous communication (Baur, 1962, hereafter I). The structure has been shown to be composed of isolated $Mg(SO_4)_2.8H_2O$ ring molecules, linked to each other by a three-dimensional network of hydrogen bonds. The positions of the hydrogen atoms were inferred from the peaks in a difference synthesis projection parallel to [100] and from crystal-chemical considerations. Seven of the eight crystallographically different hydrogen atoms participate in the hydrogen bonding system. The eighth hydrogen atom H_{IIb} seems not to be involved in a hydrogen bond†. The oxygen atoms situated nearest to H_{IIb} are, except the corresponding water oxygen of course, O'_{II} and O_{II} at about 2·4 and 2·6 Å respectively. In all previous neutron diffraction investigations of hydrates (compare the review paper by Hamilton, 1962) the hydrogen atoms were shown to take part in hydrogen bonding. The distance from the hydrogen atom to the oxygen atom acting as acceptor in the hydrogen bond has never been reported to be longer than 2·07 Å. The latter value occurs for H $\cdots$ O in $Li_2SO_4.H_2O$ (Smith, Peterson & Levy, 1961) and in $CuSO_4.5H_2O$ (Bacon, 1962b). Since hydrogen positions based on X-ray data are not very accurate a neutron diffraction investigation was undertaken with the purpose of defining more precisely the uncommon arrangement around H_{IIb}. Infrared evidence is of no help in this particular instance, since the infrared spectrum of $MgSO_4.4H_2O$ shows only a very broad band between 3200 and 3600 cm^{-1} and the contributions of the different hydrogen bonds cannot be separated.

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† There is an error in I: in the discussion of this point 'H_{IIa}' has been printed instead of 'H_{IIb}'.

Experimental

Single crystals of $MgSO_4.4H_2O$ were prepared in the way described in I. A crystal of $2·6 \times 2·9 \times 3·4$ mm^3 (the long dimension being parallel to [100]) was mounted on a single-crystal diffractometer (a further development by L. M. Corliss, B. C. Frazer and J. M. Hastings of the instrument described by Pepinsky & Frazer, 1955) at the Brookhaven graphite reactor and the intensities of 176 $0kl$ reflections were measured. The crystal was then cut down to $2·6 \times 2·9 \times 2·9$ mm^3, so that it could fit also in other orientations in the primary beam and the intensities of 129 $hk0$ and 80 $h0l$ reflections were recorded. Most of the observed reflections had $\sin \theta / \lambda$-values smaller than 0·7 Å^{-1}; a few reflections lying outside this range were also measured. Since the neutron wavelength was 1·073 Å, the total scattering cross-section of hydrogen was taken as approximately 30 barns (Bacon, 1962a), and thus the linear absorption coefficient of $MgSO_4.4H_2O$ is 1·7 cm^{-1}. The corrections to the intensities because of absorption were estimated to be of the order of 1% and were consequently neglected. A total of 367 independent intensities was obtained after averaging those which were recorded in two zones. The intensities of 19 reflections were too weak to be observed. The standard deviations of the intensities were calculated from the counting statistics and under the assumption of an average accuracy of the measurement of 5%. This figure has been estimated by comparing the intensities of the same reflections recorded under different conditions. These standard deviations were used for weighting the F_o^2 in the least-squares refinement of the data.

Crystal data

The crystals of $MgSO_4.4H_2O$ were grown from solution. The corresponding mineral is called leonhardtite.

F.W. $= 192\cdot435$; $D_m = 2\cdot01$ g.cm^{-3}, $D_x = 2\cdot007(3)$ g.cm^{-3}. Monoclinic, $a = 5\cdot922(6)$, $b = 13\cdot604(4)$, $c = 7\cdot905(5)$ Å, $\beta = 90°\ 51'\ (10')$, $V = 636\cdot8(0\cdot8)$ Å^{3}*. The space group is $P2_1/n$; all atoms are in the fourfold general position: $\pm(x, y, z;\ x+\tfrac{1}{2}, y-\tfrac{1}{2}, z+\tfrac{1}{2})$.

Refinement of the structure

The calculations were performed on an IBM 7094, the local modification of the crystallographic least-squares FORTRAN program ORFLS (Busing, Martin & Levy, 1962a) being used. The nuclear scattering lengths of the atoms were taken to be (in 10^{-12}cm): $b_{Mg} = 0\cdot54$, $b_S = 0\cdot31$, $b_O = 0\cdot577$ and $b_H = -0\cdot378$ (Bacon, 1962a). The refinement was based on the F_c^2. A first calculation using the parameters from I resulted in an R value of $0\cdot40$ $(R = \Sigma||F_o^2| - |F_c^2||/\Sigma|F_o^2|)$. After five cycles of refinement, in which only the parameters of the hydrogen atoms were allowed to vary, R was reduced to $0\cdot14$. Variation of all positional parameters and subsequent refinement of anisotropic thermal parameters lowered R to $0\cdot086$. With one scale factor for each of the three zones 165 parameters were varied,

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* Throughout this paper the estimated standard deviations are given in parentheses following the values. They correspond to the last significant digits of these values.

while the number of observations is only 367. Therefore it was suspected that the thermal parameters did not correspond to physical reality but rather represented a least-squares fit to possible systematic experimental errors. In order to check the results of the refinement of the neutron diffraction data, the X-ray diffraction data from I were refined with anisotropic temperature

Table 1. *Positional parameters and their standard deviations in* MgSO$_4$.4H$_2$O

Atom	x	y	z
Mg	0·0691(4)	0·1030(2)	0·2216(3)
S	0·1957(3)	0·1070(1)	0·8263(2)
O$_I$	0·0074(6)	0·0460(2)	0·7601(4)
O$_{II}$	0·2482(7)	0·0774(2)	0·0011(4)
O$_{III}$	0·3975(8)	0·0913(3)	0·7218(5)
O$_{IV}$	0·1290(6)	0·2106(2)	0·8148(5)
O$_{wI}$	0·3583(9)	0·0740(3)	0·3589(5)
O$_{wII}$	0·7716(7)	0·1395(3)	0·0914(5)
O$_{wIII}$	0·8914(8)	0·1282(3)	0·4412(5)
O$_{wIV}$	0·1752(7)	0·2482(3)	0·2222(6)
H$_{Ia}$	0·3726(23)	0·0851(8)	0·4797(13)
H$_{Ib}$	0·4580(16)	0·0232(9)	0·3246(12)
H$_{IIa}$	0·6802(23)	0·1904(11)	0·1417(20)
H$_{IIb}$	0·6819(29)	0·0943(12)	0·0330(29)
H$_{IIIa}$	0·8018(23)	0·1855(8)	0·4560(16)
H$_{IIIb}$	0·9207(20)	0·0980(9)	0·5533(12)
H$_{IVa}$	0·3167(18)	0·2645(8)	0·2753(18)
H$_{IVb}$	0·5771(20)	0·1938(6)	0·7249(12)

(a) (b) (c)
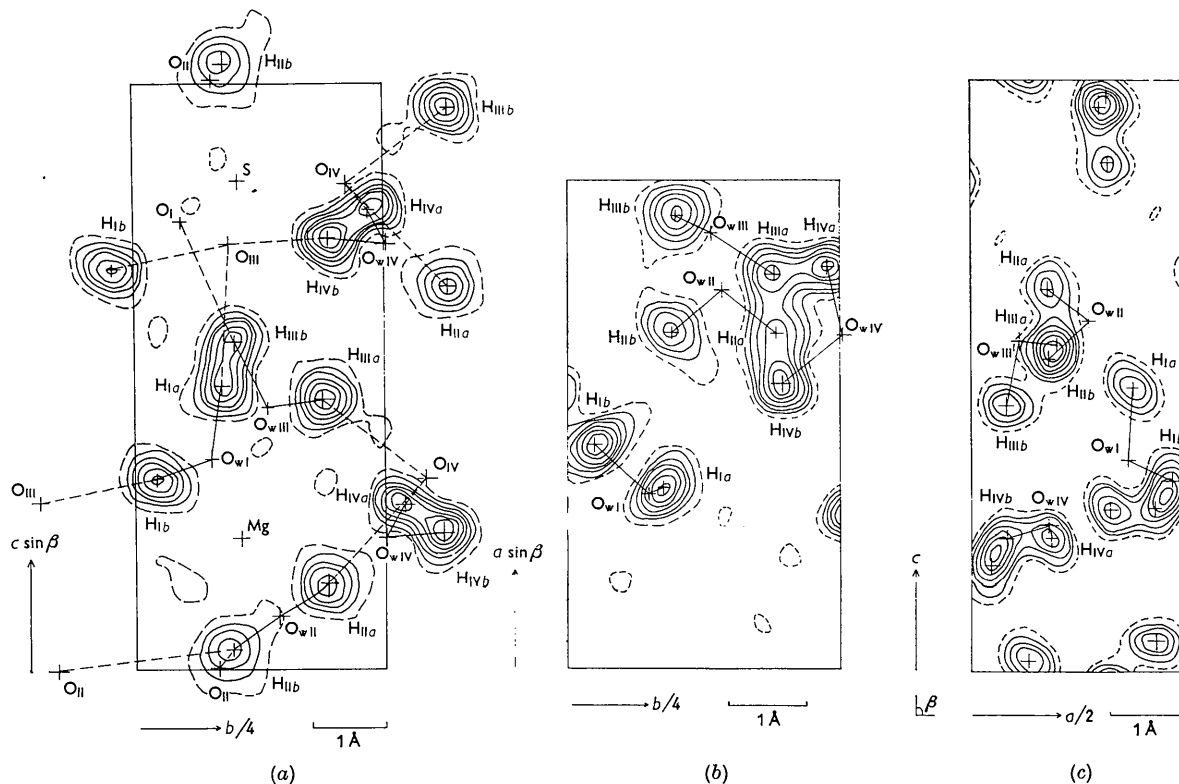
Fig. 1. Nuclear scattering density of MgSO$_4$.4H$_2$O computed with $(F_0 - F_{heavy})$, thus showing the contributions of the hydrogen atoms only. Positive contours are omitted, zero contour dashed. (a) Projection along [100]. Contour interval $0\cdot18 \times 10^{-12}$ cm.Å^{-2}. Positions of heavy atoms marked by crosses. O$_w$–H connected by heavy lines, H ————— O by dashed lines. Largest positive peak $0\cdot33 \times 10^{-12}$ cm.Å^{-2}. (b) Projection along [001]. Contour interval $0\cdot18 \times 10^{-12}$ cm.Å^{-2}. Largest positive peak $0\cdot45 \times 10^{-12}$ cm.Å^{-2}. (c) Projection along [010]. Contour interval $0\cdot25 \times 10^{-12}$ cm.Å^{-2}. Largest positive peak $0\cdot63 \times 10^{-12}$ cm.Å^{-2}.

factors. These data were recorded photographically on a precession camera and had been refined previously by successive $(F_o - F_c)$ projections parallel to [100] and [001], with different isotropic temperature factors for each kind of atom. The 427 reflections from the $hk0$ and $0kl$ zones were weighted according to the scheme of Hughes (1941). The scattering curves for Mg, S, O and H were taken from a compilation of

Table 2. $MgSO_4.4H_2O$: thermal parameters and their standard deviations

The definition of the Debye–Waller temperature factor is: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$; and B is $\frac{4}{3}(\beta_{11}.a^2 + \beta_{22}.b^2 + \beta_{33}c^2 + 2\beta_{13}ac\cos\beta)$.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B (Å²)
Mg	0·0068(4)	0·0014(1)	0·0039(2)	−0·0004(2)	0·0016(39)	0·0001(1)	1·0(0·1)
S	0·0066(3)	0·0011(1)	0·0033(2)	−0·0002(1)	−0·0041(19)	0·0002(1)	0·9(0·1)
O_I	0·0097(7)	0·0013(1)	0·0060(4)	−0·0009(3)	−0·0063(13)	0·0003(2)	1·3(0·1)
O_{II}	0·0109(9)	0·0020(1)	0·0042(4)	0·0010(4)	−0·0004(10)	−0·0002(2)	1·4(0·1)
O_{III}	0·0105(9)	0·0019(2)	0·0055(4)	0·0005(4)	0·0004(13)	−0·0003(2)	1·4(0·1)
O_{IV}	0·0116(9)	0·0012(1)	0·0072(5)	0·0003(3)	0·0044(12)	0·0003(2)	1·4(0·1)
O_{wI}	0·0131(10)	0·0022(2)	0·0065(5)	0·0016(4)	−0·0029(13)	−0·0002(2)	1·7(0·1)
O_{wII}	0·0131(10)	0·0027(2)	0·0070(5)	0·0015(4)	−0·0041(11)	−0·0003(3)	1·9(0·1)
O_{wIII}	0·0190(11)	0·0028(2)	0·0063(4)	0·0029(4)	0·0023(14)	−0·0001(3)	2·1(0·1)
O_{wIV}	0·0098(8)	0·0017(1)	0·0096(6)	0·0001(3)	0·0010(58)	−0·0001(3)	1·7(0·1)
H_{Ia}	0·0242(34)	0·0032(5)	0·0109(14)	0·0042(40)	−0·0042(24)	−0·0012(9)	2·8(0·4)
H_{Ib}	0·0162(24)	0·0058(6)	0·0101(14)	0·0053(14)	−0·0019(22)	−0·0014(10)	3·0(0·5)
H_{IIa}	0·0214(30)	0·0075(9)	0·0177(21)	0·0043(26)	−0·0013(34)	−0·0021(16)	4·3(0·6)
H_{IIb}	0·0380(55)	0·0068(10)	0·0282(45)	−0·0102(23)	−0·0106(86)	0·0014(23)	5·8(0·9)
H_{IIIa}	0·0228(35)	0·0039(5)	0·0127(17)	−0·0009(20)	0·0027(50)	0·0006(10)	3·1(0·5)
H_{IIIb}	0·0255(35)	0·0057(7)	0·0083(12)	0·0008(20)	−0·0025(23)	−0·0009(11)	3·3(0·5)
H_{IVa}	0·0130(26)	0·0052(7)	0·0115(17)	−0·0002(15)	−0·0003(104)	−0·0028(14)	2·9(0·4)
H_{IVb}	0·0166(25)	0·0030(4)	0·0083(13)	−0·0009(12)	0·0032(88)	−0·0010(8)	2·2(0·3)

Table 3. $MgSO_4.4H_2O$, observed and calculated F^2 in units of 10^{-24} cm per unit cell, multiplied by a scale factor of 10

The signs given to the F_c^2 are those of the F_c

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H  K  L OBS CALC    H  K  L OBS CALC    H  K  L OBS CALC    H  K  L OBS CALC    H  K  L OBS CALC    H  K  L OBS CALC    H  K  L OBS CALC
0  2  0  87  94     0  6  3  62  56    .0  3  6   8   -3    0 10  9  11    3    2 17  0  85 110     6  0  0  33  -31     3  0  1  28  -28
0  4  0 284 -315    0  7  3 243 -226    0  4  6  23   15    0 11  9 10  -12     2 18  0  78  84     6  1  0  26  -27     3  0 -1 490 -511
0  6  0 727 -714    0  8  3  84  -82    0  5  6 191 -167·   0 10 10  39   38    3  1  0  31  28     6  2  0  11   -3     3  0  3 235 272
0  8  0 126 135     0  9  3 243 -246    0  6  6  44  -47    0  1 10 133 -124    3  2  0 102  -98    6  3  0 173 -160    3  0 -3 367 371
0 10  0 125 -122    0 10  3  35  -40    0  7  6  76   83    0  2 10  30  -26    3  3  0 258 232     6  4  0 265 297     3  0  5  72  81
0 12  0  25  -20    0 11  3 200 224     0  8  6 130 -144    0  3 10  15   -9    3  4  0   8    7     6  5  0  35  -32    3  0 -5 290 -284
0 14  0  54  52     0 12  3 137 151     0  9  6  49   45    0  4 10   9  -10    3  5  0   6    7     6  6  0   5    2     3  0  7  46  48
0 16  0  13  -3     0 13  3 309 315     0 10  6 166 167     0  5 10   2   -5    3  6  0  11    7     6  7  0  64  57     3  0 -7 233 -236
0 18  0  17  -3     0 14  3  27   29    0 11  6 125 122     0  6 10  12   -2    3  7  0  35  -34    6  8  0  11  -10    3  0  9  76  71
0 20  0  61  48     0 15  3  1C   14    0 12  6  21   22    0  7 10 327 340     3  8  0  87  78     6  9  0  11   -6    3  0 -9  10   5
0  1  1 118 118     0 16  3  53  -41    0 13  6 285 -321    0  8 10   3   -0    3  9  0 186 -187    6 10  0  75  -88    3 0-11   0  -2
0  2  1   2    0    0 17  3   5   -3    0 14  6  87   79    0 10 10  51   56    3 10  0   5   -3     6 11  0   0   -2     4  0 -2 431 478
0  3  1  16  -14    0 18  3  21   25    0 15  6   9    0    0  1 11 118 101     3 11  0   6   -6     6 12  0   8   -8     4  0  4  29   0
0  4  1  19   21    0 19  3 253 -258    0 16  6   3   -0    0  2 11   5    8    3 12  0  30  -31    6 13  0  81 -100    4  0 -4 401 369
0  5  1   3    0    0  0  4  55   43    0 18  6  12   12    0  0 12  28   33    3 13  0   0   -0     7  1  0  16  -18    4  0  6 120 -109
0  6  1 282 257     0  1  4  14   -2    0  1  7   8   -5    0  6 12   0   -0    3 14  0   0   -1     7  2  0   6   -6     4  0 -6   6   5
0  7  1  42  -39    0  2  4  70   66    0  2  7  75   75    0  8 12  18  -20    3 15  0  12  -11    7  3  0  13   20    4  0  8  96 116
0  8  1  11    6    0  3  4 108   97    0  3  7  23   28    1  1  0 280 274     3 16  0   0    1     7  4  0  48   43    4  0 -8 252 253
0  9  1   6    0    0  4  4  21   24    0  4  7 103 -111    1  2  0 462 -515    3 17  0   9   11     7  5  0  65   65    4  0 10  82  95
0 10  1  13    6    0  5  4  38   34    0  5  7  51  -55    1  3  0  31  -31    3 18  0 211 186     7  6  0  32   34    4 0-10   0  10
0 11  1  40   36    0  6  4  71  -79    0  6  7  11    6    1  4  0  32  -34    4  0  0   5   -3     7  7  0  22  -22    5  0  1 292 327
0 12  1  53   54    0  7  4 429 -393    0  7  7   1    2    1  5  0  81   80    4  1  0  61   63    7  8  0  14  -22    5  0 -1  28  17
0 13  1   9    9    0  8  4   7    1    0  8  7  67  -67    1  6  0 342 -356    4  2  0  78   71    7  9  0  16  -13    5  0  3 183 175
0 14  1   4   -2    0  9  4 165 151     0  9  7  10    7    1  7  0   6    5    4  3  0 381 -401    7 10  0  63  -74    5  0 -3   0   1
0 15  1   6   -1    0 10  4   5   -6    0 10  7  11   11    1  8  0 869 915     4  4  0  18  -20    8  0  0 172 161     5  0  5  58  -54
0 16  1  37  -20    0 11  4   8   -6    0 11  7   3    3    1  9  0  30   27    4  5  0  22   25    8  1  0  50  -42    5  0 -5  11  ≒7
0 17  1  44  -45    0 12  4  11    7    0 12  7  28   18    1 10  0 245 242     4  6  0  35   19    8  2  0   8    4     5  0  7  37  -31
0 18  1 190 -220    0 13  4 288 246     0 13  7  66   58    1 11  0 126 -128    4  7  0  27  -21    8  3  0   0    4     5  0 -7  39  36
0  0  2 526 -537    0 14  4 135 -138    0 14  7. 12   11    1 12  0 104 -107    4  8  0  17  -10    8  4  0   5    6     5  0  9   0  -0
0  1  2  47   47    0 15  4  28  -27    0  0  8  37   27    1 13  0 283 -284    4  9  0  12   14    8  5  0   0   -3     5  0 -9  71  -80
0  2  2  34  -28    0 16  4  15  -15    0  1  8 338 260     1 14  0  70  -61    4 10  0 119  -97    8  6  0  29   24    5  0 11  29   2
0  3  2  36   29    0 17  4  13    2    0  2  8 259 264     1 15  0   0   -0    4 11  0  47  -37    8  7  0  18   13    5  0-11 356 -320
0  4  2  10   13    0 20  4  57   64    0  3  8 104 101     1 16  0   0    1    4 12  0   0   -1     8  8  0 121 -118    6  0  2  14  13
0  5  2  12    7    0  1  5 220 210     0  4  8  19    7    1 17  0   0   -0    4 13  0   2    4     1  0  1 181 205     6  0 -2 356 -320
0  6  2 556 563     0  2  5  37  -41    0  5  8   5    0    1 18  0   5    5    4 14  0  15  -11    1  0 -1   4   -3     6  0  4  14  13
0  7  2   8    0    0  3  5   4   -0    0  6  8  99  -92    1 19  0  97   97    4 15  0  46  -52    1  0  3 157 -180    6  0 -4 140 -153
0  8  2   6    6    0  4  5 327 289     0  7  8 480 -490    2  0  0  20  -19    4 16  0   6    8     1  0 -3 193 -200    6  0  6  89  -82
0  9  2 266 -257    0  5  5   4    2    0  8  8 123 -122    2  1  0  36  -39    4 17  0  49   46    1  0  5 220 231     6  0 -6  29  28
0 10  2 110 -120    0  6  5 117 116     0  9  8   7    6    2  2  0   3   -0    5  1  0 106 104     1  0 -5   7    1     6  0  8  26  32
0 11  2  43   36    0  7  5 303 -315    0 10  8  35  -41    2  3  0 188 286     5  2  0  10   -2    1  0  7  12  -15    6  0 -8  58  -55
0 12  2  25  -23    0  8  5  19   20    0 11  8   4   -5    2  4  0  19   14    5  3  0  71   76    1  0 -7 106 -113    7  0  1 149 -142
0 13  2  94  -92    0  9  5  16   16    0 12  8 126 143     2  5  0 190 -199    5  4  0  84  -83    1  0  9  11  -10    7  0 -1  26  25
0 14  2 344 342     0 10  5 352 -349    0 13  8  51   52    2  6  0  14    6    5  5  0 140 -128    1  0 11 101 -106    7  0  3  97  -93
0 15  2   6    1    0 11  5  45   40    0 16  8   0    0    2  7  0  57   54    5  6  0  32   33    1 0-11  21  -24    7  0 -3  26  -29
0 16  2 136 122     0 12  5  53  -38    0  1  9  44   46    2  8  0  72  -78    5  7  0   7   -8     2  0  2  44  -42    7  0  5  48  -42
0 17  2   6   -2    0 13  5  19  -20    0  2  9   5    6    2  9  0  43  -29    5  8  0  26   32    2  0 -2 219 -223    7  0 -5  84  84
0 18  2  38  -38    0 14  5  1C    6    0  3  9   8  -11    2 10  0  11   -5    5  9  0  50  -55    2  0  4   2   -3     7  0  7  48  47
0 20  2 311 -315    0 15  5  14    7    0  4  9   3    0    2 11  0  38  -31    5 10  0  32   35    2  0 -4 372 457     7  0 -7  50  32
0  1  3  21   16    0 16  5   5    1    0  5  9  62  -52    2 12  0  53  -60    5 11  0   0   -1     2  0  6  40  -33    8  0  2   4   -3
0  2  3 204 -200    0 17  5   1   -0    0  6  9  16  -19    2 13  0  64  -68    5 12  0  62  -56    2  0 -6 292 -311    8  0 -2  49  44
0  3  3  15    7    0  0  6  72  -58    0  7  9  14    2    2 14  0 112 -103    5 13  0   5    1     2  0  8   7    9     8  0  4   0  -5
0  4  3 271 -268    0  1  6  44  -43    0  8  9  94   87    2 15  0  15   17    5 14  0   0    0     2  0 -8   8    6
0  5  3 129 -131    0  2  6  53  -51    0  9  9  24  -24    2 16  0  19  -24    5 15  0  43  -45    2  0 10 192 -209
                                                                                                   2 0-10  54  -54
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Ibers (1962). Only 82 parameters were varied: two scale factors, 30 positional and 50 thermal parameters for the heavy atoms. Because of lack of $h0l$ or hkl data β_{13} could not be determined. No attempt was made to vary the parameters of the hydrogen atoms; they were fixed at the positions found by neutron diffraction. In three cycles R was lowered from 0·087 to 0·071 ($R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$). The agreement between the two sets of positional parameters derived for Mg, S and O is excellent. In only two of the 30 parameters is the difference between two corresponding parameters slightly larger than twice the standard deviation of the less accurate of the two parameters; none of the differences between them is significant. For the thermal parameters the agreement is good; only for three of the 50 thermal parameters their difference is possibly significant. Thus neutron diffraction data from a spectrometer, recorded by a BF_3-counter, and X-ray diffraction data collected on a precession camera, by photographic methods, yield very similar results, which indicates that no serious systematic errors have been introduced in the measurements. Nevertheless one cannot view the resulting thermal parameters with the same confidence as the

Table 4. *Interatomic distances and bond angles*

(a) Bonded distances in SO_4 and $MgO_2(O_w)_4$ groups

Mg-O_I	2·082(4) Å		S-O_I	1·480(4) Å
Mg-O_{II}	2·083(5)		S-O_{II}	1·468(4)
Mg-O_{wI}	2·052(8)		S-O_{III}	1·478(6)
Mg-O_{wII}	2·087(5)		S-O_{IV}	1·466(5)
Mg-O_{wIII}	2·072(5)			
Mg-O_{wIV}	2·072(4)			
Weighted mean value 2·077(2)			Weighted mean value 1·473(2)	

(b) Shape and orientation of the water molecules

		Distance H_a-H_b	Angle H_a-O_w-H_b	Sum of angles Mg-O_w-H_a Mg-O_w-H_b H_a-O_w-H_b	Angle O-O_w-O	Dihedral angle between planes H_a-O_w-H_b and O-O_w-O
$(O_{III})H_{Ia}$-O_{wI}-H_{Ib}	(O_{III}')	1·577 Å (15)	110·4°(0·8°)	354·2°(0·6°)	105·2°(0·2°)	9·7°(0·9°)
$(O_{IV})H_{IIa}$-O_{wII}-H_{IIb}	(O_{II}')	1·565 (24)	111·0 (1·5)	351·1 (1·0)	146·8 (0·2)	58·9 (1·4)
$(O_{IV})H_{IIa}$-O_{wII}-H_{IIb}	(O_{II})	1·565 (24)	111·0 (1·5)	351·1 (1·0)	91·8 (0·2)	9·1 (0·9)
$(O_{IV})H_{IIIa}$-O_{wIII}-H_{IIIb}	(O_{I})	1·578 (16)	108·7 (1·0)	357·3 (0·4)	137·5 (0·2)	3·9 (0·6)
$(O_{IV})H_{IVa}$-O_{wIV}-H_{IVb}	(O_{III})	1·574 (16)	108·5 (1·0)	353·6 (0·9)	114·2 (0·2)	11·6 (1·1)
Weighted mean values:		1·575 (9)	109·6 (0·5)			

(c) Geometry of the hydrogen bonds

	Distances				Angles	
	O_w-H	O_w-O	H-O	H to line O_w-O	O_w-H-O	H-O_w-O
O_{wI}-H_{Ia}-O_{III}	0·969 Å (10)	2·884 Å (5)	1·919 Å (10)	0·073 Å (10)	173·6°(0·8°)	4·3°(0·6°)
O_{wI}-H_{Ib}-O_{III}'	0·951 (13)	2·754 (5)	1·818 (12)	0·136 (12)	167·6 (1·1)	8·2 (0·7)
O_{wII}-H_{IIa}-O_{IV}	0·968 (15)	2·835 (5)	1·948 (15)	0·319 (12)	151·3 (1·1)	19·2 (0·7)
O_{wII}-H_{IIb}-O_{II}'	0·931 (17)	3·042 (5)	2·388 (18)	0·548 (18)	127·1 (1·4)	38·7 (1·2)
O_{wII}-H_{IIb}-O_{II}	0·931 (17)	3·282 (6)	2·588 (16)	0·581 (16)	131·7 (1·6)	36·1 (1·1)
O_{wIII}-H_{IIIa}-O_{IV}	0·952 (13)	2·860 (6)	2·063 (12)	0·439 (11)	140·2 (1·0)	27·5 (0·7)
O_{wIII}-H_{IIIb}-O_{I}	0·989 (10)	2·833 (6)	1·847 (10)	0·069 (14)	173·8 (0·9)	4·0 (0·7)
O_{wIV}-H_{IVa}-O_{IV}	0·958 (13)	2·831 (5)	1·901 (11)	0·189 (17)	162·9 (1·5)	11·4 (1·1)
O_{wIV}-H_{IVb}-O_{III}	0·981 (10)	2·734 (5)	1·753 (10)	0·026 (10)	177·7 (0·9)	1·5 (0·6)

Weighted
    mean value: 0·967   (5)

(d) Orientation of the water molecules relative to the magnesium ions

	Angle	Distance Mg-H		Angle	Distance Mg-H
Mg-O_{wI}-H_{Ia}	123·5°(0·6°)	2·710 Å (11)	Mg-O_{wIII}-H_{IIIa}	122·0°(0·7°)	2·700 Å (13)
Mg-O_{wI}-O_{III}	124·4 (0·3)		Mg-O_{wIII}-O_{IV}	96·6 (0·2)	
Mg-O_{wI}-H_{IIa}	120·3 (0·6)	2·662 (9)	Mg-O_{wIII}-H_{IIIb}	126·7 (0·8)	2·779 (10)
Mg-O_{wI}-O_{III}'	118·1 (0·3)		Mg-O_{wIII}-O_{I}	124·1 (0·3)	
Mg-O_{wII}-H_{IIa}	116·2 (0·8)	2·660 (13)	Mg-O_{wIV}-H_{IVa}	119·1 (0·7)	2·673 (11)
Mg-O_{wII}-O_{IV}	97·0 (0·2)		Mg-O_{wIV}-O_{IV}	125·4 (0·3)	
Mg-O_{wII}-H_{IIIb}	123·9 (1·1)	2·719 (17)	Mg-O_{wIV}-H_{IVb}	126·0 (0·8)	2·765 (9)
Mg-O_{wII}-O_{II}'	85·2 (0·2)		Mg-O_{wIV}-O_{III}	118·4 (0·2)	
Mg-O_{wII}-O_{II}	146·5 (0·2)				

positional parameters because there are, owing to the employment of projection data only, strong correlations of certain thermal parameters. The positional parameters however are virtually uncorrelated. Tables 1 and 2 show the results of the refinement. The B's in Table 2 are the isotropic B's equivalent to the anisotropic temperature factors (Hamilton, 1959). All positional and thermal parameters pertaining to the hydrogen atoms are based on the neutron diffraction data solely, as are the β_{13} for all the other atoms. Their standard deviations are those obtained from the variance–covariance matrix. The parameters for Mg, S and O are the weighted mean values of the results of both the neutron and X-ray data refinements. Their standard deviations have been calculated under the assumption that the X-ray and the neutron diffraction data represent independent measurements of the same quantity. This is not strictly true here because the experiments were performed on different specimens. Nevertheless it was felt justified in this case since both crystals were grown under the same conditions and the agreement of the thermal parameters indicates that no serious discrepancies exist in the degree of perfection of these crystals.

In Table 3 the neutron diffraction data are presented. The comparison of observed and calculated structure amplitudes does not reveal any systematic deviations which could be explained by extinction. In order to check the validity of the refinements $F_o - F_{c \text{ (heavy)}}$-projections were prepared along the three principal axes. They are shown in Fig. 1. No details which would suggest a disordered arrangement of the hydrogen atoms can be seen.

Discussion

The refinement of the neutron diffraction data has changed no essential feature of the structure of $MgSO_4.4H_2O$ as determined in I. Notably no significant changes in the individual Mg–O,O_w and S–O distances have occurred. The positions of the hydrogen atoms have been confirmed within 0·2 Å. However, the positions of the hydrogen atoms are known now with considerably better accuracy and some information on the thermal motion has been gained.

The interatomic distances and angles and their standard deviations are shown in Table 4. They have been calculated by means of the ORFFE program (Busing, Martin & Levy, 1962b). The standard deviations include the effects of correlations between parameters. The water oxygen O_{wI} and the sulfate oxygen O_{III} are the only atoms for which there is a noteworthy correlation of positional parameters. Therefore the short distance Mg–O_{wI} need not be considered significantly different from the mean value of Mg–O. This mean value for Mg–O,O_w of 2·07$_7$ Å is very similar to the corresponding value of 2·06$_9$ Å in $Mg(NH_4)_2(SO_4)_2.6H_2O$ (Margulis & Templeton, 1962). The mean S–O bond length of 1·47$_3$ Å in $MgSO_4.4H_2O$

compares favorably with the values of 1·47$_2$ Å in $Mg(NH_4)_2(SO_4)_2.6H_2O$ and 1·47$_1$ Å in $Li_2SO_4.H_2O$ (Larson, 1961). The mean value of the O–H distance is 0·96$_7$ Å and thus very similar to corresponding values reported for other hydrates; for instance in $CuSO_4.5H_2O$ (Bacon, 1962b) the mean O–H distance is 0·96 Å. The H–H distances of all four water molecules lie within very close limits (Table 4b); the weighted mean value is 1·575 Å. The mean H–H distance in $CuSO_4.5H_2O$ is 1·58 Å, but the individual values scatter much more: from 1·54 to 1·63 Å. The mean value of the angle H–O–H is 109·6°, and is thus essentially the tetrahedral angle. It is significantly different from the water vapor value in equilibrium position, which is reported to be 104° 27′ (Herzberg, 1945). The sum of the bond angles around the water oxygen atom has an average value of 354°, which indicates that the bisector of the angle H–O–H is inclined on the average 20° to the line Mg–O_w. Seemingly there is no correlation between the magnitude of the angles H–O–H and O–O_w–O, which is the angle around the water oxygen to the oxygen atoms which are hydrogen bonded to it. Furthermore these angles are not coplanar.
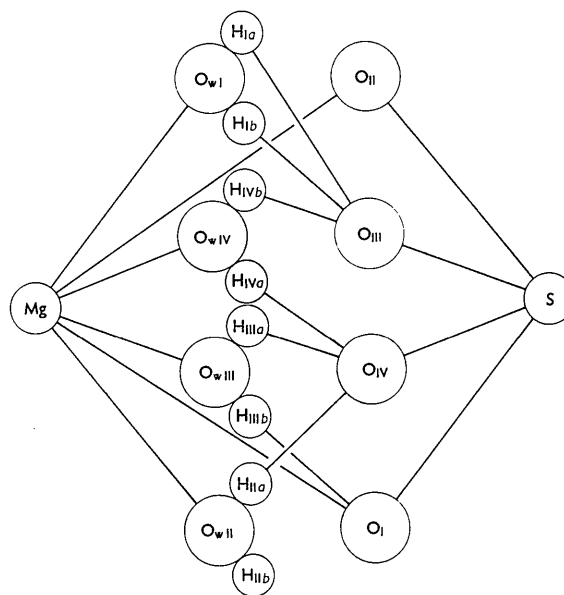

Fig. 2. Hydrogen bonding scheme of $MgSO_4.4H_2O$.

In Fig. 2 the hydrogen bonding in $MgSO_4.4H_2O$ is shown schematically. Fig. 1(a) illustrates the spatial arrangement of these hydrogen bonds. From the distances and angles in Table 4(c) the details of the hydrogen bonds can be gathered. The distance from H_{IIb} to the next sulfate oxygen atoms O'_{II} and O_{II} is 2·39 and 2·59 Å and the angles O_{wII}–H_{IIb}–O'_{II} and O_{wII}–H_{IIb}–O_{II} are around 130°. Considering these distances and angles it seems sensible to conclude that

no hydrogen bonding takes place between O_{wII} and O'_{II} or O_{II}. For purposes of comparison all distances and angles relating to H_{IIb} are given in Table 4. The geometrical arrangement around H_{IIb} is illustrated in Fig. 3. The thermal motion of H_{IIb} is the largest and most anisotropic one of all the hydrogen atoms. This is considered to be a supporting evidence for the conclusion that H_{IIb} is not involved in a hydrogen bond. Even apart from the rather extreme case of H_{IIb} it can be seen from Table 4(c) that all the hydrogen bonds are more or less bent; the next largest deviation is the one of the angle O_{wIII}–H_{IIIa}–O_{IV}, which is 140° and the hydrogen atom is at a distance of 0·44 Å
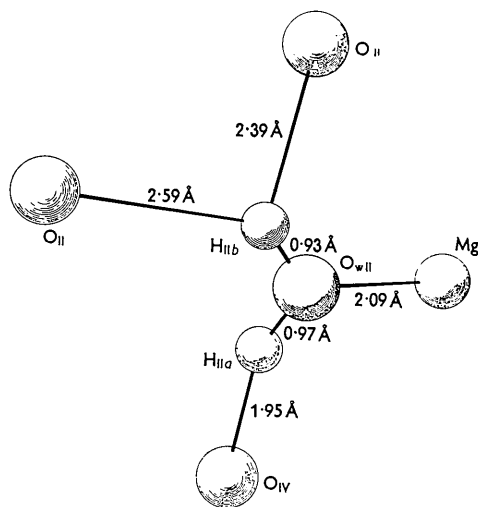
Fig. 3. Surrounding of water molecule O_{wII} in $MgSO_4.4H_2O$.

from the line O_{wIII}–O_{IV}. This deviation is the largest so far found for hydrogen-bonded water. It is comparable to the bent hydrogen bond in dimethylglyoxime where the angle O–H–N is 140° (Hamilton, 1961). Contrary to H_{IIb}, atom H_{IIIa} does not show a significant anisotropy of its thermal motion, nor is this motion extremely large. This indicates that in spite of the bending and the large H_{IIIa}–O_{IV} distance of 2·06 Å it really is hydrogen bonded. More constant than the orientation of the water molecules relative to the sulfate oxygen atoms is their orientation with respect to the magnesium ions. While the angles Mg–O_w–O vary over a range of 28°, between 97° and 125°, the angles Mg–O_w–H scatter only within 11°, from 116° to 127°. All the distances Mg–H lie within the rather narrow limits of 2·66 to 2·78 Å. If H_{IIIa} were situated on the line connecting O_{wIII} and O_{IV}, the distance Mg–H_{IIIa} would be reduced to 2·38 Å. This does not happen apparently because of the electrostatic repulsion between the magnesium ion and the hydrogen atom. Thus the orientation of the water molecules in $MgSO_4.4H_2O$ seems to be a compromise

between the requirements of the hydrogen bonding and the interaction between the cation and the water molecule dipole.

The root-mean-square components of thermal displacement, along the principal axes of the ellipsoid of thermal motion, are presented in Table 5. The directions of the principal axes were also determined, but their standard deviations are rather large and they are not presented here in detail. The mean values of the angles between the long principal axis (3) of O_w and O with the lines connecting them to Mg and S respectively are 92°(2°) and 83°(3°), while the short axes (1) make an angle of 22°(5°) and 27°(10°) with these lines. The root-mean-square thermal displacements along the short axes of O_w and O have approximately the same magnitude as the thermal displacement of their

Table 5. *Root-mean-square thermal displacements along principal axes*

Atom	Axis 1		Axis 2		Axis 3	
Mg	0·090 Å	(26)	0·116 Å	(6)	0·127 Å	(18)
S	0·038	(32)	0·099	(8)	0·146	(11)
O_I	0·053	(18)	0·107	(7)	0·185	(7)
O_{II}	0·114	(6)	0·121	(10)	0·153	(9)
O_{III}	0·123	(12)	0·136	(10)	0·143	(13)
O_{IV}	0·104	(8)	0·107	(10)	0·179	(8)
O_{wI}	0·113	(15)	0·138	(8)	0·180	(11)
O_{wII}	0·109	(10)	0·152	(8)	0·189	(8)
O_{wIII}	0·123	(12)	0·148	(10)	0·207	(9)
O_{wIV}	0·125	(8)	0·132	(9)	0·175	(7)
H_{Ia}	0·135	(57)	0·170	(17)	0·247	(29)
H_{Ib}	0·127	(17)	0·173	(13)	0·262	(15)
H_{IIa}	0·174	(24)	0·226	(18)	0·288	(21)
H_{IIb}	0·148	(31)	0·273	(29)	0·354	(32)
H_{IIIa}	0·174	(28)	0·201	(24)	0·215	(28)
H_{IIIb}	0·155	(13)	0·212	(19)	0·237	(17)
H_{IVa}	0·151	(42)	0·163	(46)	0·243	(17)
H_{IVb}	0·140	(62)	0·158	(17)	0·197	(41)

central atoms, while the displacements in their long axes are appreciably larger. This thermal motion may be explained by assuming that the groups oscillate as rigid bodies around the central atoms. The root-mean-square amplitude of angular oscillation is estimated to be about 4° for the SO_4 group. In cases where an appreciable angular oscillation of a group takes place a correction for the distance from the ligand to the central atom has to be applied (Cruickshank, 1956; Peterson & Levy, 1957). Such a correction has been computed here for all S–O and Mg–O_w distances but the differences of the corrected and uncorrected values are not significant. The mean value of the S–O distance is changed from 1·47₃ to 1·47₉ Å, and of the Mg–O_w distances from 2·07₇ to 2·08₁ Å. — The long principal axes of the hydrogen atoms are similarly at right angles to the line connecting them to the water oxygens. But here the assumption of rigid body motion of the molecule is less reasonable.

Conclusion

From the orientation of the water molecules in $MgSO_4.4H_2O$, as revealed by the neutron diffraction study, it can be concluded: (1) that the hydrogen bonds in a salt hydrate can be more bent than was known from previous investigations, (2) that a hydrogen atom of a water molecule need not necessarily participate in a hydrogen bond, (3) that the orientation of the water molecule in a salt hydrate is not only determined by the hydrogen bond geometry, but by the electrostatic forces between it and the cation as well.

References

Bacon, G. E. (1962a). Neutron Diffraction. Oxford: Clarendon Press.

Bacon, G. E. (1962b). Proc. Roy. Soc. A. 266, 95.

Baur, W. H. (1962). Acta Cryst. 15, 815.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962a). Oak Ridge National Laboratory ORNL-TM-305.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962b). Oak Ridge National Laboratory ORNL-TM-306.

Cruickshank, D. W. J. (1956). Acta Cryst. 9, 757.

Hamilton, W. C. (1959). Acta Cryst. 12, 609.

Hamilton, W. C. (1961). Acta Cryst. 14, 95.

Hamilton, W. C. (1962). Ann. Rev. Phys. Chem. 13, 19.

Herzberg, G. (1945). Molecular Spectra and Molecular Structure, Vol. II. New York: Van Nostrand.

Hughes, E. W. (1941). J. Amer. Chem. Soc. 63, 1737.

Ibers, J. A. (1962). In International Tables for X-ray Crystallography. Vol. 3, Table 3.3.1A. Birmingham: Kynoch Press.

Larson, A. C. (1961). Abstracts of Boulder, Colorado, meeting of A.C.A., p. 13.

Margulis, T. N. & Templeton, D. H. (1962). Z. Kristallogr. 117, 344.

Pepinsky, R. & Frazer, B. C. (1955). Rev. Sci. Instrum. 26, 402.

Peterson, S. W. & Levy, H. A. (1957). Acta Cryst. 10, 70.

Smith, H. G., Peterson, S. W. & Levy, H. A. (1961). Oak Ridge National Laboratory. Ann. Progr. Rep. Chem. Div. ORNL-3176, 80.

Kikuchi Pattern from a Silicon Wedge

By H. A. Fowler

National Bureau of Standards, Washington 25, D.C., U.S.A.

Under special conditions of illumination at 80 keV, the Kikuchi pattern of a thin single-crystal silicon wedge shows a dark cross within the intersection of the 110 and 101 dark zones. The pattern is interpreted as a combination of Bragg reflection effects, acting on the continuum of electrons produced by inelastic scattering.

In a series of extinction-contour studies on silicon single crystals, a dark Kikuchi figure has been repeatedly observed, which does not lend itself to interpretation as a simple defect line or band. Special conditions of thickness and illumination are required to emphasize the effect. It is similar to phenomena described qualitatively for other materials by Moliere (1961) and Selme (1963).

The silicon sample is a flake, of approximately one micron thickness, cut from a dislocation-free silicon single crystal* and finished by mechanical polishing, then etched, according to the methods of Dash (1956, 1958, 1959). The orientation is normal to a [001] axis. The flake has been mechanically broken, so as to provide cleavage surfaces, some of which form irregular wedges with the front or back faces; in these wedges a considerable degree of transmission is obtained at 80 keV.

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