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On the Crystal Chemistry of Salt Hydrates. III. The Determination of the Crystal Structure of $FeSO_4 . 7\,H_2O$ (Melanterite)*

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$FeSO_4.7\,H_2O$ crystallizes in space group $P2_1/c$ with $a = 14{\cdot}072$, $b = 6{\cdot}503$, $c = 11{\cdot}041$ Å, $\beta = 105° \; 34'$, $Z = 4$. The crystal structure had been determined from Patterson and Fourier syntheses using F_{h0l} and F_{hk0} data. The refinement was done by the method of least squares employing 738 observed structure factors from the zones *hk*0, *h*0*l*, 0*kl*, *h*3*l* and *hk*1. The final *R* value, including the contribution of the hydrogen atoms is 4·5%. The iron ions occupy special positions and are surrounded octahedrally by six water molecules each. The six water oxygens form hydrogen bonds to the tetrahedral sulfate group and to the seventh water molecule which is not coordinated to Fe^{2+}. The mean bond length of Fe–O(w) is $2{\cdot}12_4$ Å, of S–O $1{\cdot}47_4$ Å and of O–H · · · O 2·82 Å. One of the iron-coordinated water oxygen atoms receives an 'outward' hydrogen bond from the seventh water oxygen atom. The bond from iron to this water oxygen is 2·19 Å and thus significantly longer than the mean Fe–O(w) bond length.

Introduction

Monoclinic $FeSO_4.7\,H_2O$ is the stable solid phase between $-1{\cdot}82$ and 56·6 °C in contact with a saturated water solution of $FeSO_4$ (Fraenckel, 1907). It occurs in nature as an oxidation product of iron-containing sulfides and is called melanterite. $FeSO_4.7\,H_2O$ belongs to a series of compounds $M^{2+}SO_4.nH_2O$, where M^{2+} is a cation with an approximate ionic radius of 0·7 Å. The mono-, tetra- and penta-hydrates are known to crystallize each in one form only, whereas the hexa- and the hepta-hydrate both occur in two different forms (Groth, 1908). The crystal structures of the hexahydrates are known. Beevers & Lipson (1932) determined the structure of the tetragonal $NiSO_4.6H_2O$; Zalkin, Ruben & Templeton (1962) reported the structure of the monoclinic $CoSO_4.6H_2O$. Of the heptahydrates, only one structure has been described: the orthorhombic form of $NiSO_4.7\,H_2O$ (Beevers & Schwartz, 1935). No details were known about any of the monoclinic heptahydrates, though Leonhardt & Ness (1947) published the cell constants and the space group of $FeSO_4.7\,H_2O$. In addition they stated essentially correct positional parameters for the sulfur atom and gave the correct positions of the iron atoms. The present investigation has been undertaken as part of an extensive study of salt hydrates (I: Baur, 1962*a*; II: Baur, 1964*a*; IV: Baur, 1964*b*). A preliminary account has been published (Baur, 1962*b*).

Experimental

Green crystals of $FeSO_4.7\,H_2O$ were grown at 35 °C from an aqueous solution of sulfuric acid saturated with $FeSO_4$. Crystal plates of approximately $0{\cdot}2 \times 2{\cdot}0 \times 2{\cdot}0$ mm^3 were ground perpendicular to [100], [010] and [001]. 0*kl*, *h*0*l*, *hk*0, *h*3*l* and *hk*1 data were collected on a precession camera, the multiple exposure technique being used (Mo $K\alpha$ radiation, Zr filter). In order to prevent decomposition, the crystals were coated with a protective layer of a synthetic resin. The intensities of 738 independent reflections were measured with a recording microphotometer. The intensities of an additional 288 reflections were below the detection limit. The cell constants were derived from the precession photographs (Mo $K\alpha$(mean) = 0·7107 Å).

The intensities were reduced to F_o using a Lorentz–polarization factor program written by the author for an IBM 650 computer with indexing registers and floating point arithmetic. This program is based on the formulas of Waser (1951) and Burbank (1952). The calculations for the first stages of the structure determination were carried out on an IBM 650 computer with the structure factor program by Shiono (1959) and a two-dimensional Fourier synthesis program written by the author. This latter program is especially fast since it takes advantage of the indexing registers and also because the whole first summation is stored internally on the magnetic drum. The ultimate refinement of the structure was performed on an IBM 7094 computer at Brookhaven National Laboratory, with the use of local modifica-

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tions of the FORTRAN crystallographic least-squares program ORFLS and the function and error program ORFFE (Busing, Martin & Levy, 1962*a*, *b*), as well as of the Fourier synthesis program FORDAPER by Allan Zalkin.

Crystal data

$FeSO_4.7H_2O$ is monoclinic, with $a = 14{\cdot}072(10)$,* $b = 6{\cdot}503(7)$, $c = 11{\cdot}041(10)$ Å and $\beta = 105° 34(5)'$; $V = 973(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}897(4)$, $D_m = 1{\cdot}895$ g.cm^{-3} (Moles & Crespi, 1927). Because of the characteristic extinctions, $h0l$ only present with $l = 2n$, $0k0$ only with $k = 2n$, $P2_1/c$ was chosen as space group. The $a:b:c$ calculated from the above cell constants is $2{\cdot}164:1:1{\cdot}698$. Groth (1908) gives $a:b:c = 1{\cdot}1828:1:1{\cdot}5427$, $\beta = 104° 16'$; recalculated to the present setting this corresponds to $a:b:c = 2{\cdot}169:1:1{\cdot}689$, $\beta = 105° 28'$. The matrix for the transformation from Groth's setting to the present one is $(\frac{1}{2}0-\frac{1}{2}/0\frac{1}{2}0/\frac{1}{2}0\frac{1}{2})$.

Determination of the structure

Since the intensities of the reflections with h, k and l all $2n$ or all $2n+1$ were observed to be on the average stronger than those with mixed indices, it was assumed that the iron atoms occupied the special positions (*a*) 000, $0\frac{1}{2}\frac{1}{2}$ and (*d*) $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, thus forming a face-centered arrangement. Positions (*a*) and (*d*) have the point symmetry $\bar{1}$, as have the other two special positions (*b*) and (*c*). Thus (*b*) and (*c*) cannot be expected to be occupied since neither the sulfur atom nor the oxygen atoms of the SO_4 group, nor a water oxygen atom can have a surrounding with this symmetry. Therefore all other atoms must lie in the fourfold general position (*e*): $\pm(xyz;\ x, \frac{1}{2}-y, \frac{1}{2}+z)$. The Patterson projection along [010] was readily interpreted on this assumption. It resembles closely a double electron-density projection, since the Fe–S and Fe–O vectors from the two different Fe positions both form an image of the structure; the S–O and O–O vectors are too weak to change this picture substantially. A first structure factor calculation, which included the Fe atoms and the SO_4 group with positional parameters derived from the Patterson projection, yielded an $R = 0{\cdot}53$ $(R = \Sigma||F_o| - |F_c||/\Sigma|F_o|)$ for the reflections with $\sin\theta/\lambda < 0{\cdot}38$ Å^{-1}. A Fourier synthesis calculated with 76 F_{h0l} revealed the positions of all the water oxygen atoms. The 231 F_{h0l} (including non-observed reflections) were refined by 11 cycles of consecutive F_o or $(F_o - F_c)$ syntheses and structure factor calculations to $R = 0{\cdot}071$. The last difference syntheses were performed with only the reflections having $h = 2n+1$, to which the Fe atoms do not contribute. Since the Patterson projections along [001] and [100] were not easily interpretable, the y parameters were obtained from the [010] projection: assuming the bond length of S–O to be 1·48 Å, of Fe–O(w) 2·12 Å and of O–H · · · O 2·82 Å, the heights of all the atoms were calculated from their x and z parameters. The y parameters thus derived were used as a starting point for refining the 143 F_{hk0} (including non-observed reflections) by difference syntheses. In eight cycles, R was lowered from 0·36 to 0·078. The electron-density projections parallel to [010] and [001] are shown in Fig. 1.

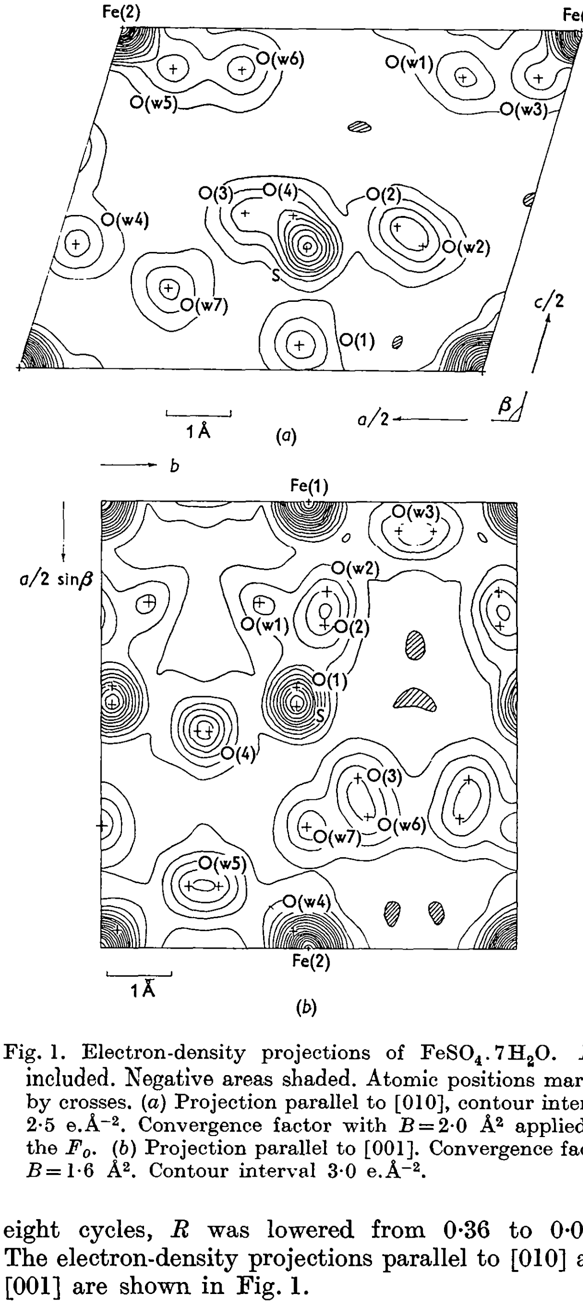

Fig. 1. Electron-density projections of $FeSO_4.7H_2O$. F_{000} included. Negative areas shaded. Atomic positions marked by crosses. (*a*) Projection parallel to [010], contour interval 2·5 e.Å^{-2}. Convergence factor with $B = 2{\cdot}0$ Å^2 applied to the F_o. (*b*) Projection parallel to [001]. Convergence factor $B = 1{\cdot}6$ Å^2. Contour interval 3·0 e.Å^{-2}.

The final refinement was carried out on 738 nonzero $h0l$, $hk0$, $0kl$, $h3l$ and hkl reflections by the method of least-squares, the weighting scheme of

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

Hughes (1941) being used. By two cycles of refinement with isotropic temperature factors R was lowered from 0·081 to 0·072. Three more cycles of refinement, employing anisotropic temperature factors, brought R down to 0·054. In the last refinement 125 parameters (36 positional parameters, 84 thermal parameters and 5 scale factors) were varied.

At this stage the hydrogen atoms were taken into account. Their positions were calculated under the following assumptions:

(1) The O–H distance is 0·97 Å; the angle H–O–H is 109·5°.

(2) The hydrogen atoms lie in the plane defined by the water oxygen atom and the two oxygen atoms to which this water oxygen is hydrogen bonded.

(3) The hydrogen atoms are as far as possible separated from the cation to which the water oxygen atom is bonded. For O(w7), which is not coordinated to an Fe^{2+} ion, instead the midpoint of the positions of the two hydrogen atoms which form hydrogen bonds to O(w7), was chosen as 'cation' position.

The assumptions (2) and (3) are not strictly valid, as is known from the neutron diffraction studies of $CuSO_4.5H_2O$ (Bacon, 1962) and $MgSO_4.4H_2O$ (Baur, 1964*a*). The positions derived for the hydrogen atoms in this way are therefore expected to be correct only within 0·1 to 0·2 Å. That these positions are reasonable is supported by the fact that, on inclusion of the hydrogen atoms in the structure factor calculation, R was lowered to 0·045 (for all observed reflections). Moreover a difference projection along [010], computed with $F_o - F_{c(\text{heavy})}$, shows the positions of all the hydrogen atoms as well as can be expected in the presence of an iron atom (Fig. 2). The distances between the hydrogen atoms themselves are sensible. The shortest H–H distance is 2·11 Å (H(57)–H(74)); all other H–H distances are above 2·23 Å. But even a distance of 2·11 Å is not precluded since distances of 2·12 Å between hydrogen atoms from different water molecules have been found by neutron-diffraction in crystals of $Na_2CO_3.NaHCO_3.2H_2O$ (Bacon & Curry, 1956) and $CrK(SO_4)_2.12H_2O$ (Bacon & Gardner, 1958).

The final positional and thermal parameters are given in Tables 1 and 2, the calculated positions of the hydrogen atoms in Table 3. The B's in Table 2 are the isotropic B's equivalent to the anisotropic tem-

Table 1. $FeSO_4.7H_2O$, *positional parameters and their standard deviations*

Atom	x	y	z
Fe(1)	0·0000	0·0000	0·0000
Fe(2)	0·5000	0·5000	0·0000
S	0·2267(1)	0·4709(3)	0·1763(1)
O(1)	0·2045(3)	0·4705(8)	0·0368(3)
O(2)	0·1371(3)	0·5369(7)	0·2116(4)
O(3)	0·3075(3)	0·6157(7)	0·2267(4)
O(4)	0·2556(3)	0·2643(6)	0·2247(5)
O(w1)	0·1129(4)	0·3853(9)	0·4322(5)
O(w2)	0·1005(3)	0·9574(7)	0·1822(5)
O(w3)	0·0305(3)	0·7937(7)	0·4323(4)
O(w4)	0·4797(3)	0·4590(9)	0·1797(4)
O(w5)	0·4313(3)	0·2850(8)	0·4418(4)
O(w6)	0·3536(3)	0·8594(7)	0·4404(5)
O(w7)	0·3637(3)	0·0048(6)	0·1142(5)

Table 2. $FeSO_4.7H_2O$, *probable positions of the hydrogen atoms*

Atom	x	y	z
H(11)	0·148	0·259	0·461
H(12)	0·126	0·428	0·354
H(22)	0·124	0·817	0·196
H(24)	0·156	0·051	0·198
H(31)	0·090	0·870	0·469
H(32)	0·979	0·887	0·387
H(43)	0·421	0·514	0·198
H(47)	0·536	0·475	0·253
H(54)	0·375	0·275	0·369
H(57)	0·413	0·359	0·508
H(61)	0·297	0·910	0·465
H(63)	0·331	0·776	0·365
H(74)	0·313	0·077	0·143
H(76)	0·334	0·894	0·058

Table 3. $FeSO_4.7H_2O$. *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 (Å^2)
Fe(1)	0·0022(1)	0·0081(3)	0·0036(1)	−0·0003(1)	0·0010(1)	−0·0004(2)	1·50(5)
Fe(2)	0·0020(1)	0·0105(3)	0·0028(1)	−0·0004(1)	0·0006(1)	0·0004(2)	1·50(5)
S	0·0018(1)	0·0084(3)	0·0032(1)	−0·0001(1)	0·0006(1)	−0·0005(2)	1·40(5)
O(1)	0·0031(2)	0·0148(11)	0·0034(3)	−0·0015(4)	0·0011(2)	0·0002(6)	2·00(15)
O(2)	0·0031(2)	0·0137(9)	0·0061(4)	0·0014(4)	0·0027(2)	0·0013(7)	2·30(15)
O(3)	0·0029(2)	0·0150(10)	0·0055(3)	−0·0029(4)	0·0003(2)	−0·0033(7)	2·50(15)
O(4)	0·0031(2)	0·0101(8)	0·0055(4)	0·0017(3)	0·0003(3)	0·0019(7)	2·20(15)
O(w1)	0·0065(3)	0·0238(14)	0·0076(4)	0·0073(6)	0·0052(3)	0·0042(9)	3·70(20)
O(w2)	0·0039(2)	0·0125(9)	0·0069(4)	−0·0001(4)	0·0002(3)	0·0019(8)	2·80(15)
O(w3)	0·0030(2)	0·0104(8)	0·0058(3)	−0·0010(4)	0·0005(2)	0·0013(7)	2·30(15)
O(w4)	0·0030(2)	0·0207(13)	0·0034(3)	0·0000(4)	0·0012(2)	0·0008(7)	2·40(15)
O(w5)	0·0042(2)	0·0168(10)	0·0049(3)	0·0031(5)	0·0011(3)	0·0005(7)	2·70(15)
O(w6)	0·0026(2)	0·0171(11)	0·0065(3)	−0·0009(4)	0·0007(2)	−0·0042(8)	2·50(15)
O(w7)	0·0041(2)	0·0112(10)	0·0069(4)	0·0002(4)	0·0009(3)	−0·0019(8)	2·70(15)

Table 4. $FeSO_4 . 7H_2O$, *observed and calculated structure factors*

Non-observed F_o are marked by a minus sign

K=0 L=0

H	OBS	CALC
0		604
1	-1	2
2	43	38
3	21	-19
4	76	71
5	-3	-3
6	59	59
7	35	-36
8	99	101
9	58	57
10	39	41
11	24	-23
12	20	20
13	-4	3
14	41	41
15	22	-23
16	14	13
17	6	5
18	14	14

K=0 L=2

H	OBS	CALC
0	52	51
1	76	-74
-1	78	79
2	121	129
-2	152	168
3	90	87
-3	26	-22
4	62	63
-4	7	7
5	48	46
-5	80	79
6	69	70
-6	100	103
7	13	14
-7	33	-33
8	72	70
-8	17	-16
9	10	-11
-9	12	11
10	40	40
-10	50	49
11	10	11
-11	39	39
12	55	56
-12	-4	-2
13	22	-24
-13	35	-37
14	21	21
-14	48	48
15	-4	-4
-15	14	13
16	29	28
-16	16	16
17	-4	-2
-17	11	-10
18	13	13
-18	16	17
-19	7	8

K=0 L=4

H	OBS	CALC
0	101	97
1	120	124
-1	112	-116
2	62	63
-2	18	15
3	25	22
-3	70	-71
4	86	85
-4	86	85
5	18	18
-5	53	-55
6	36	35
-6	101	99
7	7	9
-7	59	59
8	9	8
-8	71	71
9	21	22
-9	47	-47
10	66	72
-10	10	9
11	-4	-2
-11	12	-13
12	20	20
-12	53	53
13	-4	0
-13	7	-7
14	34	33
-14	12	13
15	19	18
-15	-4	-2
16	8	8
-16	54	57
17	10	-10
-17	-4	-3
-18	8	8
-19	7	-7

K=0 L=6

H	OBS	CALC
0	59	59
1	34	-34
-1	37	35
2	6	3
-2	93	92
3	-3	-5
-3	103	-106
4	93	91
-4	82	80
5	9	-9
-5	29	26
6	40	40
-6	23	23
7	23	-24
-7	47	-47
8	52	54
-8	51	50
9	20	22
-9	8	8
10	32	33
-10	64	65
11	24	-25
-11	9	-8
12	40	41
-12	8	6
13	12	13
-13	29	29
14	23	23
-14	36	36
15	7	-5
-15	-4	-3
-16	16	17
-17	10	11
-18	32	32
-19	-3	-2

K=0 L=8

H	OBS	CALC
0	17	-18
1	11	-10
-1	15	-15
2	24	23
-2	59	60
3	30	30
-3	18	19
4	42	44
-4	16	15
5	24	-24
-5	17	18
6	25	24
-6	91	92
7	12	13
-7	17	17
8	38	38
-8	-4	-1
9	20	-19
-9	46	-48
10	17	16
-10	45	45
11	-4	2
-11	35	36
12	28	26
-12	36	35
13	-3	-2
-13	-4	3
-14	22	25
-15	24	24
-16	31	30
-17	23	-22
-18	11	11
-19	14	13

K=0 L=10

H	OBS	CALC
0	29	29
1	-4	-2
-1	8	7
2	41	42
-2	29	28
3	18	-18
-3	9	11
4	12	12
-4	50	52
5	8	5
-5	32	-32
6	31	31
-6	28	29
7	12	-12
-7	8	8
8	8	9
-8	68	73
9	-5	-3
-9	-4	-8
10	24	24
-10	26	25
11	-3	-0
-11	-4	-4
-12	55	56
-13	-4	4
-14	11	10
-15	12	-10
-16	31	33
-17	16	16
-18	-3	10

K=0 L=12

H	OBS	CALC
0	30	30
1	15	-15
-1	17	16
2	20	19
-2	30	30
3	13	-12
-3	-4	4
4	43	42
-4	33	33
5	8	-7
-5	9	8
6	-4	2
-6	29	30
7	6	-7
-7	15	-17
-8	11	11
-9	17	18
-10	37	40
-11	-4	-0
-12	29	27
-13	8	7
-14	18	17
-15	-3	-3
-16	-2	-7

K=0 L=14

H	OBS	CALC
0	8	7
1	7	-5
-1	10	10
2	32	31
-2	28	28
3	10	12
-3	-4	8
-4	-4	5
-5	8	-7
-6	26	25
-7	27	23
-8	16	18
-9	10	-10
-10	20	19
-11	-3	4
-12	19	20

K=1 L=0

H	OBS	CALC
1	20	-18
2	11	-8
3	17	16
4	75	74
5	51	-49
6	23	23
7	42	42
8	11	10
9	7	6
10	-3	1
11	14	14
12	-3	2
13	-3	-2
14	-4	4
15	-4	4
16	-4	-0
17	-3	-0
18	-3	3

K=2 L=0

H	OBS	CALC
0	161	174
1	10	9
2	35	33
3	75	-73
4	52	52
5	7	-5
6	81	78
7	58	-57
8	79	79
9	31	33
10	57	61
11	21	-21
12	13	15
13	22	24
14	42	44
15	7	-6
16	11	10
17	9	10
18	24	26

K=3 L=0

H	OBS	CALC
1	20	18
2	31	-31
3	12	12
4	20	21
5	16	-16
6	35	-36
7	10	-10
8	19	18
9	11	-10
10	10	-10
11	21	-21
12	12	12
13	5	4
14	-4	-3
15	8	-8
16	6	6
17	11	11

K=4 L=0

H	OBS	CALC
0	115	115
1	-3	3
2	39	39
3	31	-30
4	82	83
5	36	36
6	22	21
7	19	-18
8	57	59
9	13	12
10	22	23
11	13	-13
12	24	25
13	6	5
14	27	28
15	6	-5
16	12	12

K=5 L=0

H	OBS	CALC
1	37	-36
2	25	25
3	38	39
4	20	20
5	23	-23
6	24	-25
7	-3	1
8	20	20
9	8	-8
10	9	-8
11	5	3
12	13	13
13	7	6
14	5	-5
15	8	-8

K=6 L=0

H	OBS	CALC
0	51	48
1	-3	-1
2	30	30
3	-3	2
4	31	30
5	14	14
6	31	33
7	17	-17
8	29	31
9	9	9
10	22	23
11	-3	2
12	12	12
13	6	5
14	26	25

K=7 L=0

H	OBS	CALC
1	13	-13
2	9	9
3	22	23
4	13	12
5	11	-11
6	17	-18
7	7	-6
8	18	18
9	6	5
10	7	-8
11	-3	-3
12	15	16

K=8 L=0

H	OBS	CALC
0	29	29
1	5	-4
2	10	10
3	8	8
4	18	18
5	-3	1
6	16	17
7	5	-3
8	20	20

K=9 L=0

H	OBS	CALC
1	12	-12
2	3	-3
3	14	15

H=0 K=1

L	OBS	CALC
1	43	-38
2	10	-12
3	33	31
4	-3	1
5	79	-74
6	-3	-5
7	18	17
8	-4	-2
9	20	20
10	-4	4
11	10	-9
12	-5	-2
13	-5	2
14	6	-1

H=0 K=2

L	OBS	CALC
1	39	40
2	16	18
3	82	75
4	48	47
5	14	15
6	125	115
7	36	36
8	23	24
9	11	-12
10	45	45
11	12	-13
12	30	31
13	-4	3
14	10	-4

H=0 K=3

L	OBS	CALC
1	8	-8
2	-3	-4
3	16	17
4	9	-9
5	37	-35
6	8	8
7	-4	-4

H=0 K=4

L	OBS	CALC
1	10	11
2	32	30
3	9	-10
4	41	41
5	35	-35
6	68	65
7	28	29
8	19	19
9	-4	-6
10	31	31
11	-4	1
12	21	22
13	15	15

H=0 K=5

L	OBS	CALC
1	10	-9
2	16	-16
3	10	8
4	18	20
5	14	-15
6	-4	-6
7	-4	3
8	-4	-4
9	15	16
10	8	8
11	8	-8
12	5	-7

H=0 K=6

L	OBS	CALC
1	31	32
2	39	38
3	6	-5
4	20	21
5	-4	-6
6	39	38
7	25	24
8	18	17
9	-4	-5
10	20	20
11	5	-5

H=0 K=7

L	OBS	CALC
1	-4	-1
2	15	-15
3	-4	2
4	-4	4
5	8	-7
6	6	-5
7	-4	1
8	12	-11
9	10	10

H=0 K=8

L	OBS	CALC
1	11	11
2	17	18
3	-4	-4
4	18	19
5	12	-13
6	14	13
7	19	17

K=3 L=0

H	OBS	CALC
18	-5	-4
19	-5	-9

K=3 L=1

H	OBS	CALC
10	-3	9
11	46	50
-11	46	49
12	22	-21
-12	22	26
13	13	13
-13	26	27
14	-5	-1
-14	-5	-6
15	30	31
-15	8	7
16	-6	-4
-16	-6	4
17	12	11
-17	25	25
18	-5	-2
-18	14	-14
19	21	21

K=3 L=2

H	OBS	CALC
10	-4	1
11	-5	0
-11	15	14
12	10	-5
-12	-4	4
13	12	-11
-13	-5	-5
14	10	-8
-14	16	-16
15	12	13
-15	8	-8
16	-6	-4
-16	14	14
17	11	-10
-17	-6	-1
18	-5	0
-18	10	-9

K=3 L=3

H	OBS	CALC
9	37	44
10	10	-13
11	11	12
-11	-4	3
12	8	4
-12	-4	-8
13	40	41
-13	40	41
14	-6	4
-14	11	11
15	14	13
-15	17	16
16	9	-8
-16	15	-14
17	23	23
-17	29	29
-18	-6	7
-19	15	15

K=3 L=4

H	OBS	CALC
8	-3	13
9	5	9
10	6	5
-10	-2	-3
11	14	-14
-11	14	-13
12	12	-12
-12	-4	-1
13	12	11
-13	-5	5
14	-6	1
-14	8	-8
15	-6	-7
-15	-6	-5
16	10	-8
-16	-7	-7
-17	-6	3
-18	11	9
-19	-5	-4

K=3 L=5

H	OBS	CALC
8	-4	-3
9	25	26
10	-5	-0
-10	24	25
11	38	39
-11	45	49
12	23	22
-12	-5	-8
13	15	13
-13	24	23
14	18	-17
-14	-5	-2
15	21	19
-15	26	26
16	14	10
-16	-6	-3
-17	11	8
-18	-6	2
-19	29	31

K=3 L=6

H	OBS	CALC
5	23	-27
6	-4	-2
7	11	12
8	17	17
9	10	-7
10	-5	-7
-10	-4	1
11	-6	6
-11	-4	-10
12	13	13
-12	18	-18
13	-6	2
-13	-5	-5
14	-5	-10
-14	-5	-5
15	-5	-2
-15	12	10
-16	-6	-1
-17	-6	-3
-18	-5	-4
-19	-5	2

K=3 L=7

H	OBS	CALC
4	24	-24
5	37	41
6	18	18
7	31	32
8	19	-19
-8	28	31
9	35	36
-9	23	25
10	-6	7
-10	8	-9
11	26	26
-11	23	22
12	12	-12
-12	16	16
13	11	10
-13	36	35
14	-5	6
-14	-5	-3
15	28	24
-15	15	14
-16	16	15
-17	20	19
-18	-5	-2
-19	-5	10

K=3 L=8

H	OBS	CALC
0	27	-27
1	10	11
-1	12	-13
2	23	23
-2	7	8
3	11	-10
-3	19	22
4	13	-13
-4	12	-12
5	11	10
-5	14	-14
6	-5	10
-6	-3	-2
7	-5	3
-7	-4	-2
8	-5	-6
-8	14	5
9	-6	3
-9	17	-17
10	-6	7
-10	-5	-7
11	14	14
-11	-5	-2
12	-5	-9
-12	17	17
13	-5	-2
-13	-5	-8
-14	-6	-4
-15	-6	-1
-16	-6	-5
-17	-6	4
-18	-5	1
-19	-4	-7

K=3 L=9

H	OBS	CALC
0	20	22
1	17	17
-1	27	29
2	15	-15
-2	22	-23
3	27	27
-3	20	19
4	18	17
-4	16	16
5	28	28
-5	46	51
6	16	-14
-6	11	-10
7	15	13
-7	19	18
8	-6	1
-8	-5	0
9	18	18
-9	52	60
10	-6	-3
-10	13	13
11	-5	9
-11	18	17
12	-5	3
-12	18	-16
13	26	22
-13	35	33
-14	10	9
-15	15	15
-16	10	-7
-17	23	22
-18	14	13
-19	22	22

K=3 L=10

H	OBS	CALC
0	17	17
1	11	-12
-1	13	-14
2	-5	-4
-2	25	-25
3	-5	-3
-3	-5	-3
4	13	13
-4	13	13
5	-5	-1
-5	-5	5
6	-6	-2
-6	-5	-1
7	-6	-4
-7	-5	-2
-8	-5	4
-9	-5	0
-10	12	-11
-11	17	-17
-12	-6	6
-13	13	13
-14	12	10
-15	-6	-1

K=3 L=11

H	OBS	CALC
0	16	-15
1	25	24
-1	35	36
2	16	15
-2	-5	3
3	25	25
-3	23	22
4	18	-18
-4	11	-10
5	17	17
-5	27	27
6	-6	-7
-6	18	17
7	25	26
-7	38	41
-8	15	-14
-9	24	25
-10	-6	-4
-11	33	33
-12	-6	-3
-13	13	9
-14	-6	5
-15	32	31

K=3 L=12

H	OBS	CALC
0	12	-13
1	-6	-9
-1	-5	3
2	-6	8
-2	-5	11
3	-6	4
-3	-5	1
4	-6	-7
-4	-5	-14
5	-6	-5
-5	-5	7
-6	-5	-0
-7	-5	1
-8	-6	-8
-9	-6	4
-10	-6	6
-11	-6	3
-12	-6	-1
-13	-6	-5
-14	-5	6
-15	-5	3

K=3 L=13

H	OBS	CALC
0	-6	5
1	27	28
-1	12	11
2	-6	-5
-2	-6	-6
3	-5	4
-3	28	28
4	-5	-1
-4	21	20
5	27	28
-5	13	11
-6	-6	-4
-7	21	22
-8	10	9
-9	23	23
-10	-6	-6
-11	11	10
-12	-5	8
-13	19	18
-14	-5	-6
-15	14	14

K=3 L=14

H	OBS	CALC
0	-5	4
1	-5	6
-1	14	-14
-2	-5	1
-3	12	11
-4	-6	10
-5	-6	-6
-6	-6	-5
-7	-6	3
-8	-5	5
-9	-5	-5
-10	-5	-3
-11	-5	2
-12	16	13

K=3 L=15

H	OBS	CALC
0	-4	6
1	9	9
-1	22	23
-2	-5	-6
-3	-5	4
-4	-5	3
-5	28	31
-6	-5	4
-7	-5	6
-8	-5	-9
-9	19	21
-10	-4	4
-11	13	13

K=1 L=1

H	OBS	CALC
1	157	157
-1	28	27
2	69	67
-2	13	9
3	49	48
-3	160	164
4	106	-108
-4	17	-19
5	70	73
-5	6	4
6	30	-29
-6	-2	2
7	90	94
-7	86	86
8	-3	-5
-8	21	21
9	48	50
-9	34	33
10	27	28
-10	34	-34
11	60	66
-11	51	51
12	32	-36
-12	47	50
13	16	18
-13	34	35
14	-4	-1
-14	16	-16
15	30	32
-15	16	16
16	-4	1
-16	15	15
17	14	15
-17	21	21
18	-4	3
-18	-4	-5
-19	9	8

K=2 L=1

H	OBS	CALC
1	19	-19
-1	38	38
2	36	34
-2	8	7
3	65	-64
-3	25	23
4	14	-14
-4	36	35
5	29	29
-5	10	-9
6	14	-12
-6	32	31
7	28	-29
-7	29	-27
8	15	16
-8	27	26
9	5	4
-9	27	27
10	7	-3
-10	-3	2
11	9	9
-11	-4	2
12	11	-11
-12	17	17
13	-4	-3
-13	9	-8
14	-4	2
-14	-4	-1
15	-4	-4
-15	-4	-6
16	-4	-6
-16	13	-12
17	-4	0
-17	9	6
18	-4	4
-18	7	7

K=3 L=1

H	OBS	CALC
1	82	84
-1	53	54
2	41	40
-2	-3	-5
3	96	99
-3	154	152
4	55	-58
-4	11	10
5	63	66
-5	36	36
6	42	43
-6	-3	4
7	49	50
-7	47	46
8	-3	-4
-8	28	27
9	42	45
-9	7	6
10	10	9
-10	37	-36

K=4 L=1

H	OBS	CALC
1	21	21
-1	27	-24
2	-3	-5
-2	-3	-5
3	17	-16
-3	28	-26
4	11	10
-4	28	27
5	23	24
-5	25	-24
6	-4	4
-6	33	-33
7	19	-20
-7	37	-35
8	-4	-4
-8	18	17
9	15	15
-9	16	15
10	22	22
-10	-4	0
11	-4	-1
-11	12	-11
12	-4	3
-12	7	-6
13	10	9
-13	11	10
14	8	9
-14	-4	-5
15	-4	-2
-15	16	-16
16	11	-12
-16	-4	-6
17	-4	5
-17	12	12
18	7	6
-18	10	10

K=5 L=1

H	OBS	CALC
1	30	28
-1	11	10
2	14	14
-2	-4	-2
3	34	36
-3	70	71
4	34	-37
-4	9	8
5	48	51
-5	19	19
6	-4	7
-6	-4	-4
7	29	26
-7	49	51
8	14	-13
-8	-4	5
9	28	30
-9	21	20
10	-4	2
-10	13	-13
11	29	29
-11	45	44
12	-4	-1
-12	16	15
13	16	17
-13	27	25
14	-4	4
-14	-4	5
15	21	22
-15	11	11
16	-4	4
-16	-4	6
17	10	9
-17	19	20

K=6 L=1

H	OBS	CALC
1	15	15
-1	18	-18
2	10	-7
-2	22	-22
3	17	-16
-3	11	10
4	24	24
-4	30	30
5	-4	1
-5	6	6
6	-4	-9
-6	20	-20
7	22	-23
-7	-4	-4
8	19	-20
-8	21	22
9	11	10
-9	16	16
10	8	8
-10	-4	5
11	-4	-5
-11	16	-15
12	-4	-5
-12	-4	4
13	9	8
-13	12	11
14	-4	-0
-14	-4	-2
15	7	-7
-15	15	-15
16	8	-8
-16	-3	-3
-17	7	8

K=7 L=1

H	OBS	CALC
1	34	33
-1	33	33
2	16	16
-2	-4	-2
3	28	29
-3	36	36
4	-4	4
-4	-4	2
5	28	28
-5	18	18
6	-4	5
-6	-4	3
7	21	22
-7	21	21
8	-4	3
-8	7	7
9	10	9
-9	20	20
10	10	8
-10	-4	-5
11	24	24
-11	14	13
12	-4	-5
-12	-4	3
13	14	14
-13	15	15
-14	10	-9
-15	11	11

K=8 L=1

H	OBS	CALC
1	10	9
-1	9	-10
2	-4	-4
-2	16	-16
3	10	-8
-3	-4	-2
4	-4	3
-4	16	16
5	16	15
-5	-4	-6
6	-4	0
-6	11	-12
7	15	-15
-7	17	-16
8	-4	-3
-8	-4	3
9	11	11
-9	13	14
10	15	15
-10	-4	-6
-11	11	-11
-12	-3	2
-13	7	11

K=9 L=1

H	OBS	CALC
1	14	14
-1	9	9
2	-4	1
-2	-4	0
3	13	13
-3	16	16
4	-4	1
-4	-4	-5
5	19	18
-5	13	14
6	-3	-4
-6	-4	6
7	11	11
-7	16	16
8	-3	3
-8	-3	2
-9	19	19

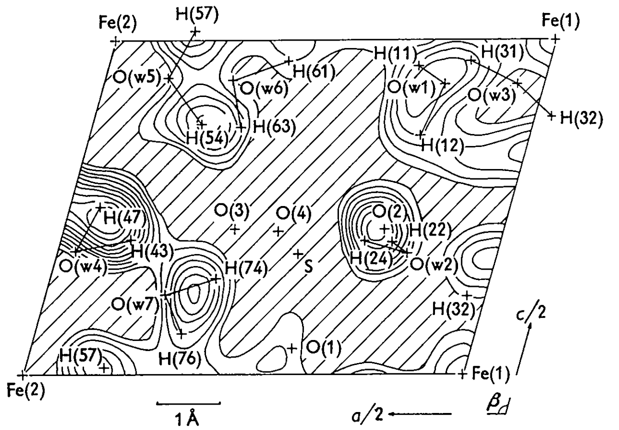

Fig. 2. Difference density projection parallel to [010] computed with $F_o - F_{c(\text{heavy})}$, thus showing the contributions of the hydrogen atoms only. 70 F_{h0l} with $\sin\theta/\lambda < 0·38$ Å^{-1} were used in the summation. Atomic positions marked by crosses; water oxygen atoms connected by lines to their corresponding hydrogen atoms. Negative areas shaded, negative contours omitted, first drawn contour is the zero contour. Largest negative peak is $-0·50$ e.Å^{-2}. Contour interval 0·09 e.Å^{-2}. Hydrogen atoms bear the numbers of the water oxygen atoms to which they belong, followed by the numbers of the sulfate or water oxygen atoms to which they form hydrogen bonds.

perature factors (Hamilton, 1959). The observed and calculated structure factors are listed in Table 4. Non-observed F_o are marked by a minus sign; the value given here for F_o is equal to $\sqrt{(\frac{1}{2}I_{\min}.\text{Lp}^{-1})}$. The atomic form factors used in computing F_c were taken from the *International Tables* (Ibers, 1962). The F_c include the contribution of the hydrogen atoms; the B of the isotropic temperature factor for the hydrogen atoms was chosen uniformly 1·3 Å^2 higher than the equivalent isotropic B of the corresponding water oxygen atoms. The R value for all the reflections including the 288 non-observed is 0·071.

Discussion of the structure

The bond distances and angles in $\text{FeSO}_4.7\text{H}_2\text{O}$ are presented in Table 5. The estimated standard deviations given have been calculated with the use of the least-squares variance–covariance matrix and therefore include the effects of correlations between parameters. None of the positional parameters is involved in high correlations. The highest correlation coefficient of 0·6 is one between two thermal parameters. The four components of the structure, *i.e.* the two different $\text{Fe(H}_2\text{O)}_6^{2+}$ octahedra, the SO_4^{2-} tetrahedron and the seventh water molecule, which is not coordinated to Fe^{2+}, are linked together by hydrogen bonds. A schematic representation of the hydrogen bonding is shown in Fig. 3, the actual spatial arrangement can be gathered from Fig. 4.

The average value of the O–H · · · O bond lengths is 2·82 Å; the spread is from 2·71 to 3·03 Å. The angles O–O(w)–O, around the water oxygen atoms to the oxygen atoms to which they are hydrogen bonded, scatter from 103° to 145°. Assuming the hydrogen positions of Table 3 to be correct, the angles

Table 5. *Interatomic distances and bond angles*

(*a*) Coordination octahedron around Fe(1)

Fe(1)–O(w1)	2·068(5) Å	
Fe(1)–O(w2)	2·144(5)	
Fe(1)–O(w3)	2·136(5)	
Mean value:	2·116(3)	
O(w1)–O(w2)	2·992(7) Å	2·965(7) Å
O(w1)–O(w3)	3·047(7)	2·897(7)
O(w2)–O(w3)	3·129(6)	2·920(6)
O(w1)–Fe(1)–O(w2)	90·5°(0·2°)	
O(w1)–Fe(1)–O(w3)	92·9°(0·2°)	
O(w2)–Fe(1)–O(w3)	94·0°(0·2°)	

(*b*) Coordination octahedron around Fe(2)

Fe(2)–O(w4)	2·096(5) Å	
Fe(2)–O(w5)	2·109(5)	
Fe(2)–O(w6)	2·188(5)	
Mean value:	2·131(3)	
O(w4)–O(w5)	2·987(7) Å	2·960(7) Å
O(w4)–O(w6)	3·057(6)	3·002(6)
O(w5)–O(w6)	3·102(7)	2·974(7)
O(w4)–Fe(2)–O(w5)	90·5°(0·2°)	
O(w4)–Fe(2)–O(w6)	91·0°(0·2°)	
O(w5)–Fe(2)–O(w6)	92·4°(0·2°)	

(*c*) SO_4 tetrahedron

S–O(1)	1·488(4) Å
S–O(2)	1·481(4)
S–O(3)	1·466(4)
S–O(4)	1·462(4)
Mean value:	1·474(2)

O(1)–O(2)	2·407(6) Å	O(1)–S–O(2)	108·4°(0·3°)
O(1)–O(3)	2·400(6)	O(1)–S–O(3)	108·7°(0·3°)
O(1)–O(4)	2·412(6)	O(1)–S–O(4)	109·7°(0·3°)
O(2)–O(3)	2·415(5)	O(2)–S–O(3)	110·1°(0·3°)
O(2)–O(4)	2·411(6)	O(2)–S–O(4)	110·1°(0·3°)
O(3)–O(4)	2·398(6)	O(3)–S–O(4)	109·9°(0·3°)
Mean value:	2·407(3)	Mean value:	109·5°(0·1°)

(*d*) Hydrogen bonds

O(w1)–O(1)	2·748(7) Å		
O(w1)–O(2)	2·733(7)	O(1)–O(w1)–O(2)	121·4°(0·2°)
O(w2)–O(2)	2·785(7)		
O(w2)–O(4)	2·901(6)	O(2)–O(w2)–O(4)	123·3°(0·2°)
O(w3)–O(1)	2·857(6)		
O(w3)–O(2)	2·928(6)	O(1)–O(w3)–O(2)	114·0°(0·2°)
O(w4)–O(3)	2·803(6)		
O(w4)–O(w7)	2·725(6)	O(3)–O(w4)–O(w7)	110·5°(0·2°)
O(w5)–O(4)	2·950(6)		
O(w5)–O(w7)	2·714(7)	O(4)–O(w5)–O(w7)	102·6°(0·2°)
O(w6)–O(1)	2·821(6)		
O(w6)–O(3)	2·770(6)	O(1)–O(w6)–O(3)	121·2°(0·2°)
O(w7)–O(4)	2·766(6)		
O(w7)–O(w6)	3·027(7)	O(4)–O(w7)–O(w6)	145·0°(0·2°)
Mean value:	2·82	Mean value:	120°

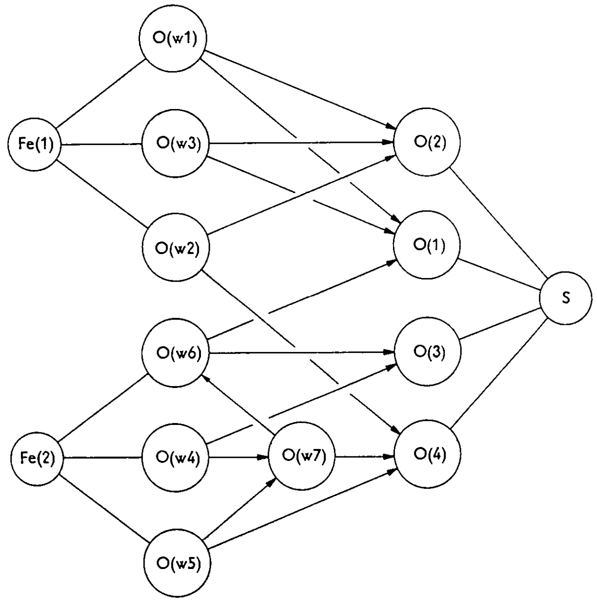

Fig. 3. Hydrogen bonding scheme of $FeSO_4 . 7H_2O$.

O(w)–H–O range (with one exception) from 160° to 180°, the angles H–O(w)–O from 0° to 13°, the angles Fe–O(w)–H from 113° to 124°, the distances H · · · O from 1·75 to 1·83 Å. The exception is the hydrogen bond from O(w7) to O(w6) where O(w6)–H(76)–O(w7) is 148°, H(76)–O(w7)–O(w6) is 23° and H · · · O is 2·17 Å. The assignment of this hydrogen bond is not quite unambiguous. The water oxygen atoms O(w1) through O(w6) have each only two contacts to sulfate oxygen atoms or to O(w7) which can be explained as hydrogen bonds (bond distances between 2·71 and 2·95 Å; see Table 5(*d*)). O(w7) instead has three such contacts to O(4), O(3) and O(w6). The sulfate oxygen atom O(4) at a distance of 2·77 Å seems clearly to be hydrogen bonded to O(w7). The distances of O(3) and O(w6) to O(w7) are 3·02 and 3·03 Å, the angles O(4)–O(w7)–O(3) and O(4)–O(w7)–O(w6) are 97° and 145° respectively. On purely geometrical grounds it cannot be decided whether O(3) or O(w6) is the acceptor atom of the hydrogen bond from O(w7), or if the bond is a bifurcated one. It seems however more probable that the bond goes to O(w6) since this assignment is in better accord with the difference

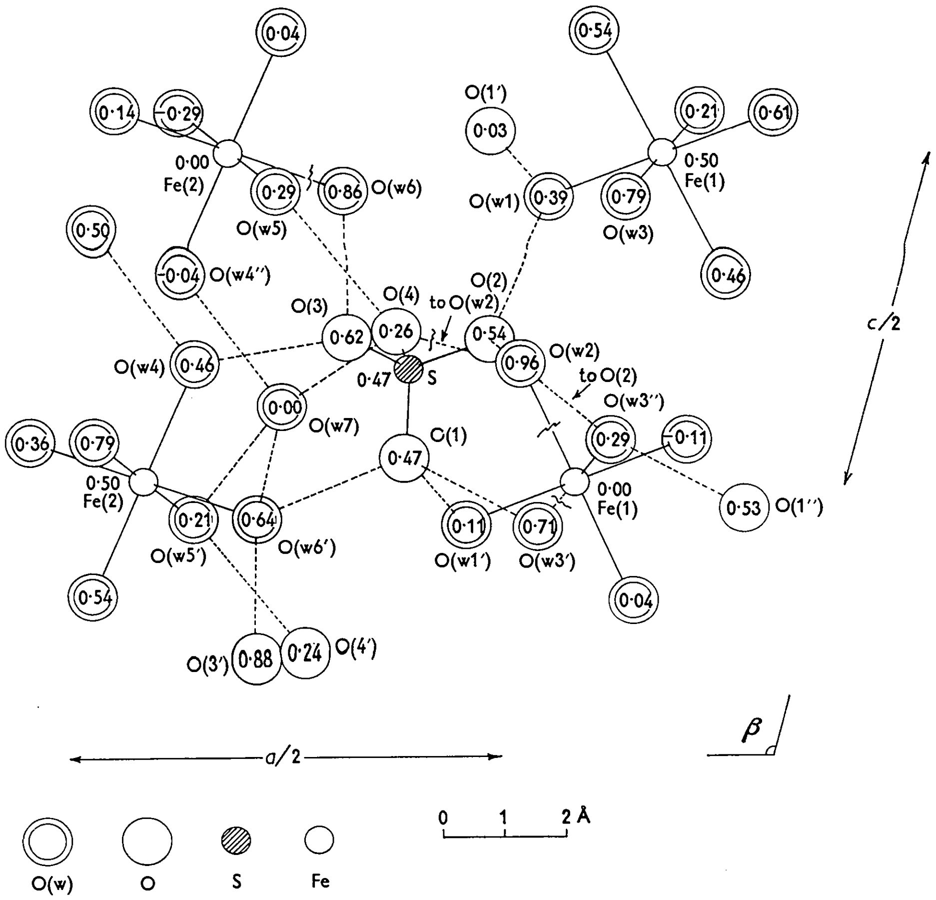

Fig. 4. Schematic projection parallel to [010] illustrating the hydrogen bonding system. The numbers in or near the circles representing the atoms are the *y* parameters of these atoms. Hydrogen bonds shown by dashed lines.

map parallel to [010]. Further supporting evidence is to be found in the fact that the distance Fe(2)–O(w6) is 2·19 Å and thus significantly longer than the average Fe(2)–O(w) distance of 2·13 Å. This is similar to the differences in bond lengths of Mg–O(w) in $MgSO_4.7H_2O$ (Baur, 1964*b*), where the water oxygen atoms which act as acceptor atoms of hydrogen bonds have an average Mg–O(w) bond length of 2·10 Å, while for the ones which are bonded to Mg only, Mg–O(w) is 2·05 Å. These differences in bond lengths can be understood in terms of Pauling's electrostatic valence rule: a point which has been discussed at greater length in part I (Baur, 1962*a*). The coordination octahedron around Fe(1) is distorted in a similar way, although not quite so pronounced, as in FeF_2 (Baur, 1958). In FeF_2 there are two Fe–F bonds of 1·99 Å and four of 2·12 Å; in $FeSO_4.7H_2O$ there are around Fe(1) two O(w1) at a distance of 2·07 Å and four water oxygen atoms (O(w2) and O(w3)) at 2·14 Å. Dunitz & Orgel (1960) interpret tentatively this kind of distortion around Fe^{2+} by a Jahn–Teller mechanism. In the present case however it is possible that this short distance is only apparent. Although one has to be cautious in interpreting the thermal parameters since they are much more liable than positional parameters to be affected by systematic errors in the data, it seems safe to conclude from Table 6 that the thermal motion of O(w1) is significantly more anisotropic than that of the other water oxygen atoms. The thermal displacements of the water oxygen atoms O(w2) through O(w6) and of Fe(1) and Fe(2) can be interpreted as rigid body motions of the whole groups. The directions of the smallest thermal displacement (axis 1 in Table 6) of the water oxygen atoms are at an average angle of 12°(2°) with the line connecting them to the iron atoms. The displacement of O(w2) through O(w6) along the bond Fe–O(w) is of approximately the same magnitude as the displacement of the central iron atom. The other two axes, of intermediate and largest thermal displacement (axes 2 and 3 in Table 6) are at average angles of 94°(4°) and 83°(3°) with the respective Fe–O(w) lines. The displacements of O(w1) along axes 1 and 3 are very different from those of all the other water oxygen atoms. It seems that O(w1) is moving (at least partly) independently of the rest of the group. The correction of the bond distance for thermal motion assuming that Fe(1) and O(w1) move independently (Busing & Levy, 1957) changes Fe(1)–O(w1) from 2·07 to 2·11 Å. This correction therefore brings the distance Fe(1)–O(w1) into somewhat better accord with the distances Fe(1)–O(w2) and Fe(1)–O(w3).

Table 6. $FeSO_4.7H_2O$, *root-mean-square thermal displacements along principal axes* (Å)

Atom	Axis 1	Axis 2	Axis 3
Fe(1)	0·130(2)	0·135(2)	0·150(2)
Fe(2)	0·127(2)	0·135(2)	0·154(2)
S	0·128(2)	0·129(3)	0·141(3)
O(1)	0·133(7)	0·154(6)	0·194(7)
O(2)	0·125(7)	0·164(8)	0·210(6)
O(3)	0·110(8)	0·194(6)	0·210(6)
O(4)	0·121(8)	0·181(7)	0·196(7)
O(w1)	0·115(10)	0·180(8)	0·309(7)
O(w2)	0·154(8)	0·180(6)	0·227(7)
O(w3)	0·138(7)	0·163(6)	0·200(8)
O(w4)	0·134(6)	0·167(5)	0·212(6)
O(w5)	0·154(7)	0·169(6)	0·228(6)
O(w6)	0·140(7)	0·166(7)	0·228(8)
O(w7)	0·147(9)	0·191(6)	0·215(7)

The mean bond length for the six different Fe–O(w) bonds in $FeSO_4.7H_2O$ is $2\cdot12_4$ Å (uncorrected for thermal motion). Reliable information on Fe^{2+}–O(w) distances is scarce; the value found here can be compared with the mean value for Fe–O,O(w) of 2·122(5) Å in $FeSO_4.4H_2O$ (I) and of 2·140(13) Å in $Fe(H_2O)_6.SiF_6$ (Hamilton, 1962). The differences between these values are not significant. The mean value for the Fe–O(w) bond length in $FeSO_4.7H_2O$ is changed to 2·138 Å if the correction for thermal motion is applied to all the distances, namely a correction assuming independent motion for the distance Fe(1)–O(w1) and assuming in-phase motion for all the other Fe–O(w) distances. The bonding angles O(w)–Fe–O(w) scatter from 86·0° to 94·0°, the differences between them are significant; so are the differences between the O(w)–O(w) distances in the octahedra, which range from 2·90 to 3·13 Å. The mean value of the S–O distances in the sulfate group is $1\cdot47_4$ Å; the corresponding value in $MgSO_4.4H_2O$ (Baur, 1946*a*) is $1\cdot47_3$ Å. Since the thermal ellipsoids of the sulfate oxygen atoms are similarly oriented in respect to the sulfur atom, as are the water oxygen atoms to the iron atom (the average angles of the axes 1, 2 and 3 with the lines S–O are 14°(3°), 94°(2°) and 93°(3°)), rigid body motion of the whole sulfate group may be assumed and the in-phase correction for thermal motion applied to the bond distances: the average S–O bond length becomes then $1\cdot48_5$ Å. The O–S–O angles are close to the tetrahedral value; the deviations of the O–O distances within the sulfate group from their mean value are not significant.

Beevers & Schwartz (1935) made it a point in their description of the orthorhombic crystal structure of $NiSO_4.7H_2O$ that the octahedral coordination of water around a divalent cation like Ni^{2+} is always different from that around a trivalent ion like Al^{3+}. In the first case there should always be two water oxygen atoms in the octahedron receiving hydrogen bonds from an outside water molecule. This in fact is true for tetragonal $NiSO_4.6H_2O$ (Beevers & Lipson, 1932) and for orthorhombic $NiSO_4.7H_2O$ (the latter structure has been fully confirmed by a refinement of the isostructural $MgSO_4.7H_2O$ (Baur, 1964*b*)). But it does not hold for the monoclinic structure of $CoSO_4.6H_2O$ (Zalkin, Ruben & Templeton, 1962) or for $FeSO_4.7H_2O$, as has been demonstrated here.

In both these structures there are two crystallographically different $M^{2+}(H_2O)_6$ octahedra in special positions, and in each structure only one out of the two octahedra is of the type reported for the nickel sulfate hydrates.

It is a pleasure to thank W. C. Hamilton for valuable discussions. The first part of this study (performed in Göttingen) was supported by the Deutsche Forschungsgemeinschaft.

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Short Communications

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Acta Cryst. (1964). **17**, 1174

The symmetry of phases in the reciprocal lattice. A correction.

By J. W. Jeffery, *Birkbeck College Crystallography Laboratory, University of London, England* and E. F. Bertaut, *Laboratoire d'Électrostatique et de Physique du Métal, Grenoble, France*

(*Received* 17 *June* 1964)

The criticism of the paper by Jeffery (1963) contained in the penultimate two paragraphs of Bertaut's (1964) note on the above subject is invalid, since it rests on a misreading of the original paper.

The error is due to the fact that in the relation between the phase α_{hkl} and the symmetry-related phase $\alpha_{h'k'l'}$, Bertaut (1964) writes α_{hkl} as the dependent variable on the L.H.S., whereas Jeffery (1963) writes $\alpha_{h'k'l'}$ (see his first equation) in this position.

The actual statement in the tables (Jeffery, 1963) is not

$$\alpha_{hkl}=\alpha_{\bar{k}hl}+3(\pi/2)l$$

as misread by Bertaut (1964), but should be read

$$\alpha_{\bar{k}hl}=\alpha_{hkl}+3(\pi/2)l$$

in conformity with Bertaut's result.

The final conclusion is that Buerger's early geometrical method (1949) used in Jeffery's (1963) paper and the algebraic method (Bertaut, 1964) yield the same results, as would be expected.

The opportunity is taken to correct a minor misprint in Jeffery's paper. Under *Application to the tetragonal space groups* (p. 1239) the L.H.S. of the four equations should be $\alpha_{\bar{k}hl}$ *not* $\alpha_{\bar{h}kl}$.

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